IMPROVED QUALITY BITUMEN AS A BINDER IN FLEXIBLE PAVEMENT THROUGH NEW ADDITIVES AND IN-SITU POLYMERIZATION

By

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DECLARATION CERTIFICATE

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no materials previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the University or other institute of higher learning, except where due acknowledgment has been made in the text.

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled **“Improved Quality Bitumen as a Binder in Flexible Pavement Through New Additives and In-Situ Polymerization”** submitted by **Mr. Rabindra Kumar Padhan** to University of Petroleum and Energy Studies, Dehradun for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by him under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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(RABINDRA KUMAR PADHAN)

LIST OF SYMBOLS

Å	Angstrom (unit of length)
Cst	Centistokes
^{0}C	Temperature in Celsius scale
Cm	Centimeter
Cm/Min.	Centimeter/Minute
G	Gram
H	Hour
K	Temperature in Kelvin scale
Kg	Kilogram
KN	Kilo Newton
Lit	Liter
Ml	mille liter
Mm	Millimeter
MPa	mille Pascal

Pa	Pascal
S	Second
w/w	Weight/Weight

LIST OF ABBREVIATIONS

ASTM	American Society For Testing And Materials
BIS	Bureau Of Indian Standards
BP	Boiling Point
BBR	Bending Beam Rheometer
CRM	Crumb Rubber Modified
CR	Crumb Rubber
CRMB	Crumb Rubber Modified Bitumen
DSR	Dynamic Shear Rheometer
EN	European Norm
EVA	Ethylene Vinyl Acetate
IS	Indian Standard
IR	Infra Red

MMT	Million Metric Tones
MT	Million Ton
MP	Melting Point
MSCR	Multiple Stress Creep Recovery Test
NMR	Nuclear Magnetic Resonance
PET	Poly (ethylene terephthalate)
PMB	Polymer Modified Bitumen
PAV	Pressure Aging Vessel
PVC	Poly (vinyl chloride)
PPA	Poly Phosphoric Acid
SP	Softening Point
SBS	Styrene Butadiene Styrene
RTFO	Rotating Thin Film Oven Test
TFOT	Thin Film Oven Test
UV	Ultra Violet

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EXECUTIVE SUMMARY

Bitumen is a visco-elastic material, which remains as residue after vacuum distillation of the crude oil. It is a complex mixture of organic compounds which cannot be classified exactly and therefore, their components are broadly grouped into asphaltenes and maltenes. The maltenes can be subdivided into saturates, aromatics, and resins. Asphaltenes are highly polar complex material of high molecular weight. Bitumen is extensively used for road constructions because of its excellent binding characteristics and low cost. However, increased stress on highways due to heavier loads, higher tire pressures and severe climatic conditions are causing premature failures, high temperature rutting, low temperature fatigue and stripping of road pavement.

Various additives such as antistripping agent, reactive polymer, thermoplastic & thermo elastic polymer etc. are known to improve the performance of bituminous pavements. Out of these various additives styrene butadiene styrene (SBS) is generally used as thermo elastic polymers to improve elastic and rheological properties of bitumen and therefore, globally being used for bitumen modification in large volume. However, SBS modified bitumen shows some serious problems such as phase separation when stored at high temperature for long time and also have

tendency to degrade on exposure to heat, oxygen and UV light. These conditions generally lead to undesirable aging of bitumen and polymer degradation thus affecting the overall performance of SBS modified bitumen.

Researchers are employing alternative materials such as scrap tires and waste plastics for bitumen modification. Large volumes of scrap tires and waste plastic are generated now a day's causes environmental pollution which motivates the researchers to use these waste materials for bitumen modification. However, crumb rubber and waste plastic modified bitumen have some issues regarding storage stability as crumb rubber and plastic particles settles at the bottom of container which causes difficulty in transportation of these modified bitumen and therefore restricts their use for bitumen modification.

Waste plastics and waste tires rubber have been used to get storage stable polymer modified bitumen but use of plastics incorporated bitumen was also found to have storage stability issues. Therefore, in consideration of the preceding literature review and keeping above issues in mind, PET derivatives and other additives have been synthesized from waste plastics which in turn lead to several bituminous applications. The study conducted in the present thesis have been summarised as below.

1. The waste PET derivatives synthesized in present thesis acts as antistripping agents for bituminous application to avoid moisture ingress in road pavement. Bitumen doped with these synthesized PET derivatives was found to possess 100% antistripping properties.

2. In order to ensure better dispersion of polymers in bitumen, the present thesis also described the innovative approach for in-situ polymerization of terepthalamide derivatives (derived from waste PET) with methylene diphenyl diisocyanate (MDI) in the body of bitumen to synthesize polyurea and polyurethane. Insitu polymerized polymer modified bitumen was found to possess high storage stability and also enhance the rheological properties of bitumen.

3. In this thesis, we have also synthesized aminated polyvinyl chloride by the reaction of waste polyvinyl chloride with polyamines and studied their affects on the physico-chemical properties of bitumen.

4. In addition to this, another objective of this thesis is to develop storage stable polymer modified bitumen with high elastomeric properties by using reactive polyoctenamer polymer along with cross linking agent in bitumen. The combination of reactive polyoctenamer along with cross linking agent was found to promote anchoring of crumb rubber in bitumen to produce storage

stable crumb rubber modified bitumen. The use of reactive polymer to develop polymer modified bitumen & crumb rubber modified bitumen also avoid milling operation which further make the products cost effective and energy efficient.

5. The present research work also provides an alternate way for the disposal of waste plastics keeping the environment free of pollution. This may contributes a significant role in **Swachh Bharat Abhiyan** which is a national level campaign by the Government of India.

CHAPTER 1

Introduction & Literature Review

1.1 Introduction

1.1.1 Historical Prospective of Bitumen

Bitumen, a black or dark brown non-crystalline thermoplastic viscous material, has been used for centuries as a building material, sealant, adhesive and waterproofing agent [**1**]. A tarry fluid with a characteristic smell, oozing out of rocks or floating in lake waters is well known to man from time immemorial. As early as 3500 BC, the Sumerians used asphalt as an adhesive for bricks and sealant for water crafts. In 2000 BC, Babylonians built bridges, wells, tunnels, sewers, roads, etc., including the Tower of Babel with asphalt as a bonding material. The Indus valley civilization of Harappa and Mohanjo-dero, in around 300 BC used asphalt for waterproofing bathrooms. In biblical times Noha's ark was waterproofed with asphalt. Under the Pharaohs, the Egyptians mummified their dead with, amongst other things, with bitumen recovered from Dead Sea [**2**]. The widespread use of bituminous binders first began at the end of the 19th century with the advent of pneumatic tyre industry. Up to this time roads were constructed using broken stones, cemented with wet fine aggregates. Such roads had serious shortcomings such as dusty clouds in dry summer weather and surface erosion in wet conditions. Initially coal tar, available as by product of coal gas industry, was used to prevent erosion with limited success. As late as the sixties, Tar and bitumen were used in roughly equal quantities as road binders. The decline in coal Tar availability and other problems associated with it, led to gradual switch over to bitumen as the predominant material for use as an ideal road binder.

Bitumen are derived from crude oil, which in turn originates from the remains of marine organisms such as, phytoplankton, algae and other vegetable matters which gets deposited on the ocean bed [**3**] or earth crust. This accumulated biomaterial, over billions of years, gets converted into crude oil, under the effect of huge heat and the enormous weight of the upper layers of earth. This crude oil eventually gets trapped in impermeable rock forming large underground reservoirs. The crude oil can sometimes rise through faults in the layers above, coming to the ground surface. Crude oil compositionally is a mixture of hydrocarbons with varying but small proportions of non hydrocarbon constituents and some trace of metals. Most crude oil is now extracted from underground by drilling [**3**].

1.1.2 Chemistry of Bitumen

Bitumen, a non-crystalline black or dark brown viscous material, is substantially soluble in carbon disulphide (CS_2) solvent. Bitumen obtained from different sources of crude oil, has different composition of hydrocarbon. The bitumen content of crude petroleum oil can vary between 10% and 40% or even higher percentage. The crude is classified into three broad types based on the residue left behind on distillation of crude oil, these are: (a) bitumen containing mainly cyclic hydrocarbon and aromatic (b) paraffin based which mainly contain alkanes giving paraffin wax as residue (c) bitumen and paraffin based which mainly contain naphthenic hydrocarbon and aromatic giving mixture of bitumen and paraffin wax as residue [**4**].

Chemically bitumen is a complex mixture of hydrocarbons of high molecular wt and minor amounts of heteroatom containing molecules of high boiling points and with functional groups such as oxygen, nitrogen, oxygen and sulphur. These heteroatoms impart functionality and polarity to the molecules and may disproportionately contribute to the properties of bitumen [**5**]. Heavy metals like vanadium and nickel usually exist in trace amounts in the form of inorganic salts and oxides or in porphyrinic structures [**6**]. Although there is only a minor amount of these functional groups in the bitumen, they strongly influence the properties of bitumen and its interaction with other materials, such as stone aggregates.

Table 1.1 Elemental Composition of Bitumen

Element	Range
Carbon	88-82%
Hydrogen	11-8%
Sulphur	6-0%
Nitrogen	1-0%
Oxygen	1.5-0%

As bitumen is extracted from crude oil, which has variable composition according to its origin, the precise breakdown of hydrocarbon groups in bitumen is difficult to determine. However, elementary analysis of bitumen manufactured from a variety of crude sources shows that range of composition may be as shown in Table 1.1

The precise composition of bitumen varies according to the crude sources. Although the chemical composition is very complex as per Whiteoak [**2**], it is possible to separate bitumen into four main chemical compositions. These are:

✓ Asphaltenes
✓ Maltenes or Resins
✓ Aromatics
✓ Saturates

These four groups are not well defined and there is inevitably some overlap between these groups. The overall properties of the bitumen are determined by the combined effect of these fractions.

Asphaltenes are n-heptane insoluble black or brown amorphous solids having carbon, hydrogen in addition with small amount of nitrogen and Sulphur. They are highly polar, complex materials of high molecular weight (between 1,000 to 100,000). Asphaltenes typically constitute 5 to 25% of the bitumen. The asphaltenes content has a considerable effect on the rheological characteristics of bitumen [7]. Increasing the asphaltenes content produces harder bitumen with a lower penetration, higher softening point and higher viscosity. In short, asphaltenes define the stiffness and rigidity of the bitumen constituent. Within the medium of bitumen, asphaltenes tend to associate together to form micelles of high molecular weight. On heating the gel structure of the micelles is broken down, which however gets reformed on cooling. Prolonged heating of bitumen may lead to irreversible breakdown of asphaltene composition.

Resins are n-heptane soluble dark brown in colour, solid or semi-solid and high polar in nature. The high polar nature makes the resins very strong adhesive. The average molecular weight ranges from 500-50,000. The resins part of the bitumen act as a peptising or dispersing agent for the asphaltenes, therefore an increase in resins results in a solution (sol) structure, whereas a reduction forms a gelatinous (gel) structure in the bitumen. Resins mainly work as stabilizers, which hold every constituent together in the bitumen [**8**].

Aromatics have the lowest molecular weight naphthenic aromatics compound and form the major proportion of the bitumen (40-65%). They have a very low polarity and form a dark brown viscous liquid that acts as a dispersion medium for the other high molecular weight aromatic like asphaltene in the bitumen. Aromatics have an average molecular weight in the range of 300-20,000. They are responsible for the adhesive properties of the bitumen.

Saturates are similar to base oil consisting of straight and branch aliphatic hydrocarbon chains which together give the fluid properties of the bitumen. They have the lowest average molecular weight like aromatics, white or straw in colour and forms 5-20 % of the total bitumen.

1.1.3 Production of Bitumen

Of the wide variety of crude oils commercially available, only a limited number are considered to be suitable for producing bitumen of the required quality. The bitumen content of crude petroleum oil can vary between 10% to 40% or even higher percentage. Residues from the distillation of meticulously selected crude oils provide the base materials for bitumen production. Bitumen refining separates the lighter fractions from the residues. Several manufacturing methods are used to produce specification bitumen’s depending on the crude source and processing capabilities available. Often a combination of processes is practiced. The illustration (Fig.1.1) shows a compilation of the main process employed in refinery.

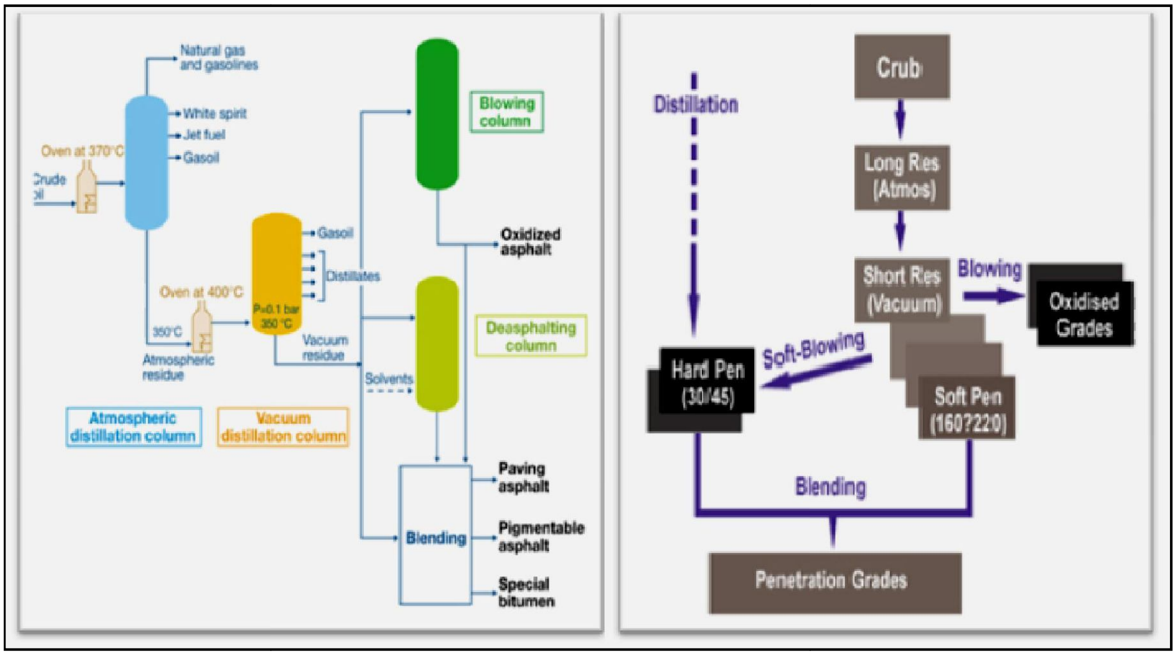

Fig.1.1 Typical Bitumen Production Scheme

Distillation

The most common refining process for producing bitumen is straight reduction from crude oil using atmospheric and vacuum distillation. In the above diagram (Fig.1.1), initially atmospheric distillation is used to separate lighter fuel fractions and heavier component at the bottom. The heavier fraction left out in the kettle after distillation is known as an atmospheric residue. The atmospheric residue is introduced into a vacuum distillation unit, where due to pressure reduction; lighter fraction is recovered without any significant thermal cracking of the molecules. Depending upon the specification grade required, the remaining residue called short residue can be used as such or further processed either as a component or blown further to the desired penetration/viscosity grade.

Solvent de-asphalting

Specific solvents can also be used to separate the lubricant and bitumen components of crude without damaging their chemical structure. Solvents like propane, butane, pentane etc. are used in solvent deasphalting process called ROSE Process. It separates asphaltenic residue from short residue. The deasphalted residue is hard bitumen which are used in blends to produce the desired specification grade product.

Oxidation

Bitumen can be further processed by blowing air through it at elevated temperatures (280°C on average) to alter its physical properties for commercial applications. Depending on the degree of oxidation, oxidized bitumen could be of two distinct types: air rectified and oxidized. Oxidized bitumen have a distinctive consistency at room temperature and a rubbery nature. The process of oxidation increases the stiffness and softening point of the bitumen and considerably alters key physical properties. Varying the length of the oxidation or air blowing process varies the extent of the reaction and produces distinctive end products. Oxidized bitumen are used in roofing applications, while air rectified bitumen are used in paving applications and some roofing applications.

Blending

The final bitumen product can be produced to technical specification either directly in the refining process or by blending bitumens of different physical properties and solvents. Blending of higher and lower viscosity residues in the required proportions may take place at the refinery, at terminals or at a third party facility, where blend components and finished products can be easily transported and distributed for use.

1.1.4 Characterization of Bitumen using Various Test Methods

There are many conventional test methods such as penetration, softening point and viscosity were used to evaluate the quality and consistency of bitumen binders during the 19th centuries. These conventional grades of bitumen are termed as penetration grade. Penetration grade is determined by the softening point and the penetration test methods.

Penetration

The penetration measures the consistency of the bitumen at a given standard conditions of service temperature (25°C), time (5 Sec), and load (100 g). The test method is described in ASTM D5.

Viscosity

Viscosity tests measure the time required for the bitumen binder to flow through a calibrated glass viscometer. Viscosity values are obtained at 60°C and 135°C. Viscosity specifications are based on absolute viscosity, which is calculated by pulling the bitumen through the viscometer with a vacuum at 60°C and whereas kinematic viscosity, the bitumen flow under its own weight at 135°C. Kinematic viscosity is related to dynamic viscosity of the bitumen binder in which capillary tube viscometer is used to measure the time required for a fixed quantity of material to flow through a standard orifice. In India generally a specification IS: 73 (4th revision) (Table 1.2) is followed at present for road works in general.

Softening Point

The softening point is the temperature at which the bitumen soften enough to allow the balls enveloped in bitumen to fall a distance of 25 mm into the bottom plate. Softening point determine the temperature susceptibility of bitumen binder within the temperature range of 30-157°C using the ring and ball apparatus immersed in distilled water or ethylene glycol. The test method is described in ASTM D36.

Table 1.2 Requirement for Paving Bitumen (4th revision is: 73; *clause* 6.2)

Sr.No	Characteristics	Paving Grade				Method of Test, Reference to IS No.
		VG 10	VG 20	VG 30	VG 40	
1	Penetration at 25°C, 100g, 5 s, 0.1 mm, *Min*	80	60	45	35	IS 1203
2	Absolute viscosity at 60°C, Poises,	800–1200	1600-2400	2400-3600	3200 4800	IS 1206 (Part 2)
3	Kinematic viscosity at 135°C, cSt, *Min*	250	300	350	400	IS 1206 (Part 3)
4	Flash point, (Cleveland open cup), °C, *Min*	220	220	220	220	IS 1448 P:69
5	Solubility in trichloroethylene, percent, *Min*	99.0	99.0	99.0	99.0	IS 1216
6	Softening point (R&B), °C, *Min*	40	45	47	50	IS 1205
Tests on residue from rolling thin film oven test (RTFOT)						
7	Viscosity ratio at 60°C, *Max*	4.0	4.0	4.0	4.0	IS 1206 (Part 2) IS 1208
8	Ductility at 25°C, cm, *Min*,	75	50	40	25	IS 1206 (Part 2) IS 1208

1.1.5 Superior Performing Asphalt Pavements (Superpave) Test

Unfortunately, both softening point and the penetration only measure the bitumen sample at a specific temperature and they do not give any correct indication of how the binder would perform at a wide range of temperatures, which the bituminous pavement might normally experience during the road construction time and also during its lifetime. Therefore, these tests are considered empirical and unreliable to predict bituminous pavement performance [**9**]. Since conventional tests as above were unable to predict a correct correlation with the performance of the bitumen pavement in-service, the strategic Highway Research Program (SHRP) was initiated in the late 1980s in the United States. The aim was to develop realistic specifications for bitumen binder based on the bitumen and bituminous pavement performance parameters. The concept behind the Superpave development was to develop performance based tests and specifications for hot mix asphalt binders which performs well in-service [10-11]. The Superpave PG specification (AASHTO MP1) requires the physical properties of the binder to be specified at the temperature ranges in which the material will be used with primary aim to preclude the three primary forms of distress in HMA: rutting, fatigue cracking, and thermal cracking. The temperature range where the specified properties are met is defined as the binder grade, and this range spans from the very high temperatures the binder is exposed to during production and construction to the large range from high to low temperatures the binder is subjected to in service. Both short- and long-term aging are considered in the PG system through the use of the rolling thin film oven test (RTFOT) and the pressure-aging vessel (PAV), respectively. The associated binder grade selection process uses environmental data for a specific highway section (HS) to select the grade required for use in HMA that will provide adequate performance at a selected reliability level. The Superpave specification tests which received global acceptability, consider bitumen's fundamental physical properties which directly relate to field performance. It was found that rheology is the best way to characterize the performance properties of bitumen's gel structures. Rheology is the study of deformation and flow of matter. Now a day's the dynamic shear rheometer (DSR) and bending beam rheometer (BBR) are essential parts of the hot mix asphalt specification and are recognized as the most potentially valuable tools. For hot mix, DSR testing is done at the high pavement temperature, and BBR testing is done at a temperature to characterize the rheology at the low pavement temperatures.

Dynamic Shear Rheometer (DSR)

The Dynamic Shear Rheometer (DSR) is a dynamic oscillatory test apparatus that can be used to describe the viscous and elastic behaviour of bitumen over a range of temperatures and frequencies. DSR measures the complex shear modulus (G*) and phase angle (δ) of bitumen. Complex shear modulus (G*) indicates the recoverable elastic response and delta (δ) is recoverable and non-recoverable deformation of bitumen binder. Performance-based properties for hot mix asphalt binders are determined by the DSR for a minimum strength modulus (G*/sin (δ) and a maximum phase angle (δ). The higher the strength modulus is, the better would be the resistance to deformation. The lower the phase angle, the more it is able to recover its original shape after being deformed by a load. Multi Stress Creep Recovery (MSCR) mode of operation of DSR gives a more accurate characterization of percent recovery (recoverable strain) and J_{nr} values (inverse of stiffness) and is particularly more relevant to modified bitumen. Lower J_{nr} means the residue is more resistant to deformation, flow or bleeding. Since SHRP research was conducted on unmodified bitumen only, it was argued that Superpave PG specifications may not therefore completely cover the requirements desired from polymer modified binders. Therefore, the US also considered the so-called "PG Plus" specifications for modified bitumen binders. Under these specifications, empirical tests such as elastic recovery in ductility test were incorporated to ensure that the modified bitumen does have adequate amount of elastomeric polymer.

Bending Beam Rheometer (BBR)

The Bending Beam Rheometer (BBR) test provides a measure of low temperature stiffness and relaxation properties of bitumen. These parameters give an indication of bitumen binder ability to resist low temperature cracking. BBR gives valuable information like other Superpave binder tests; the actual temperatures anticipated in the area where the bitumen binder will be used. BBR measures the stiffness and m-value. Stiffness is a measure of the thermal stresses developed in the Hot Mix Asphalt (HMA) as a result of thermal contraction. The slope of the stiffness curve, m, is a measure of the rate of stress relaxation. The maximum stiffness criteria of 300 MPa and the minimum m-value criteria of 0.30 has been recommended in performance graded binder specifications (ASTM: D 6682), which is generally an accepted value for mitigating low-temperature cracking.

Moisture Susceptibility Test for Bituminous Mixture

There have been number of test methods developed and applied in the past to predict the moisture susceptibility of asphalt mixes. The evaluation methods commonly used to assess moisture susceptibility of bitumen are classified into two categories: qualitative tests and quantitative strength tests. The Boiling Water Test (ASTM D-3625) is qualitative tests, while the Modified Lottman Test (AASHTO T283) and Immersion-Compression Test (AASHTO T165) are quantitative strength tests.

Modified Lottman Indirect Tension Test

The test procedures include testing of unconditioned and moisture conditioned samples to assess the impacts of water on indirect tensile strength. Dry samples are compacted to 7% air voids, conditioned in a 25°C water bath for 2 hours to reach the required testing temperature, and them tested. Moisture conditioned samples are compacted to the same density, subjected to vacuum saturation to a target threshold, then conditioned using an optional freeze thaw cycle and/or submersion in a water bath of 60°C for 24 hours. After conditioning, the sample is submerged in a 25°C water bath for 2 hours to bring the conditioned samples to the required test temperature. The output of the test is the tensile strength ratio (TSR), defined as the ratio of wet to dry indirect tensile strength. The TSR (AASHTO T283) was adopted by the superpave system as a critical parameter in mix design.

Immersion-Compression Test

According to the Immersion-Compression Test (AASHTO T-165) six cores are utilized. Each core is four inches in diameter and four inches in height. The cores are compacted with a double plunger at 3,000 psi for two minutes. An air void content of 6% is attained. The six cores are split into two groups. The first control group is a group. The second group is conditioned in a water bath at 49°C for four days or at 60°C for one day. After conditioning the required time, the unconfined compressive strength of each core is found. A testing temperature of 25°C and a loading rate of 0.2 in/min are used. The retained compressive strength is calculated. The minimum required retained strength of 70 percent is specified by many agencies [12]. However, the Immersion-Compression Test has produced retained the strengths close to 100 percent, even when stripping is higher in the cores. Thus, this test is not much sensitive enough to measure moisture damage.

Boiling Test

The boiling test is well established as a simple and effective method to evaluate moisture susceptibility on the loose bituminous mixture. With this test method the adhesion quality is determined based on the remaining percentage of the coated area by visual observation. In applications to Hot Mix Asphalt (HMA), the coating is assessed only after boiling to evaluate moisture sensitivity because in most cases the material is fully coated prior to conditioning. As an output this test evaluates stripping through the use of coating loss. For the Boiling Water Test, the loose bituminous mix is added to boiling water. The bituminous mix is allowed to remain in the boiling water for 10 minutes. Moisture damage is measured by observing the loose bituminous mix in the water. The percentage of the total visible area of the aggregate that retained its original coating of bituminous mix is rated as either above or below 95 percent. One of the deficiencies of the current standard is that the coating is assessed visually. Alternatively, three methods, namely absorption method, the mass loss method, and image analysis has also been studied to evaluate the degree of stripping of the coating.

1.1.6 Requirement of Additives for Bitumen

To meet the demands of technological and demographic changes, the use of polymer modified bitumen has become increasingly important. Increased stress on highways due to heavier loads, higher tire pressures, and ever rising traffic counts are causing premature failures of flexible pavements. Severe climates, always a source of concern and an increased emphasis on safety have prompted research towards the amelioration of highway paving materials. As the network of highways ages, the demand for quality maintenance and recycling products is becoming more important than that for new construction. To address these problems, the highway engineer and researcher has turned to modification for custom design of pavement materials.

1.1.7 Classification of Additives for Improving Bitumen Quality

Bitumen are modified with a number of additives and broadly classified polymeric and other chemical modifiers as follows (Fig.1.2)

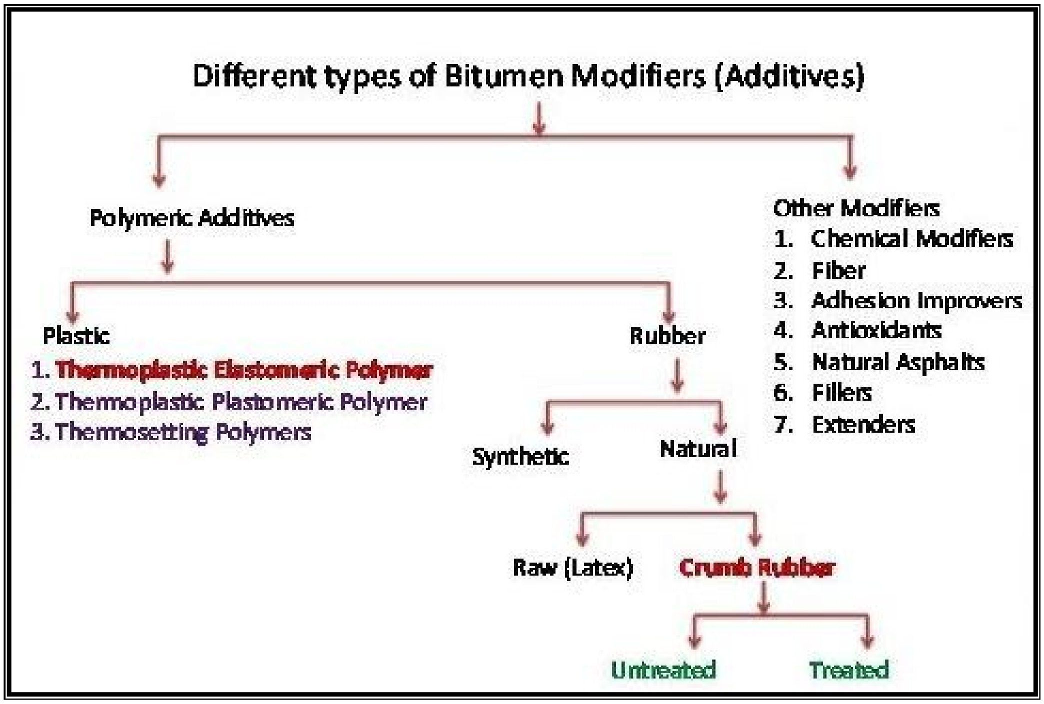

Fig.1.2 Classification of Additives for improving bitumen Quality

Polymers as Potential Additives

Polymer modification has been increasingly employed in asphalt concrete, primarily for control of short-term permanent deformation (rutting). At the same time, polymer based modification of bitumen typically improves binder’s ductility, thereby providing a binder that is more durable to pavement stress and deformation [14]. There is also evidence that polymer modifiers may improve the aging characteristics of a binder so that the deleterious impact of oxidative aging is delayed, leading to a more durable pavement.

While all of these effects positively impact the durability of polymer-modified pavements, there is a need to quantify these improvements and their duration in the presence of oxidative aging process. Such an improved understanding will lead to better modified binder selection and to a better cost benefit analysis, thereby leading to more efficient use of funds. The term “polymer” simply refers to a very large molecule made by chemically reacting smaller molecules (monomers) with one another either in long chains or clusters. The sequence and chemical structure of the monomers from which it is made determines the physical properties of a specific polymer.

Polymers, most often used in modifying bitumen, can be grouped into two general categories: elastomers and plastomers. As the name implies, elastomers can be stretched like a rubber band and recover their shape when the stretching force is released. Therefore, elastomers have the ability to resist permanent deformation (rutting). Elastomers therefore improve elasticity, cyclic loading properties, adhesion, durability, impact resistance, resilience and toughness etc. Several different types of elastomeric polymers are used for modifying bitumen. Typical examples of elastomers are: natural rubbers, styrene-butadiene-rubber (SBR), styrene-butadiene-styrene (SBS), and Neoprene. However, plastomer form tough, rigid, three dimensional networks within the bitumen. These plastomer give high initial strength to the bitumen to resist heavy loads. However, they have lower strain tolerance and may crack at high strains. Examples of plastomers for modifying bitumen are: ethylene vinyl acetate (EVA); ethylene butyl acrylate (EBA); polyethylene; and ethylene-methyl-acrylate (EMA) copolymer. Most highway agencies in the United State primarily specify and use elastomers. Plastomers use in road making is virtually nonexistent.

1.1.8 Supply & Demand Scenario of bitumen in India

The fastest growing Indian economy will further demand a good road transport network with a high quality pavement structure, to cater to emerging very heavy traffic-both in terms of number and axle loading. Road-laying under the Golden Quadrilateral project and the North-South and East-West corridors project of National

Highways Authority of India (NHAI) has been quantitatively significant. According to the budget estimates of the Ministry of Shipping, Road Transport and Highways, Govt. of India, 5,694 km of road-laying and four-laning project, out of a total of 5,846 kilometers, are targeted for completion in the present fiscal year. While these road development projects help in adding considerable infrastructural assets, their construction and subsequent maintenance phases require huge amount of suitable pavement materials.

With the fast growing Indian road transportation infrastructure demand, the road network is undergoing a challenging development of high quality pavement structure under National Highways Development Programmes (NHDP), Golden Quadrilateral project and the East-West and North-South corridors project of National Highways Authority of India, State Highways Improvement Programmes (SHIPs), Bharat Nirman, Pradhan Mantri Gram Sadak Yojana (PMGSY) etc. where a huge budget provision has been made by the Government of India. The average annual demand of bitumen in India is around 4 MMT (million metric tonnes) and it is estimated that bitumen alone cost nearly 45% of the overall bituminous pavement road construction cost [**13**]. With the unprecedented growth of road construction industry, local demand has exceeded the bitumen production and supply which is adversely affecting the completion of many road projects in time. The industry has also witnessed sharp cost escalations in bitumen binder over the years. Due to continuing rapid modernization and strong growth in road building construction, India today represents one of the largest and fastest growing bitumen markets and driving the demand further needing significant import of quality bitumen and bituminous products. However, in India predominant grade of bitumen in use still is VG-20 which is equivalent to PG 64-22 grade. There is an urgent need to use more and more PG 76-22 grade (which can only be made through blending with suitable polymer chemistry) for heavily trafficked roads.

1.2 Literature Review

Bibliographic studies were conducted to understand the knowledge available in area of additive application to improve bitumen which is the focus of the current research work. This literature review related to present work consists of four parts; the first part deals with the effect of antistripping additives in bitumen. The key topic in the second part is to study the reactive polymer modified bitumen. The third part describes the in-situ polymerization in bitumen matrix. Last part describes the laboratory approaches used to evaluate the rheological properties of the blended two or more polymers in bitumen.

1.2.1 Antistripping Additives for Bitumen

Bitumen in pure form is not suitable for recent roads and current heavy traffic, therefore, forced engineers to modify bitumen to improve its performance during service life [**15**]. The modified binders are more stable under heavy loads, braking, accelerating forces and shows increased resistance to permanent deformation in hot weather. It resists fatigue loads and having better adhesion of aggregates with binders. Literature search indicated that use of antistripping chemicals in bitumen is in practice the world over for several decades and a variety of chemistries, both organic and inorganic have been examined.

Curtis in his review article on ‘Liquid Antistripping Chemicals’ reported examples of some basic additives which have been used in the past and include primary alkyl amines, e.g., lauryl amine, stearyl amine, and the alkylene diamines, particularly the alkyl-substituted alkylene diamines, e.g., N-stearyl-1,3-propylene diamine [**16**]. Carlo Gravarini & G. Rinaldi reported good antistripping property of a product derived from the reaction of tetra ethylene pentamine (TEPA) & formaldehyde (CH_2O) [**17**]. Al-Handy reported use of starch as more cost effective binder modifier for road pavements and more specifically for special paving construction sites when fuel or chemical resistance is desired [**18**]. Evans E.D claimed significant antistrip property in the reaction product of ozonized fatty acids and polyamines [**19**]. Sawatzky, H reported that nitrogen containing fraction derived from sewage sludge, improves the adhesion of asphalt to aggregate in asphalt concrete [**20**]. Rick A reported the use of Tall Oil to increase the adhesivity of bitumen to mineral aggregates [**21**]. Hesberger reported the use of Dihydroxy aluminium sulphonates as an antistripping agent in bitumen [**22**]. Jack N. Dybalski of Armak Company recommended treatment of aggregates with cationic type surfactants to get maximum antistrip behaviour [**23**]. D.N. Little & Jon A. Es reported the use of lime as antistrip agent which also gives certain additional advantages such as stiffening of bituminous binder, control of fracture growth at low temperature, reducing aging effect and altering plastic properties of bitumen [**24**]. The literature survey indicates some chemical transformations have been reported in literature. Shukla reported reaction of PET with ethanolamine using acetic acid, sodium acetate and potassium sulphate as a catalyst which was completed in 8 hours, resulting in bis (2-hydroxyethylene) terephthalamide (BHETA) [**25**]. The paper reports use of PET material and amine in molar ratio of 1:6 with maximum conversion efficiency into bis (2-hydroxy ethylene) terphthalamide (BHETA) in the range of 68.2 to 83.2% under different catalytic conditions and temperature range of 170^{o}C to 180^{o}C. Magda E.T. et al studied chemical recycling of post consumer PET bottle using ethanolamine and dibutyl tin oxide (DBTO), sodium acetate, cetyl trimethyl ammonium bromide as catalyst at 190^{o}C in about 62% yields and used the reaction product in developing anticorrosion paints [**26**]. Spychaj T reported aminolysis and aminoglycolysis of waste PET in which experiments were conducted at 200-210°C (with a molar ratio of recurrent polymer unit to amine of (1:2) [**27**]. The amines used were diethylenetriamine, triethylenetetramine and their mixtures, p-phenylenediamine or triethanolamine. The products thus developed were tried out as a hardener for liquid epoxy resin. From the prior art information it becomes clear that in PET aminolysis process to recycle waste PET, the conditions used were quite severe and makes use of a range of catalysts, some of which are quite costly and hazardous. The literature survey indicates that there is no report of using the PET derived compounds as antistripping agent in bitumen. There are also no reports of using the product derived from PET by aminolysis for any applications in the petroleum industry in general and bitumen in particular.

In the light of foregoing literature search, the **Chapter 2** describes the synthesis of terephthalamide derivative from poly (ethylene terpthalate) (PET) waste by aminolysis reaction and their successful test as antistripping additives for bitumen. The results indicated a comparable performance of terephthalamide products, to commercially used antistripping chemicals.

1.2.2. Reactive Polymer Modified Bitumen

To meet the demands of technological and demographic changes, the use of polymer modified bitumen has become increasingly important. Increased stress on highways due to heavier loads, higher tire pressures, and ever rising traffic counts are causing premature failures. Severe climates, always a source of concern, and an increased emphasis on safety have prompted research towards the highway paving materials. As the network of highways ages, the demand for quality maintenance and recycling products is becoming more important than that for new construction. To address these problems, the highway engineer and researcher has turned to modification for custom design of pavement materials.

Among many different additives used in bitumen modification, the Polymeric additives broadly classified as thermoplastics, thermosets, thermoplastic elastomers and the rubbers have been more common. Currently, the most commonly used polymer for bitumen modification is the thermoplastic elastomers such as styrene-butadiene-styrene triblock copolymer (SBS). SBS, as an elastomer, improves the high temperature performance, rutting resistance, resist heavy traffic load with the elasticity of bitumen and therefore globally used for bitumen modification in large volume at present. However, due to thermodynamically unstable nature of bitumen containing SBS, it shows some serious problems such as early phase separations when stored at high temperature, tendency to degrade on exposure to heat, oxygen, and UV light etc. [**28-31**]. These conditions generally lead to undesirable ageing of bitumen and polymer degradation, thus affecting the overall performance of the blend. Such observation has led to research studies for improving the modified bitumen properties through the use of novel additives and other polymers. Some polymers called reactive polymers are being considered as novel bitumen modifiers which may improve bitumen polymer compatibility and also reduce the amount of additive required. These reactive polymers are known to perform via forming chemical bonds with some bitumen molecules, thus improving the mechanical behavior, storage stability and temperature susceptibility of the resulting binder. Some research being carried out in this area is described below:

Polyphosphoric acid (PPA), a short chain reactive oligomer has been used in modified bitumen for quite some time now. J.F. Masson [**32**], while reviewing the PPA's use in bitumen, concluded that PPA cannot dissociate and react with bitumen unless enclaves of high dielectric constant exist in bitumen. The PPA, when used in the appropriate ratio, helps blended bitumen in improving its high temperature characteristics. As per Yudollahi G et al [**33**] PPA reacts with some functional groups present in bitumen, breaks asphaltene agglomerates into individual particles and helps create better distribution of asphaltene in the maltene phase and thus improves the elastic behavior of the bitumen.

Roghanizad [**34**] studied the rheological behavior of bitumen containing 5% precipitated calcium carbonate coated with a thin layer of a polymeric compound and demonstrated that it increases the rutting resistance and good storage ability. Using FTIR and SEM, he demonstrated that agglomeration of asphaltene particles has been prevented.

Chemically modified crumb rubber asphalt (CMCRA) prepared by Memon G.M [**35**] through chemical treatment with hydrogen peroxide of the crumb rubber resulted in improved elastic recovery property of the bitumen and showed good performance both in the lab and in the field tests which lasted for the six years under different environmental and weather conditions.

S. Keyf et al [**36**] studied two reactive polymers namely ethylene terpolymer (SRETP) and ethylene terpolymer(ETP) supplied by Du Pont to improve features of 60/70 penetration grade modified bitumen used on highways. A new asphalt compound with increased softening point and decreased penetration and ductility values was reportedly formed. On testing it showed decreased sensitivity towards temperature and increased rutting resistance behaviour.

Giovanni Polacco [**37**] studied the viscosity functions of bitumen blended with polymers such as styrene-butadiene-styrene (SBS), ethylene vinylacetate (EVA) and reactive polymer "Ethylene terpolymers" (RET) at different temperatures in steady-state rate sweep tests. He demonstrated that the first two polymers form a physical network that is swollen by the asphalt, while the latter (which is functionalized with glycidyl methacrylate) is cross linked and/or have formed chemical bonds with the molecules of asphaltenes. In the presence of SBS or EVA, at certain temperatures, the viscosity curves exhibit a Newtonian behavior at low shear rates, followed by two distinct shear-thinning phenomena.

In another article Polacco G et al [**38**] studied some reactive functional group of terpolymers of ethylene glycidyl methacrylate (GMA). The polymer was introduced into bitumen to enhance its mechanical properties. The reactive epoxy ring in GMA mainly reacted with carboxylic groups in bitumen and formed an ester link between each other. It was also observed that the epoxy ring also got opened by a hydroxyl group and a new hydroxyl group formed on the polymer main chain. In this way polymer network involving bitumen molecules could be produced. Due to the polarity and the formation of chemical bonds with bitumen molecules, the compatibility between polymers and bitumen is greatly improved, as well as the storage stability.

In another interesting literature, Pei-Hung Yeh [**39**] studied chemically modified polypropylene additive to optimize the performance of polymer modified bitumen binders containing various concentrations of isotactic polypropylene and maleated polypropylene. The bitumen blends were compared with the unmodified asphalt to assess the thermal transition properties of asphalt

M.J. Martín-Alfonso [**40**] reported the effect of processing temperature on the reaction between bitumen compounds and an isocyanate-based reactive polymer, synthesized by reaction of polymeric MDI (4,4′-diphenylmethane diisocyanate) with a low molecular weight polyethylene-glycol (PEG). Rheokinetics experiments, viscosity measurements at 60°C, atomic force microscopy (AFM) characterization, thin layer chromatography (TLC-FID) analysis and thermo gravimetric studies (TGA) were performed on the reactive polymer and on samples of MDI-PEG modified bitumen containing 2wt.% of the polymer. Results showed the existence of an optimum processing temperature for the formation of a polymer–bitumen network, reaction ability and polymer thermal degradation.

Golzin Yadollahi [**41**] recently showed that the use of reactive polymer Vestenamer®, a product of Evonic Degussa Corporation, when used in 4.5% concentration along with 1% PPA in Bitumen modified with crumb rubber (CRMB), there is a significant improvement in the tackiness properties of the blend. Crumb rubber (CR) has been used as an additive in asphalt mixes since the 1930s. CRMB is known to improve performance of asphalt mixture with respect to thermal susceptibility, elastic behavior, fatigue cracking resistance and aging stability. It is being used extensively because of its relatively lower cost and potential advantage of environment protection as CR is derived from used tyres available in large scale. CR alone as a modifier function is a non-reactive additive while Vestenamer® reacts chemically with CR and bitumen to produce a uniform, low tack, rubber-like composite. This chemical bond is attributable to the double-bond structure of the Vestenamer, which permits cross-linking with the sulphur associated with the asphaltenes and maltenes in the bitumen and creates a macro-polymer network. Vestenamer® reportedly improves the performance of pavement at high temperature conditions, where rutting is the most prevalent type of pavement distress.

In the light of foregoing literature search, the **Chapter 6** describes the properties of a reactive polymer based modified bitumen formulation made by using polyoctenamer, sulphur in bitumen and their properties was compared, with well established SBS elastomer based PMB. The storage stability, softening point, microstructure, rheological properties, Marshal Strength, Temperature susceptibility, Stripping and rutting characteristics of these blends were studied.

1.2.3 In-situ Polymerization in Bitumen

Literature search indicates that the existing art of making modified bitumen is based mostly on the physical blending of additives with bitumen, which has certain built in deficiencies such as expensive, phase separations, tendency to degrade polymer chain, hardening, etc. Such observations have led to research studies for improving the modified bitumen properties through in-situ polymerization. Very few research works are reported in literature where polymer is generated in the body of bitumen.

In US 5,039,342, **[42]** bitumen has been chemically modified by reacting ethylenically unsaturated monomers in the presence of the bituminous materials present in the asphalt. By chemically bonding long polymeric chains with asphaltene molecules it is possible to alter the physical properties of bitumen without encountering the phase separation problems experienced with physical blends of bitumen and polymer. The invention disclosed an aliphatic monomer is used e.g. styrene, butadiene, ethylene, propylene, vinyl acetate, isoprene, acrylonitrile and chlorostyrene.

In US 4,301,051, **[43]** bitumen is reacted with a polymerisable vinyl aromatic monomer and a rubbery polymer. The chemically modified asphalt can be cross linked by reaction with a cross linking agent such as a polycarboxylic acid, an organic isocyanate or an organic polyepoxide. The chemically modified asphalt compositions of the invention can be used in the treatment of glass fibers as well as in road paving applications and the like.

Sang-Yum Lee **[44]** and his co-workers introduced a novel method that could modify neat asphalt by insitu polymerization of DMP. In this paper, a polymer-forming monomer, DMP was added to the neat asphalt and polymerization occurred autonomously, without adding any external catalyst for the polymerization, only with bubbling of the air. The author showed polymer produced in the bitumen was polyphenyleneoxide (PPO) and it enhanced the mechanical properties such as the tenacity and toughness of the bitumen.

Another patent EP 2123684 A1 **[45]** discloses a method for synthesizing a homopolymer or copolymer from an alkenyl monomer such as styrene having the average molecular weight (M_w) of the homopolymer or copolymer is less than 100,000, comprising one step of polymerising process, in the presence of a bituminous component. The patent further discloses that bituminous component is less than 50wt% based upon the weight of the alkenyl monomer. They also observed that the presence of the bituminous component limits the molecular weight of the homopolymer or copolymer. Increasing the amount of the bituminous component decreases the molecular weight of the polymer. The resulting polymer contains the bituminous component, and depending on the amount of polymer present, the colour of the resulting polymer ranges from yellow to brown to black. This invention provides yellow or brown or black polymer without the need for the addition of pigments.

In the light of foregoing literature search, the **Chapter 3** describes the novel approach to prepare PMBs by using terephthalamide derivative and MDI in bitumen to form a reactive type of polymer modified bitumen and characterize the fundamental properties of the PMBs were characterised by using conventional test methods.

1.2.4. Combining Effect of Two or More Polymers in Bitumen

Some researchers have modified the bitumen binder by blended two or more polymers followed by treatment with a stabilizer, in order to improve the performance of bitumen. This section describes the cohesive effect of two polymer blend in the bitumen.

Yang Peng [**46**] and his co-worker studied the blending of Styrene-butadiene-styrene tri-block copolymer (SBS) and waste polyethylene (WPE) to modify the base asphalt in order to improve the performance of asphalt. They used a special stabilizer (mainly sulphur), SBS/PE combined asphalts showed much better storage stability at high temperature and no visible phase separation was observed under optical microscope observation. The physical properties and dynamic mechanical properties (including viscosity change and rheological characteristics) of the SBS / PE combined asphalt with and without sulphur were studied respectively.

Due to the poor compatibility between tire rubber and bitumen, the storage stability of crumb rubber-modified bitumen are normally poor at high temperature. Once agitation stops, the dispersed tire rubber particles separates quickly from the bitumen and the polymer rich phase migrates to the upper part of the storage bitumen tank, while bitumen rich phase segregates into the lower parts. This results in the binder becoming useless for paving road application [**6**]. Thus, it is necessary to improve the storage stability of tire rubber-modified bitumen for construction of paving bituminous road use.

N.F. Ghaly [**47**] studied the enhancement of the properties of crumb rubber modified asphalt binder by the addition of SBS and sulphur. The author found that tire rubber modified bitumen binder has improved the storage stability through the addition of Styrene-Butadiene-Styrene (SBS) and elemental sulphur. Golzin Yadollahi [**48**] studied the effects of CR, PPA and a commercial plastomer vestenamer (trans-polyoctenamer) on the behaviour of unmodified bitumen.

The literature review thus provides a background to understanding the affects of different types of additives such as antistripping additives derived from waste plastic, reactive polymer and in-situ polymerized product on bitumen. In consideration of the preceding literature review and keeping the aim of this thesis in mind, it was decided to use different types of additives to modify bitumen. Although researcher has developed wide varieties additives for bitumen modification, this thesis specifically focused on following topics:

- Use of terephthalamide derivative synthesis from PET waste.
- In-situ polymerization in bitumen
- Effect of Aminolysed PVC on bitumen properties
- Combining the effect of two polymers on the properties of bitumen
- Reactive polymer modified bitumen

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1.4 Scope of Present the Present Thesis

Large volumes of waste scrap tires and plastics are generated now a day's causes environmental pollution which motivates the researchers to use these waste materials for bitumen modification. However, crumb rubber and waste plastic modified bitumen have some issues regarding storage stability as crumb rubber and plastic particles settles at the bottom of container which causes difficulty in transportation of these modified bitumen and therefore restricts their use for bitumen modification.

In consideration of the preceding literature review and keeping the above issues in mind, presents thesis aims to synthesize polymeric additives from waste plastic to get cost effective and storage stable modified bitumen. The synthesized waste PET derivatives used in this thesis also act as antistripping agents for bituminous application and found to possess 100% antistripping properties.

Another objective of this study is to carry out in-situ polymerisation to develop polyurethane and polyurea by reacting methylene diphenyl diisocyanate (MDI) with polyols and polyamines respectively (derived from PET waste) in the body of bitumen. Detailed rheological properties for in-situ polymerized product were also carried out.

In this thesis, we have also synthesized aminated polyvinyl chloride by the reaction of waste polyvinyl chloride with polyamines and studied their affects on the physico-chemical properties of bitumen.

Another objective of this thesis is to develop storage stable polymer modified bitumen with high elastomeric properties by using reactive polyoctenamer polymer along with cross linking agent in bitumen. The combination of reactive polyoctenamer along with cross linking agent also found to promote anchoring of crumb rubber in bitumen to produce storage stable crumb rubber modified bitumen. The use of reactive polymer to develop polymer modified bitumen & crumb rubber modified bitumen also avoid milling operation which further make the products cost effective and energy efficient.

Therefore, the present thesis is directed to the chemically conversion of waste plastic (such as PET and PVC) into useful polymeric compounds which in turn leads to several bituminous applications. The present research work also provides an alternate commercial way for the disposal of waste plastics keeping the environment free of pollution. This may contributes an important role in **Swachh Bharat Abhiyan** which is a national level campaign by the Government of India.

CHAPTER 2

Poly (ethylene terephthalate) (PET) Polymer derived terephthalamide chemicals as novel antistripping Additive for bitumen: An environmentally friendly approach for Waste disposal

Polyethylene terpthalate (PET) is potentially a large scale environment pollutant. Aminolysis of PET as a way to chemically degrade into monomers and oligomers for the purpose of recycling is known for quite some time. As per literature information utilization of such degraded products for large scale industrial use has seen only for limited applications. The present study reports to develop a simple green chemistry based aminolysis process for conversion of environmentally hazardous waste into industrially useful anti-stripping compounds used in bitumen. It has been observed during the study that bitumen doped with PET derived product improves property of bitumen towards making it less susceptible to damage through ingress of moisture while retaining all other properties of the bitumen.

2.1 Introduction

Poly(ethylene terephthalate) (PET) is a semi-crystalline thermoplastic polyester, constitutes 18% of total polymer produced worldwide. Majority of the world's PET manufacture is for synthetic fibers with bottle production accounting for around 30% of global demand. PET used for soft drink and water bottles has grown at exceptional rates, growing at an average annual rate of approximately 4.3% during 2009–2012. Due to the nontoxic nature, durability and crystal clear transparency of PET, they find large scale use in various forms, including bottles for drinking water, soft drinks etc. Further, due to their non-biodegradability nature and current poor recycle/disposal practices, PET based polymeric product have made themselves not only omnipresent but also a major culprit for environmental pollution. In response to the growing production of PET bottles, recycling has played a major role in reducing waste by converting into alternative useful products.

Two major processes, namely mechanical recycling and chemical recycling have been applied in order to recycle used-PET. However, quality problems associated with recycled PET processed through mechanical recycling do not permit its use in the manufacture of bottles for drinking purposes. However, it is used for making low grade fibers and various other products. Since the mechanical recycle of PET waste has severe limitations, chemical recycling is considered as one of the best possible alternatives.

Chemical recycling provides a simple method of cleaving PET into its monomeric and dimeric form, which can then be used for the reproduction of plastic bottles and other industrially useful products. Due to the ester linkage of PET, it is 100 percent recyclable and can be transformed into various polyester grades, film grade and bottle grade plastic and other useful chemicals. Chemical recycling of PET polymer is divided into six groups: glycolysis, methanolysis, hydrolysis, ammonolysis, aminolysis, and other methods. However, aminolysis has been little explored as chemical recycle of PET for synthesis of industrially useful products. Shukla and Harad 2006 [**1**] have investigated aminolytic degradation of PET waste in the presence of ethanolamine with different chemicals such as sodium acetate, glacial acetic acid and potassium sulphate as catalysts. The product obtained, bis (2-hydroxy ethylene) terephthalamide (BHETA), has the potential of being a good precursor for further chemical reactions to synthesize useful products.

In recent years, one of the important developments in the field of alternate application of virgin or used plastic/rubber material (mainly, styrene butadine styrene, crumb rubber and ethylene vinylaceted, polyolefines, poly(ethylene terephthalate) waste type), is their use in making polymer modified bitumen (PMB). Currently, PMB are used in huge quantities in making road highway infrastructure. PMBs offer some definitive advantages over conventional bitumen such as lower susceptibility to seasonal temperature variations, higher resistance to deformation at elevated pavement temperatures, better adhesion, rheological properties, better age resistance properties, less cracking even in heavy axle load traffic conditions etc. [**2-6**]

However, due to high cost of popularly used polymers such as SBS, EVA etc. crumb rubber modified bitumen (CRMB) and waste plastic are used as an alternative modifiers for bitumen. However, the use of plastic in India, has just begun during the last decade, albeit slowly, due to lack of infrastructure facilities. There are also no reports of using products derived from PET waste by aminolysis for any applications in the petroleum industry sector in general and bitumen in particular. This fact motivated us to study the chemical recycling of PET waste. We have converted it to various terephthalamide derivatives and tested them as antistripping additives for bitumen. This was done inspite of the fact that there are certain reports which questions the role of nitrogen compound as antistripping additives in bitumen. For example N. Castaño [7] reported that Nitrogen based antistripping doped bitumen when stored at elevated temperatures (140 °C – 190 °C), two types of reactions are possible.

(a) **Formation of Non Active Amide Adduct**

The reaction of nitrogen based functional groups of the antistripping agents with polar functional groups of the bitumen and therefore, becomes less effective antistripping agent.

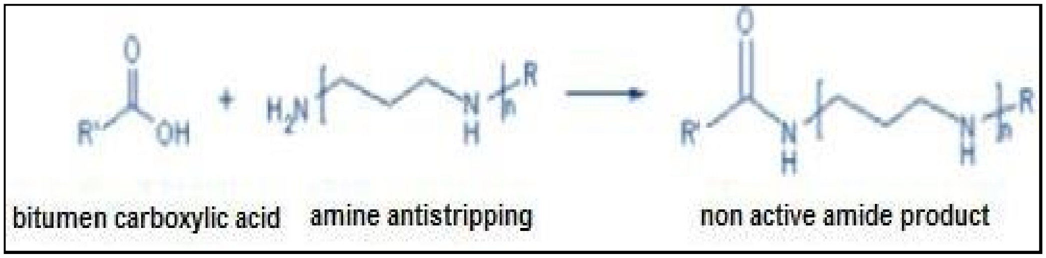

Fig.2.1 Formation of non active amide adduct

(b) Self Oxidation of the Antistripping Agents in the Bitumen

Oxidation of the nitrogen functionality of nitrogen containing anti-stripping chemical under normal use of bituminous concrete may make it a poor antistripping chemical. The oxidation process may also increase the number of functional groups present in the bitumen and these new functional groups may further react with nitrogen containing antistripping agents affecting their reactivity and performance.

We successfully attempted to overcome the above observed deficiency by focusing on the synthesis of least chemically reactive polyamide derivatives from waste PET.

In the present study, we have used waste PET bottle as a synthon and chemically converted it through a new and noncatalytic, nontoxic route into several benzamide derivatives. The developed benzamide derivatives were successfully tested as antistripping additives for bitumen. The results shows that the performance properties of waste PET derived products are comparable with commercially available antistripping agents. The works thus open a new direction for the recycling of waste PET in bituminous concrete, which may help in alleviating a major environmental pollution problem.

2.2 Experimental

2.2.1 Materials

This study specifically used PET bottle grade and virgin PET polymer. The plastic bottles were stripped of all labels and washed thoroughly with water to remove any potential contaminants. The clean bottles were cut into squares (flakes) of about 1 cm by 1 cm and dried at ambient temperature. All chemicals used in this studied are of LR grade.

2.2.2 Synthesis of Antistripping Additive

We developed a simple and general procedure for the PET aminolysis reactions as summarized below:

A three necked 500 ml round bottomed flask equipped with a heating mantle, overhead stirrer, water condenser, nitrogen gas sparging tube and a thermo well pocket containing a thermometer in the range of 100-350 ^{0}C was charged with 30 grams of PET (in the form of small cut pieces), 100 ml xylene, 60 grams of a polyamines e.g. triethylene tetraamines (TETA), tetraethylene pentamine (TEPA). Current of dry nitrogen was constantly maintained. The mixture is heated at 130 to 140 ^{o}C to reflux for 8-hours. As the PET degradation completed, the solution turned homogeneous (i.e., flakes disappeared completely). At the end of the reaction the unreacted amines if any and others by product were recovered under vacuum. The resulting product is recovered in quantitative yields is a semi-viscous liquid at ambient temperatures.

We confirmed the general applicability of the developed method by undertaking reaction of PET with ethanolamine (EA) under the same set of conditions as above. After 8 hours of reaction, we got bis(2-hydroxyethylene) terephthalamide (BHETA) in quantitative yields. The melting points (232 ^{o}C), IR spectra, mass spectrum, ^{1}H-NMR of our reaction product and a synthetic reference sample matched nicely as shown in (Fig.2.2, Fig.2.3 and Fig.2.4). Our developed process, in contrast to earlier reported methods by Shukla and Magda E.T. et al **[1, 8]**, is a simple route for eliminating the need of costly and toxic catalysts and high temperature reaction conditions. The developed method could also be classified as an example of green chemistry.

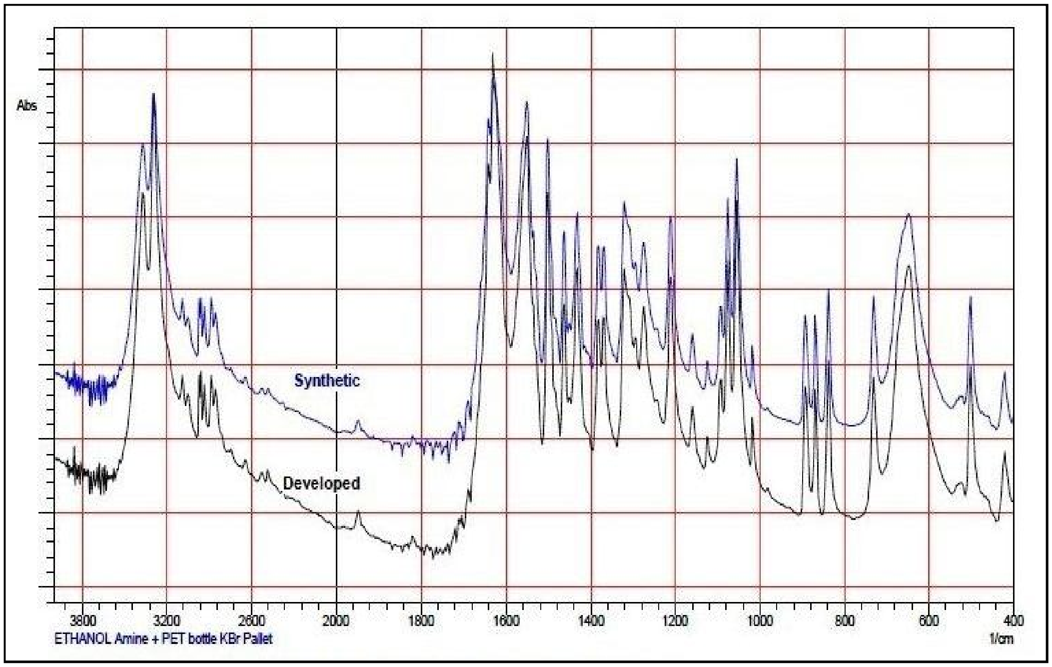

Fig.2.2 IR Spectrum of BHETA (our developed and Synthetic Product)

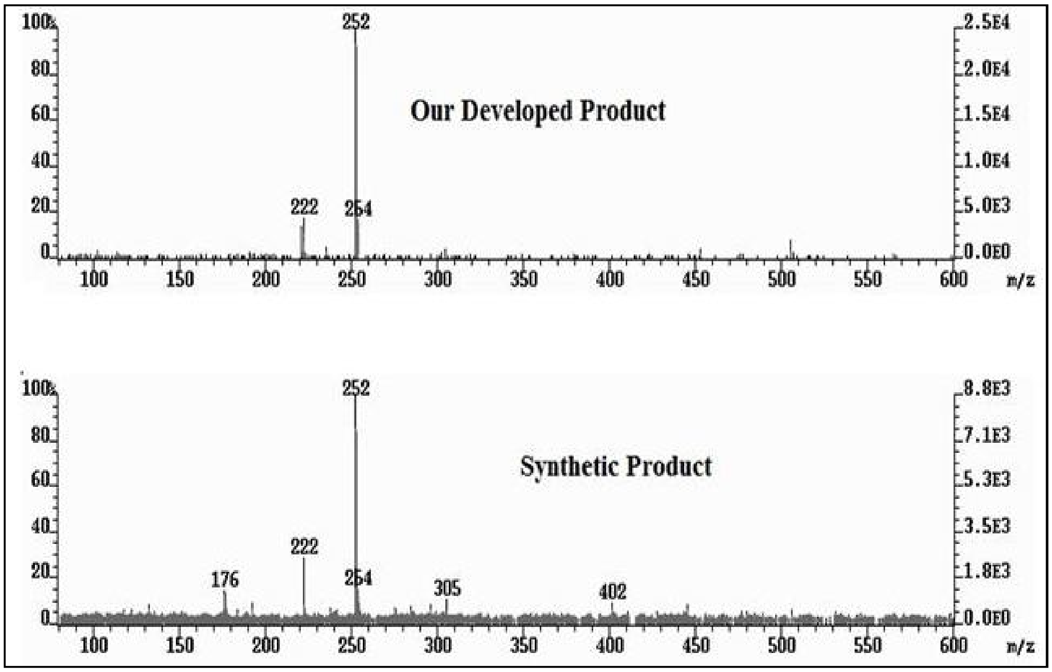

Fig.2.3 Mass Spectrum of BHETA (our developed and Synthetic Product)

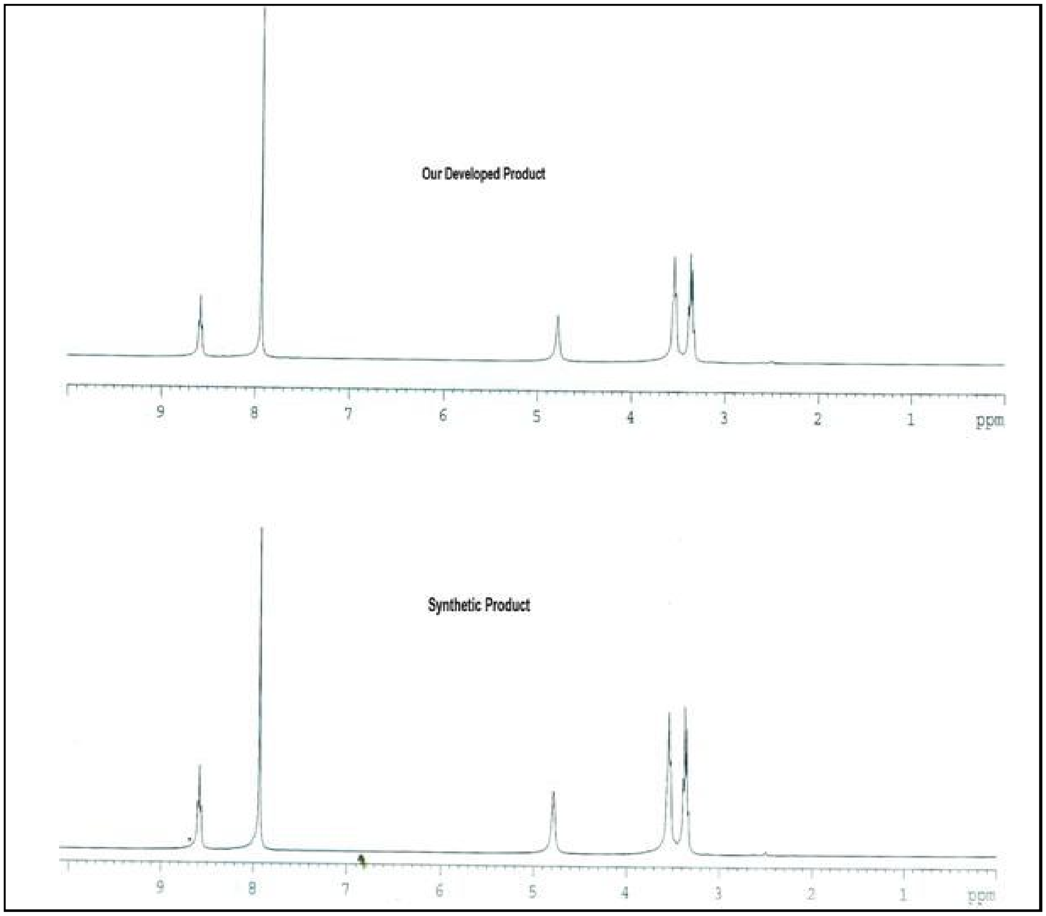

Fig.2.4 ^{1}H-NMR spectrum of BHETA (our developed and Synthetic Product)

2.3. Results and Discussion

2.3.1 Spectroscopy Characterization of Antistripping Agent

Advanced analytical techniques such as FTIR (Spectrum BX Series), Proton NMR spectroscopy (Bruker ACP-300 MHz NMR spectrometer) and Mass spectra (Micromass Autospec Ultima mass spectrometer in the field desorption (FDMS) mode) were used to characterize the reaction product. The reaction provides a product which basically appears to be the mixture of related compounds. The conversion of PET into amide is confirmed by IR analysis, which shows the disappearances of ester peak at 1735 cm^{-1} and the formation of amide peaks at 1637.8 cm^{-1} and 1547.2 cm^{-1} for TEPA amide (Fig.2.5) and 1637.6 cm^{-1} and 1544.4 cm^{-1} for TETA amide (Fig.2.6). NMR spectrum of TEPA and TETA displays chemical shift at 8.7-8.6 ppm,

(Fig.2.7 and Fig.2.8) which further confirms the presence of aromatic amide proton. The mass spectrum analysis showed a major molecular ion peak at 510 confirming the formation of TEPA derived diamide (Fig.2.9). The Molecular ion peaks at 423 and 700 indicated the presence of the monomer and dimer of terephthalamide derived from TETA respectively (Fig.2.10). However, mass spectra also showed some extra peaks at higher range. These could possibly arise from other oligomers formed during the reaction or the impurities or some other additives originally present as a part of PET composition such as copolymer, plasticizer etc.

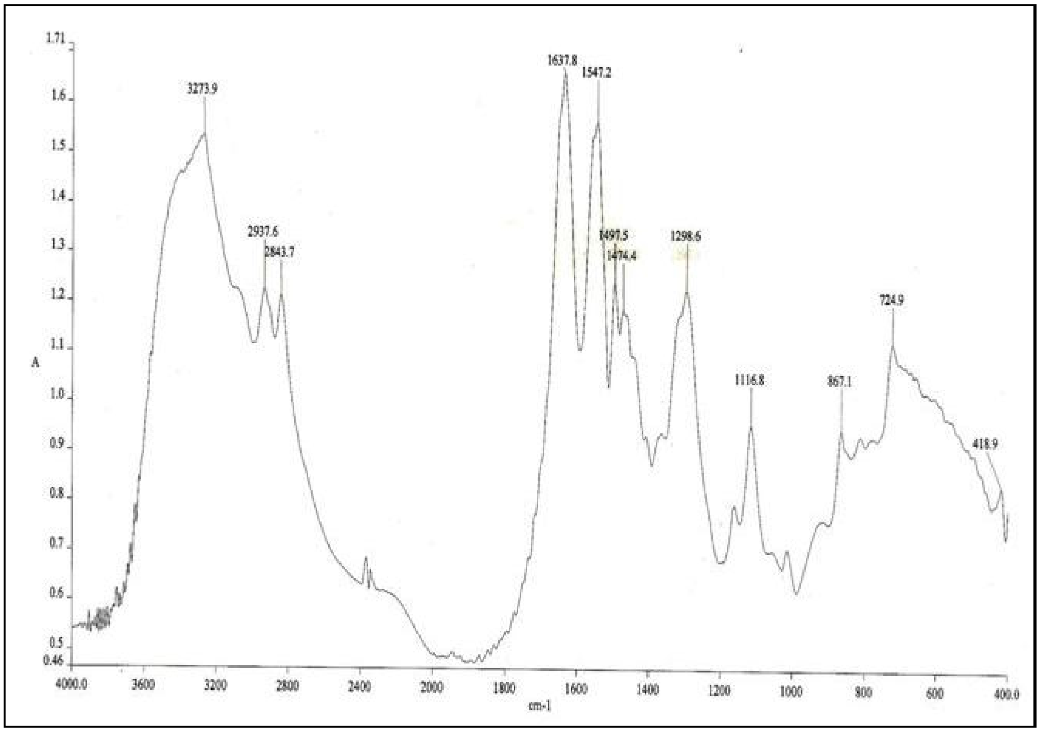

Fig.2.5 IR Spectrum of TEPA- terephthalamide

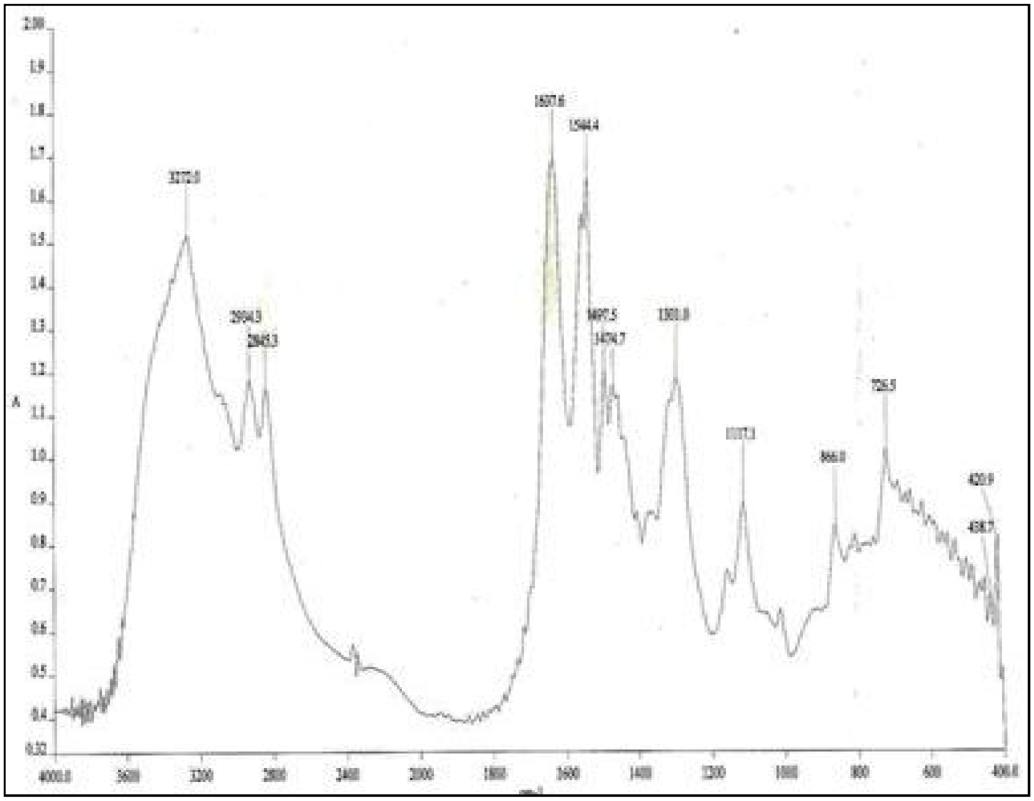

Fig.2.6 IR Spectrum of TETA- terephthalamide

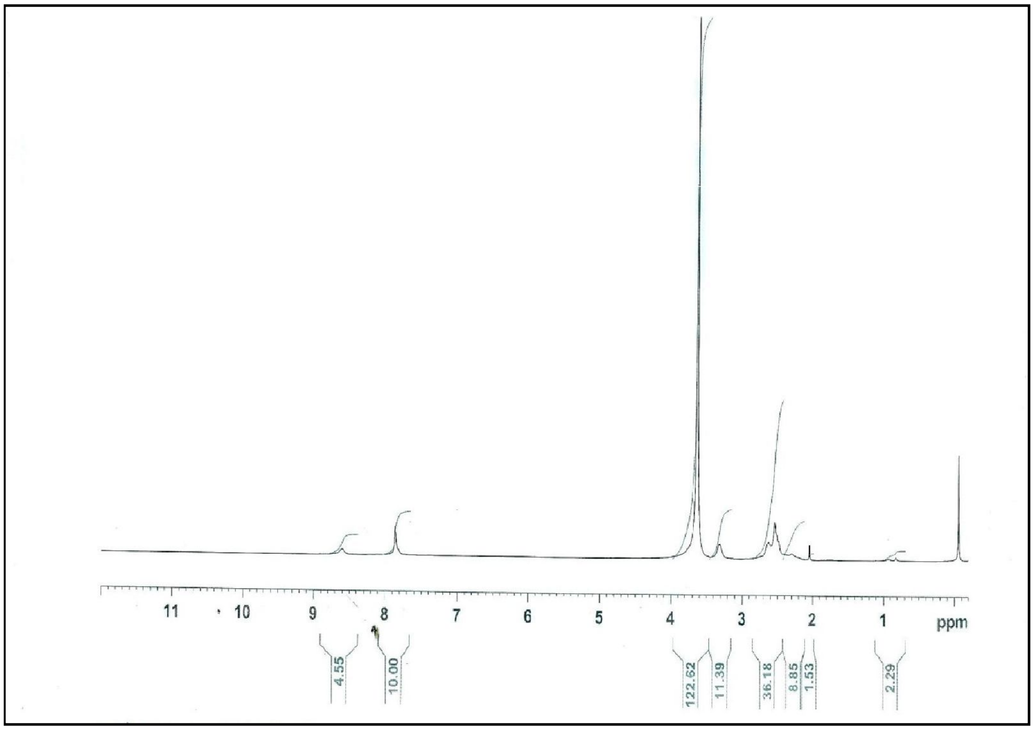

Fig.2.7 NMR Spectrum of TEPA- terephthalamide

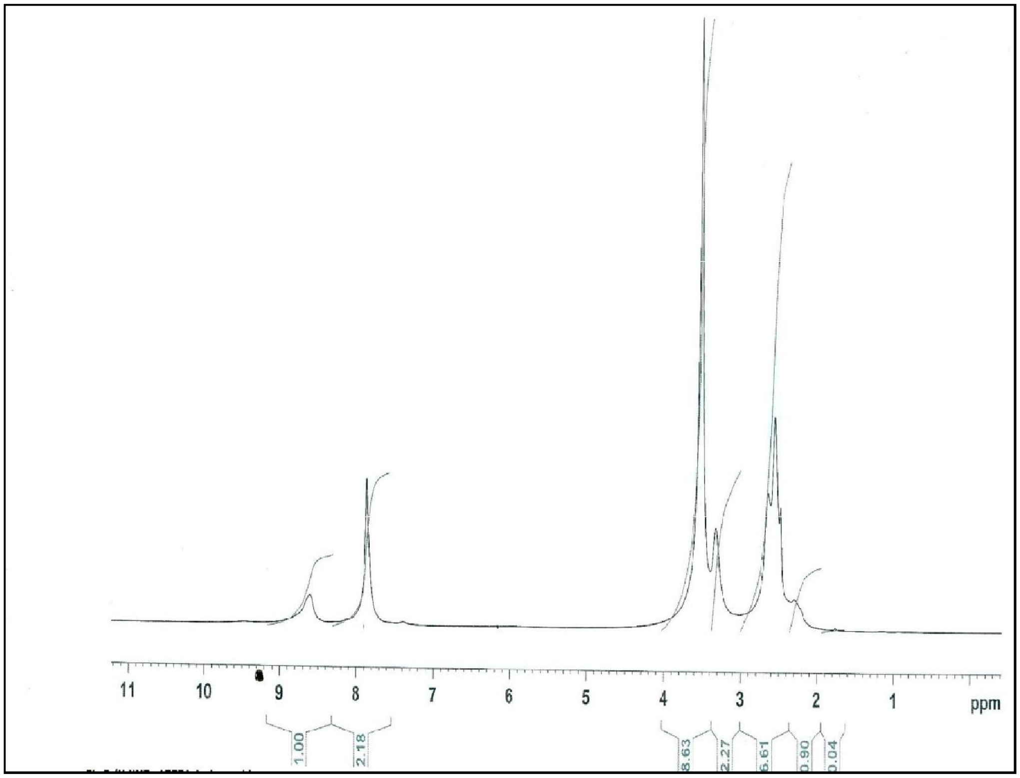

Fig.2.8 NMR Spectrum of TETA- terephthalamide

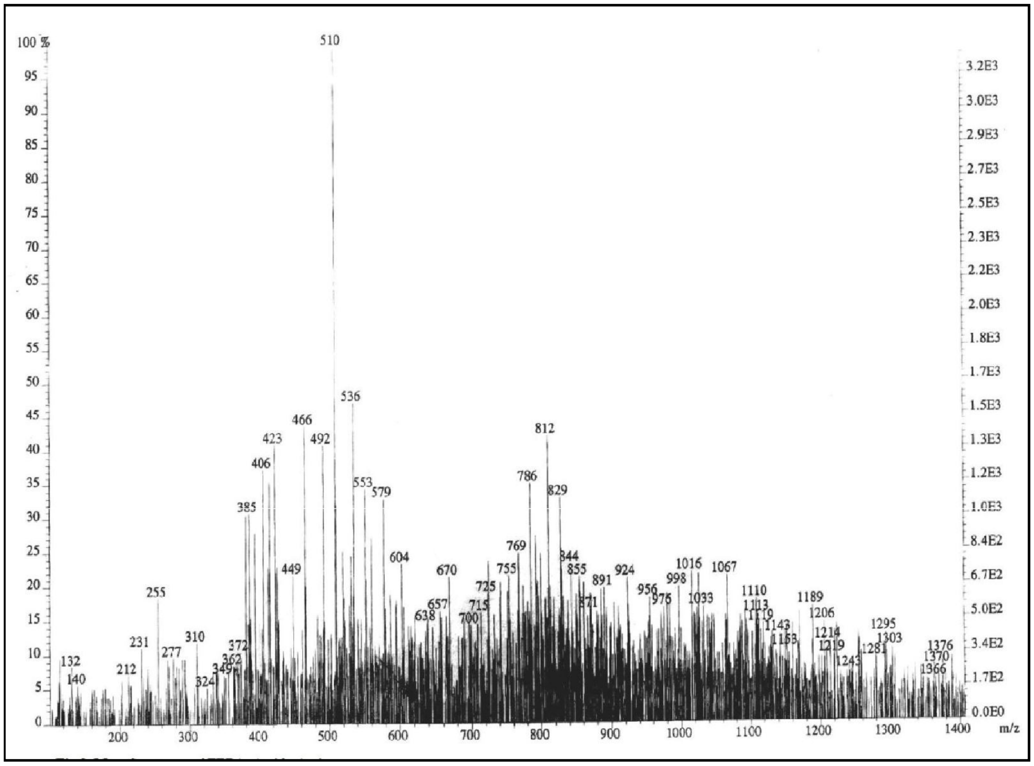

Fig.2.9 Mass Spectrum of TEPA- terephthalamide

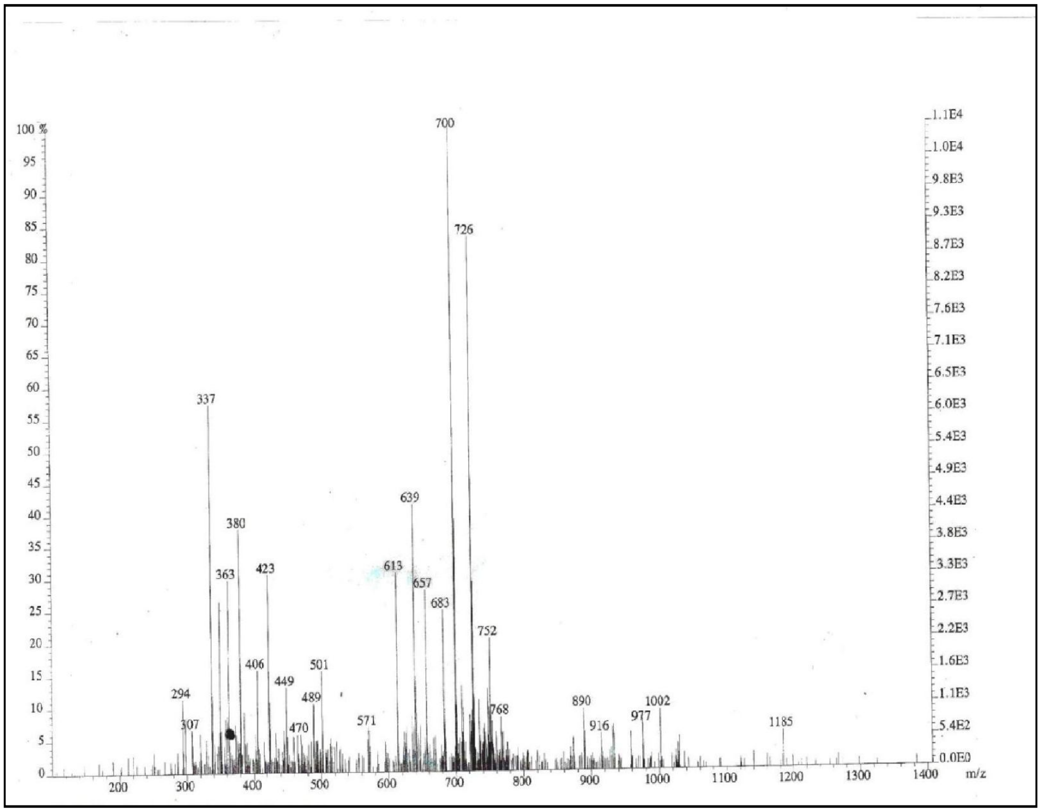

Fig.2.10 Mass Spectrum of TETA- terephthalamide

2.3.2 Evaluation of Antistripping additives

There are different performance tests which are based on laboratory and field test for evaluating antistripping properties developed over the years, but none are accepted fully correlating with real field conditions. Hot water boiling test and Marshall Stability test; as per ASTM D 3625-96 and ASTM D 6927-06 respectively, are commonly practiced to quickly asses the antistripping properties of various chemicals and aggregates.

Some of antistripping chemicals developed under this research study (code named PET-A & PET-B) were blended with bitumen in appropriate ratio and tested for physicochemical properties (Table 2.1); hot water immersion tests, (Table 2.2 and Fig.2.11). These tests confirm acceptability of developed product mixture as an antistripping chemical for bitumen and their performance is well comparable to commercial products (Table 2.2 and Fig.2.11), currently being used by the petroleum oil industry.

Table 2.1 Properties of Bitumen containing 0.5% of Developed Anti-Stripping Chemicals

Properties		Neat Bitumen	Product PET-A	Product PET-B	Referral specification
Absolute Viscosity (60^{0}c), Poise		1135	1840.79	1721.47	IS1206 (PART2)
Kinematics Viscosity (135^{0}C) (cst)		297	440.65	413.29	IS1206 (PART3)
Penetration 25 C (100g, 5s),0.1mm		87	70.3	71	IS1203/1978
Softening Point (Ring and Ball), ^{0}C, Minimum		45.5	47.5 ^{0}C	48 ^{0}C	IS 1205/1978
Ductility at 27 ^{0}C (5 Cm/Min)		100+	100+	100+	IS 1208 : 1978
Flash Point Pen Cup, ^{0}C		350	350	350	IS1209
After TFOT	Viscosity at 60 ^{0}C	3257.38	4495.27	4579.11	IS1206 (PART2
	Ratio of viscosity after TFOT and before TFOT	2.86	2.442	2.66	Requirement <4
	Ductility	100+	100+	100+	Requirement min 75 (IS1208)

PET-A: Bitumen containing reaction product of PET (bottle grade) and tetraethylene pentamines (0.5% w/w) and PET-B: Bitumen containing reaction product of PET (bottle grade) and tri-ethylene tetra-amines (0.5% w/w).

Table 2.2 Compare of hot water test result of terephthalamide antistripping versus commercial antistripping agents

Reaction products	Concentration of the antistripping additive				After TFOT (0.5%)	Passing Percentage
	0.3%	0.4%	0.5%	1.0 %		
Terephthalamide based on TETA	80-75% coated	90-85% coated	100% coated	100% coated	100% coated	
Terephthalamide based on TEPA	75-80% coated	90-85% coated	100% coated	100% coated	100% coated	90-100% coated
Commercial antistripping agent (WETFIX-AD-4F)	80-70% coated	85-80% coated	90-95% coated	100% coated	--	
Commercial antistripping agent (ZYCOSOIL)	95-90% coated	100% coated	100% coated	100% coated	---	

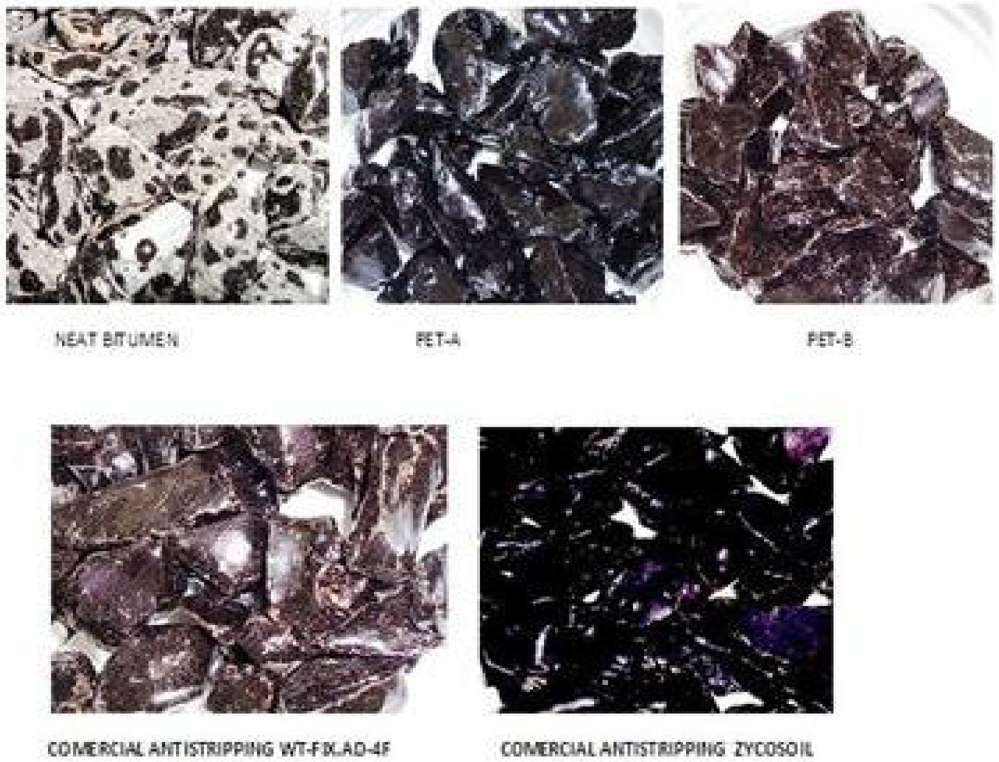

Fig.2.11 Hot Water Immersion Tests

2.3.3 Marshall Stability Test

The Marshall Stability test was done to evaluate the Marshall stability of the mix which is defined as the maximum load carried by the specimen at 60 ^{0}C and resistance to plastic deformation. The grading of aggregates selected for this project as per MORTH (2001) specifications is presented in Table 2.3. Marshall specimens were made at their optimum binder content 6% and immersed in the water bath for 24 hours at 60 ^{o}C and some other specimens were immersed in the water bath for 30 minutes at 60 ^{o}C. The results of Marshall Strength at their optimum bitumen content are shown in Table 2.4. The Marshall Stability tests were conducted on neat and developed binder mixes. It has been observed that the terephthalamide modified bitumen mix show better binding property, strength and more resistant to water. It has been observed that the stability values of mixes modified with terephthalamide have been increased significantly from 14.07 KN to 15.79 KN and 14.11 as compared to mix prepared with neat bitumen. Hence, the present research will not only strengthen the road construction but also increases the road life as well as will help to control the environment pollution. It is evident from the Table 2.4 that flow value of mix was decreasing slightly 2.48 mm in case of plain bitumen to 2.54 and 2.52 for modified binder. The decrease in flow value shows that the mixes become slightly more stable at 60 ^{0}C temperature.

Table 2.3 Gradations of Aggregate for Bituminous Concrete

Aggregate Sieve size (mm)	Requirement of MORTH	Aggregate gradation Adopted, % Passing
26.5	100	100
19.0	100	100
13.2	79-100	93.6
9.5	70-100	87.6
4.75	53-71	70.8
2.36	42-58	54.2
1.18	34-48	36.8
0.600	26-38	29.2
0.300	18-28	25.4
0.150	12-20	16.4
0.075	4-10	5.9

The retain Marshall Immersion test was done to estimate the resistance of mixtures against water. Marshall Specimens were made at their optimum binder content and immersed in the water bath for 24 hours at 60 °C. Some other marshall specimens were immersed in the water bath for 30 minutes at 60 °C too. The Index of Retained Strength (IRS) was then calculated using the following equation:

IRS= S1/S2*100% ……………………………………………………… (1)

Where: S1 = Marshall Stability for Marshal Specimens immersed in a water bath for 24 hours.

S2 = Marshall Stability for Marshal Specimens immersed in a water bath for 30 minutes.

Table 2.4 Marshall Stability Test

Compaction temperatures of all Marshall Specimens are 141^{0}C

Binder content	**(Marshall Strength KN / Flow in mm)**		
	Neat Bitumen	PET-B	PET-A
Marshall value of 5% dosage	12.45/2.49	13.76/2.01	12.95/2.35
Marshall value of 6% dosage	14.07/2.48	15.79/2.54	14.11/2.52
Marshall value of 6.5% dosage	11.68/4.08	12.05/2.79	11.24/3.10
Retained Marshall strength	74.27	84.35%	87.31%

PET-A: Bitumen containing reaction product of PET (bottle grade) and tetraethylene pentamines (0.5% w/w) and PET-B: Bitumen containing reaction product of PET (bottle grade) and triethylene tetra-amines (0.5% w/w).

All values of modified bitumen satisfy the minimum IRS requirements of 75%. These tests confirm acceptability of developed product mixture as antistripping chemical for bitumen.

2.3.4 Aging Behaviour

N. Castaño [7] reported that the real performance of the doped aged bitumen with nitrogen based antistripping agent decreases when stored at elevated temperature at 140 °C –190 °C. So following literature we focused on rheological properties of the product such as absolute viscosity at 140 ^{0}C temperatures for 30 days. The result (Fig.2.12) showed that the rate of increase in viscosity of neat binder was more as compared to doped bitumen. This result would imply that after addition of antistripping additives, the binder would be comparatively less temperature susceptible than neat binder.

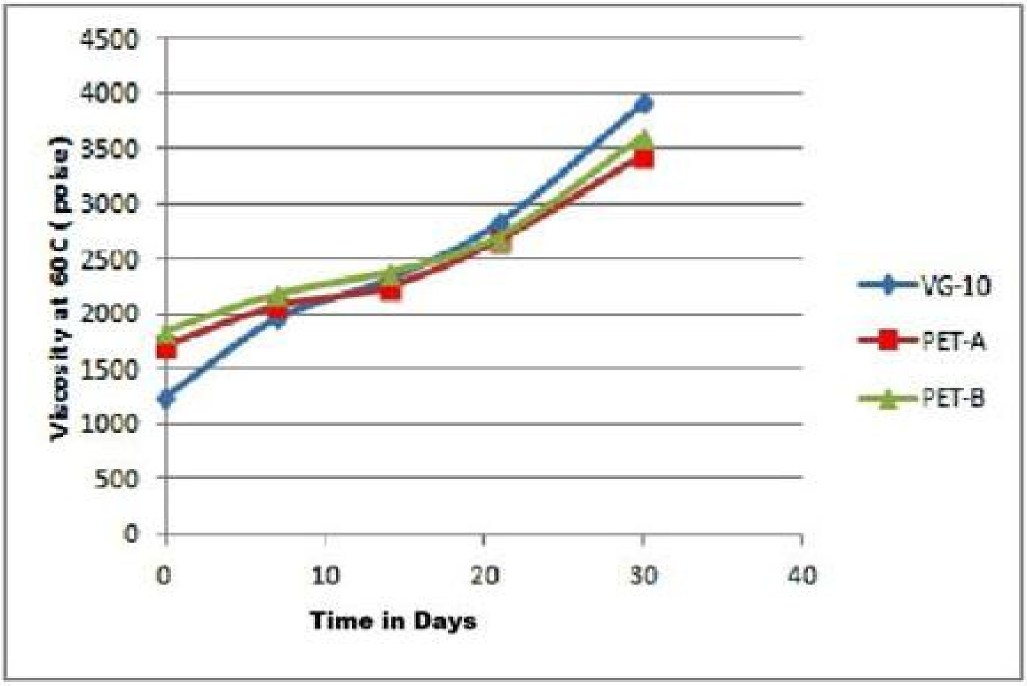

Fig.2.12 Viscosity aging effect on bitumen and dope bitumen

2.3.5 Dynamic Shear Rheometer

J. Kim [9] reported that one of the key concerns of consumers of antistripping chemicals is the fact that most amine-based liquid antistripping agents have a tendency to decrease the viscosity (analogous to reducing G*/sinδ) of the neat binder. To alleviate this, we performed dynamic shear rheometer (DSR) test on the neat binder containing 0.5% of terephthalamide derivative by weight of the binder and to determine its superpave binder performance grading against neat binder (PG 58-19 grade bitumen). DSR test results are shown in Fig.2.13, Fig.2.14, and Fig.2.15. The results showed that the RTFO aged binder for terephthalamide doped bitumen and neat bitumen, G*/sin(δ) values remained similar and also within the required limits, i.e. G*/sin(δ) values of bitumen > 2.2 kPa and G*. sinδ value < 5000 kPa confirming its rutting resistance and fatigue cracking factor almost equal to the neat binder's values.

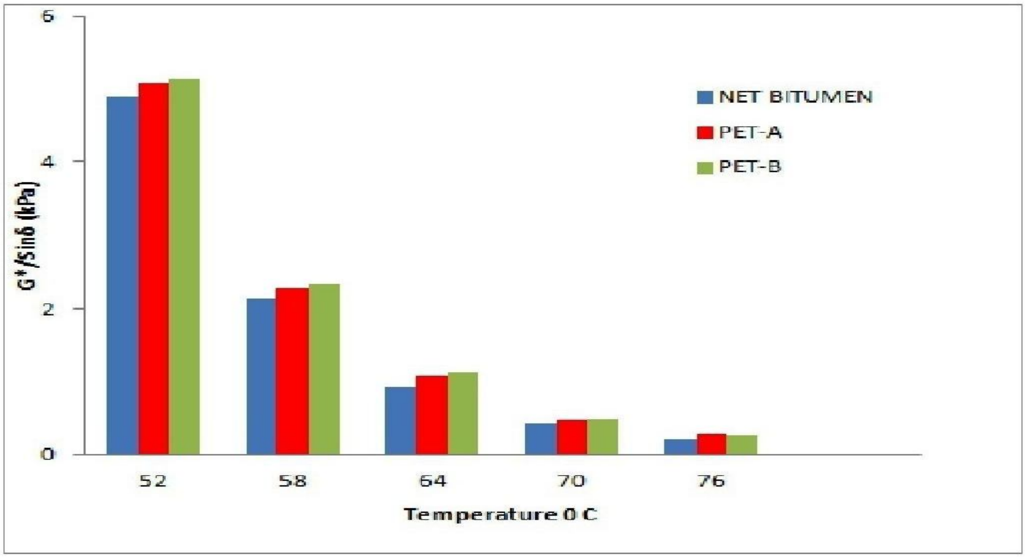

Fig.2.13 G*/Sinδ (kPa) Measured as a function of temperature of neat binder

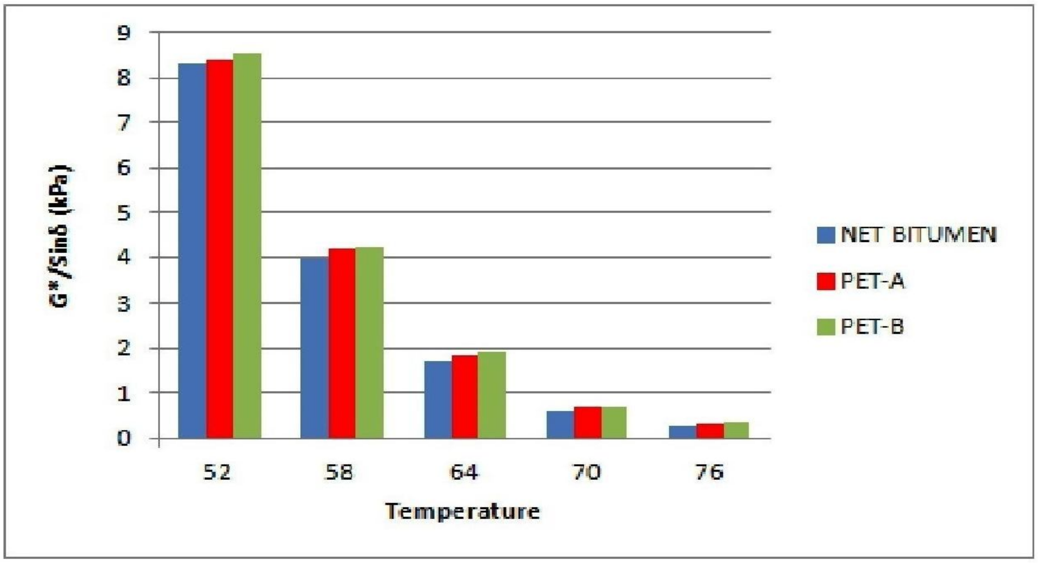

Fig.2. 14 G*/Sinδ (kPa) Measured as a function of temperature of

RTFO aged binder

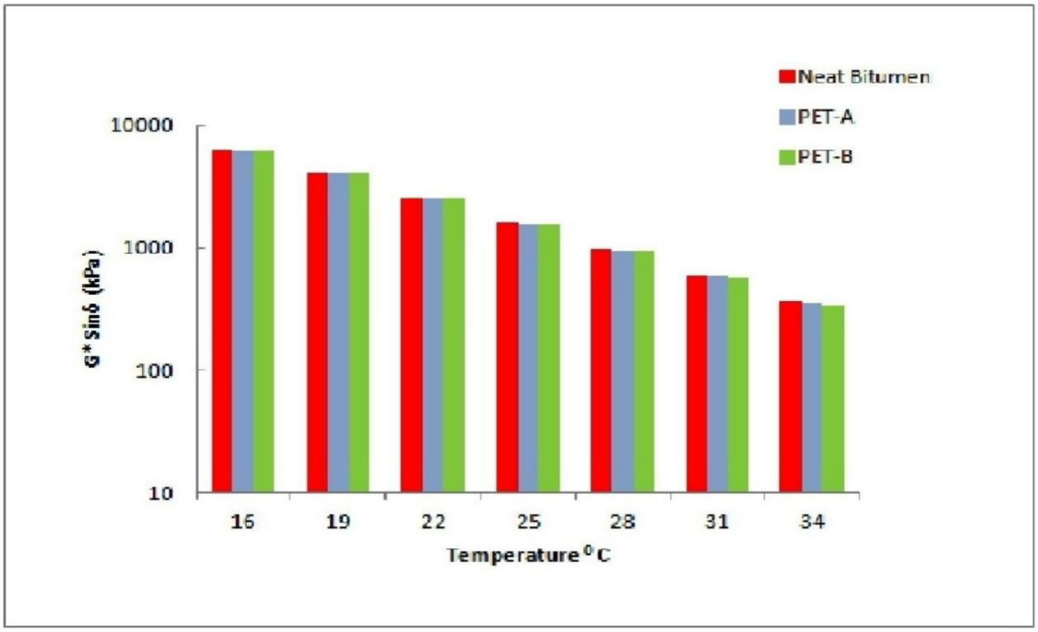

Fig.2. 15 G*.Sinδ (kPa) Measured as a function of temperature of PAV aged binder

2.3.6 Bending Beam Rheometer

In order to examine low temperature cracking properties, thin beams of bitumen were tested for creep stiffness at low temperature using the bending beam rheometer. The BBR measures the two important properties of bitumen such as stiffness and m-value. Stiffness is a measure of the thermal stresses developed in the bitumen as a result of thermal contraction. The slope of the stiffness curve, m, is a measure of the rate of stress relaxation. The maximum stiffness criteria of 300 MPa and the minimum m-value criteria of 0.300 has been recommended according to performance graded binder specifications (ASTM: D 6682), which is generally an accepted value for mitigating low-temperature cracking properties of bitumen. We carried out creep tests on PAV aged binders, at three different temperatures (-18, -12 and -6 ^{o}C) using the bending beam rheometer (TE-BBR, Cannon Instrument Company). Terephthalamide doped binder results (Fig.2.16 & Fig.2.17) were consistently matched with the desired value limits. Therefore, it would be safe to assume that unlike other reported antistripping additives for bitumen modification, the terephthalamide amine based antistripping chemicals when blended in 0.5% ratio (wt/wt) with neat bitumen shows a positive trend in binder properties in terms of both rutting and fatigue resistance and also remain within the superpave performance grade of 58-19.

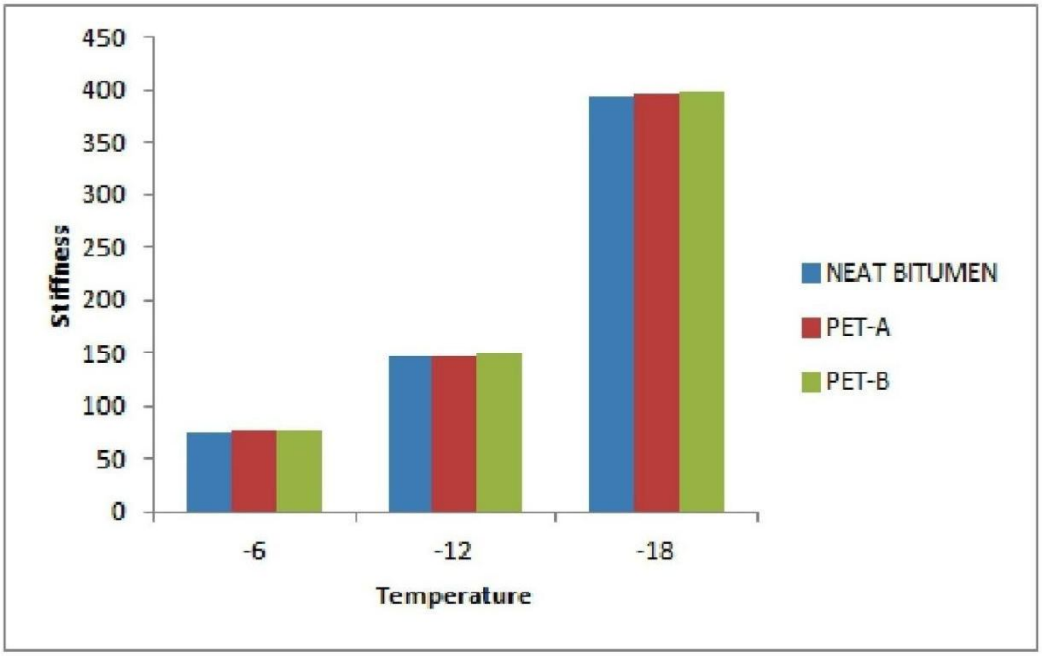

Fig.2.16 Stiffness of bitumen at different temperatures

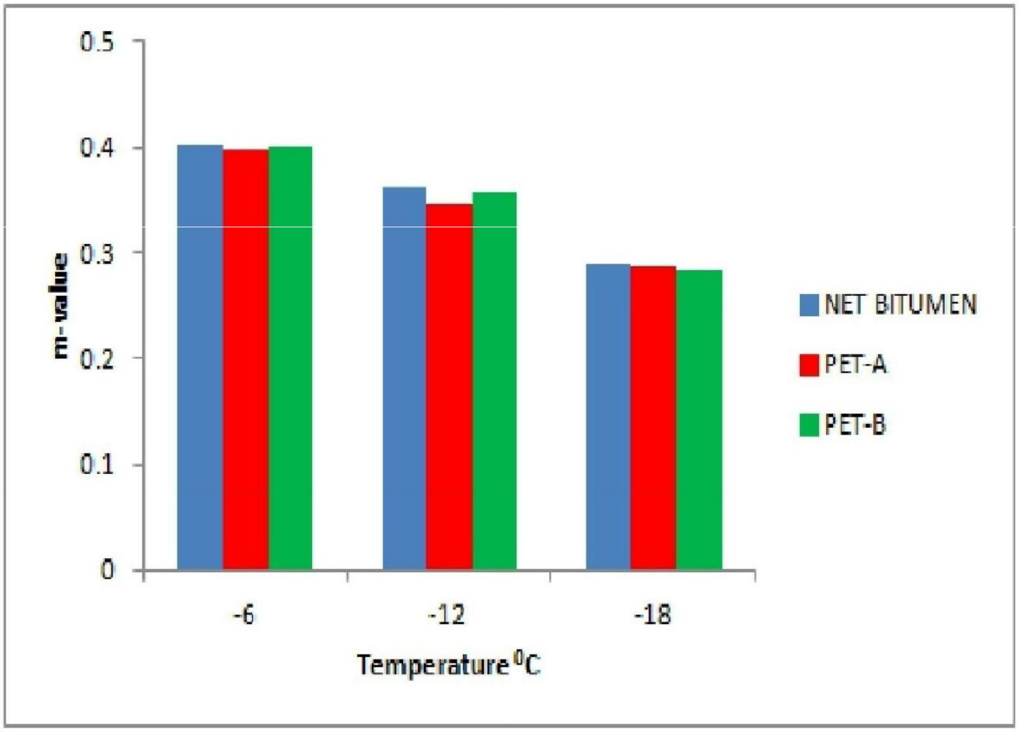

Fig.2.17 m- value of bitumen at different temperatures

2.4. Conclusions

Development of a bituminous concrete mixture with excellent antistripping properties through incorporation of small amount of a terephthalamide (derivative derived from the reaction of polyamines with waste or virgin poly(ethylene terephthalate) (PET) polymer) in bitumen is being reported for the first time in the present work. It was observed that bitumen doped with 0.3 to 0.5% of terephthalamide product showed outstanding anti-strip properties with 100% anti-strip performance in hot water immersion tests and retained Marshall Stability test. Unlike previous experience known in literature, with amine based antistripping additives, the test results showed that terephthalamide derivative did not affect the original binder properties and the binder with 0.5% terephthalamide was found to meet all the requirements of PG 58-19 grade bitumen. It was also noted from DSR results, the rutting factor (in terms of $G^*/\sin\delta$) and the fatigue resistance (in terms of $G^*. \sin\delta$) of bitumen doped with 0.5% terephthalamide binder remained quite close to the values of the neat bitumen. The use of antistripping additive synthesized under this research program adds value to conventional bitumen by providing improved adhesion between the bitumen and the aggregate surfaces particularly in the presence of moisture saturated environment. It has also been observed that moisture induced damages to the bituminous concrete doped with terephthalamide is far less as compared to conventional bitumen. The process developed in this research is an example of “green chemistry” being a single pot reaction with atom economy of high order.

2.5 References

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CHAPTER 3

Polymer Modified Bitumen (PMB) for flexible pavements through in situ polymerization reactions- a new cost effective approach

This Section of the thesis attempts to demonstrate a new approach where in-situ polymerization of monomers (monomers derived from aminolysis of Poly (ethylene terephthalate) waste) in the body of bitumen to develop storage stable polymer modified bitumen (PMB). The resulting product was found to meet the corresponding standards pavement requirements and is comparable with Styrene–butadience-Styrene (SBS) based PMB formulations. This research work, therefore, suggests not only a new technique for making PMBs but also opens a new chapter for the recycling of waste PET in bituminous concrete roads which may help in easy disposal of waste PET polymer.

3.1 Introduction

India has one of the biggest road networks in the world, aggregating to about 2.1 million miles at present. The roads in India are primarily bitumen-based macadamized roads. India produces around 4.5 MMT of bitumen per year and the demand is expected to go up significantly in the near future due to accelerated emphasis on road construction activity by the government of India. An efficient transport system is pre-requisite for sustained strong economy. Conventional bituminous materials have tended to perform satisfactorily in most highway pavement applications. However, in recent years, increased traffic load, larger and heavier vehicles, increased axle load pressures, have added to the already severe demands of load and environment on the highway system. This has led to the need of enhancing the properties of existing bituminous material. Bitumen modification offers a solution to overcome the deficiencies of bitumen and thereby improve the performance of bituminous mixtures [**1-3**]. Modified bitumen is being increasingly used these days to meet the growing requirements of quality of flexible pavements. Modified binders are more stable against heavy loads, braking and accelerating forces and show increased resistance to permanent deformation in hot weather. They resist fatigue loads and have better adhesion between aggregates and the binders.

Modified binders, using additives of varying chemistries, have been prepared by various investigators to improve basic properties of the bituminous mixes such as temperature susceptibility, fatigue resistance, anti-striping characteristics, etc. For example, primary alkyl amines, e.g., lauryl amine, stearyl amine, alkylene diamines etc [**4**], or reaction product of formaldehyde or phenol with tetra ethylene pentamine (TEPA) [**5-6**], or reaction product of ozonized fatty acids and polyamines [**7**] or more recently terephthalamide derived from the reaction of PET and TEPA [**8**] have been reported as good antistripping additives. D.N. Little [**9**] reported use of lime to give certain additional advantages such as stiffening of bituminous binder, control of fracture growth at low temperature, reducing aging effect and altering plastic properties of bitumen. Use of polyphosphoric acid (PPA) helps blended bitumen in improving its high temperature characteristics. Yudollahi. G et al [**10**] reported that PPA reacts with some functional groups present in bitumen, breaks asphaltene agglomerates into individual particles and helps to create better distribution of asphaltene in the maltene phase and thus improves the elastic behavior of the bitumen.

Most commonly used polymer for bitumen modification can be subdivided into two main categories: thermoplastic elastomers and plastomers [**11**]. Thermoplastic elastomers copolymers constitute most frequently used categories of polymers for bitumen modification, among which styrene-butadiene-styrene (SBS) is the preferred one [**12-13**]. Poly (styrene-isoprene- styrene) (SIS), which belongs to the same copolymer family, is also being frequently used for bitumen modification. Examples of the plastomeric types of polymers studied for bitumen modification are polyethylene (PE) [**14-15**] and ethylene–vinyl acetate (EVA) [**16**]. Polymer modified bitumen (PMB) are widely known to reduce thermal susceptibility and permanent deformation and enhance resistance to low-temperature cracking. At present Styrene–Butadiene–Styrene (SBS) has been accepted in many road projects owing to its good performances in both high and low temperature conditions. However, SBS degrades when exposed to atmospheric conditions and the mechanical stress [**17-18**]. Many researchers have focused on the use of cheaper materials for bitumen modification. For example, Crumb rubber (CR), a non-reactive polymer, has been used as an additive in bitumen mixes since 1930s. Crumb Rubber is known to improve performance of bitumen mixture with respect to thermal susceptibility, elastic behavior, fatigue cracking resistance and aging stability [**18-20**]. CR finds extensive use because it is relatively low cost product and also gives potential advantage of environment protection as crumb rubber (CR) is derived from used car and truck tyres which are available in large scale. Recently a new bitumen modifier class, called reactive polymers [**21-24**], has also been used for bitumen modification. These copolymers contain distinct functional groups capable of forming chemical bonds with bitumen molecules. In this case, the functional groups may able to chemically interact with hetero-atoms and reactive groups of bitumen. This process results in improving the mechanical behavior, storage stability and temperature susceptibility of the resulting binder. Reactive polymers are known to improve the performance of pavements under high temperature conditions, where rutting is the most prevalent type of pavement distress. Keyf et al [**24**] studied two reactive polymers namely ethylene terpolymer (SRETP and ETP), to improve features of 60/70 penetration grade modified bitumen used on highways. Giovanni P [**25**] studied the viscosity functions of bitumen blended with reactive polymer "Ethylene terpolymers" (RETP) at different temperatures in steady-state rate sweep tests and demonstrated that RETP functionalized with glycidyl methacrylate is chemically cross linked with bitumen. M.J. Martín-Alfonso [**26-27**] reported the reaction of an isocyanate-based reactive polymer, 4,4′-diphenylmethane diisocyanate (MDI) with a low molecular weight polyethylene-glycol (PEG). Rheokinetics experiments, viscosity measurements at 60°C, atomic force microscopy (AFM) characterization, thin layer chromatography (TLC-FID) analysis and thermo gravimetric studies (TGA) were performed on the reactive polymer. Results showed the existence of an optimum processing temperature for the formation of a polymer–bitumen network. A US patent [**28**] reports, chemically modified bitumen by reaction with an ethylenically unsaturated monomer. Phase separation behaviors of modified bitumen are improved by chemically bonding of long polymeric chains onto higher aromatics parts of bitumen. In another US patent, [**29**] bitumen is reacted with a polymerisable vinyl aromatic monomer and a rubbery polymer in the presence of a cross linking agent such as a polycarboxylic acid, or an organic isocyanate or an organic poly-epoxide. This chemically modified asphalt compositions has been recommended for use in the treatment of glass fibers or for road paving applications.

Memon G [**30**] prepares chemically modified crumb rubber asphalt (CMCRA) by treatment of crumb rubber with hydrogen peroxide and reported modified bitumen with improved elastic recovery property and good under different environmental and weather conditions. Sang-Yum Lee and his co-workers [**31**] introduced a novel method that could modify neat bitumen by in situ polymerization of dimethyl phenol (DMP). A monomer, dimethyl phenol (DMP), when added to neat bitumen in the presence of air, autonomous polymerization occurred without any external catalyst. The polymer produced in the bitumen was shown to be polyphenyleneoxide (PPO) which enhanced the mechanical properties such as tenacity and stiffness of the bitumen. In a European patent [**32**] a method for synthesizing a homopolymer or copolymer (with bituminous component less than 50wt% based upon the weight of the monomer) from an alkenyl monomer such as styrene has been disclosed in which weight average molecular weight (Mw) of the homopolymer generated is less than

100,000. The patent further discloses that increasing the amount of the bituminous component decreases the molecular weight of the polymer. Further the resulting bituminous product shows a range of color from yellow to brown to black depending on the amount of polymer present.

This section of the thesis attempts to demonstrate a new approach where in-situ polymerization of monomers (monomers derived from aminolysis of waste PET) in the body of bitumen leads to production of storage stable PMB. The developed product was found to meet with standard pavement requirement. Therefore the present work not only suggest a new process for making PMBs but also opens a new chapter for the recycling of waste PET in bituminous concrete roads.

3.2 Experimental

3.2.1 Materials

3.2.1.1 Chemicals

Triethylene tetramines (TETA), Ethanolamine, 4,4-diphenylmethane diisocyanate (MDI) and xylene were of Laboratory Reagent (LR) grade.

3.2.1.2 Aggregates

Locally available aggregates were used which had particle size of 100% passed through 19-mm sieve and were retained on a 13.2-mm sieve. The aggregates were washed by distilled water to remove all fines, dried at 105 -110 ^{0}C to constant weight and stored in airtight containers for use.

3.2.1.3 Aggregate Gradation Adopted

The grading of aggregates for bituminous mixes selected for this researc were done as per Ministry of Road transport and highways (MORTH: 2000) Specifications and is given in Table 3.1

Table 3.1 Aggregate Gradations of Bituminous Mixtures Adopted

Sieve size (mm)	Specified limits	
	Sieve size (mm) passing	Percent Adopted
19	100	100
13.5	79-100	93
9.5	70-88	89
4.75	53-71	64
2.36	42-58	56
1.18	34-48	35
0.6	26-38	27
0.3	18-28	18
0.15	12-20	12
0.075	4-10	6

3.2.1.4 Bitumen

Bitumen (VG 10 grade) was supplied by IndianOil Mathura refinery meeting BIS specification IS: 73-2006. Typical properties of bitumen used are given in Table 3.1.

3.2.1.5 Poly(ethylene terepthalate) (PET)

In our study we specifically used both bottle grade and virgin PET polymer for the production of PMB Discarded PET bottles were procured from local market. The plastic bottles were stripped of all labels and after removing caps and labels bottles were cleaned by boiling water with detergent solution followed by proper washing and drying to remove any potential contaminants. The bottles were then cut into squares (flakes) about 1cm by 1cm and their dried at ambient temperature.

3.2.2 Methods

3.2.2.1 Synthesis of terephthalamide Derivative

Experimental procedure for aminolysis reaction of PET waste was carried out according to our earlier described method [8].

A three necked 500 ml round bottomed flask equipped with a heating mantle, overhead stirrer, water condenser, nitrogen gas sparging tube and a thermo well pocket containing a thermometer was charged with 30 grams of PET polymer, 90 ml Toluene, 90 grams of amine (e.g. triethylene tetramine (TETA), Ethanol Amine). Current of dry nitrogen was constantly maintained. The mixture was refluxed for 8-hours. As the PET degradation completed, the solution turned homogeneous (i.e., Flakes disappeared completely). At the end of the reaction the unreacted polyamine, if any and glycol was recovered under vacuum.

3.2.2.2 Preparation of in-situ terephthalamide based PMB

In the present work two types of terephthalamide (viz. BHETA and TETA-terephthalamide) were taken. These terephthalamide were reacted with MDI in bitumen, at respective wt/wt ratio of (3:1.5:95.5). The reaction mixtures was heated under vigorous stirring under nitrogen atmosphere at a temperature of about 90–130 ^{0}C for 4 hours. The formation of polymer (generated in-situ) was confirmed from IR spectra (Fig.3.1& Fig.3.2). A typical FTIR spectrum of segmented polyurethane would display two carbonyl peaks: one at 1724 cm^{-1} assigned to bond C=O groups, and a second at 1712 cm^{-1} assigned to free C=O groups. The N–H group participating in the hydrogen bond displays a characteristic absorption peak between 3273 and 3442 cm^{-1}. IR spectra of all the polyurea are similar in almost all aspects and assessment of all the spectra reveals that the spectra comprise of urea linkages. The IR bends at 1663 - 1609 cm^{-1} and 1234-1220 cm^{-1} confirm the urea linkage.

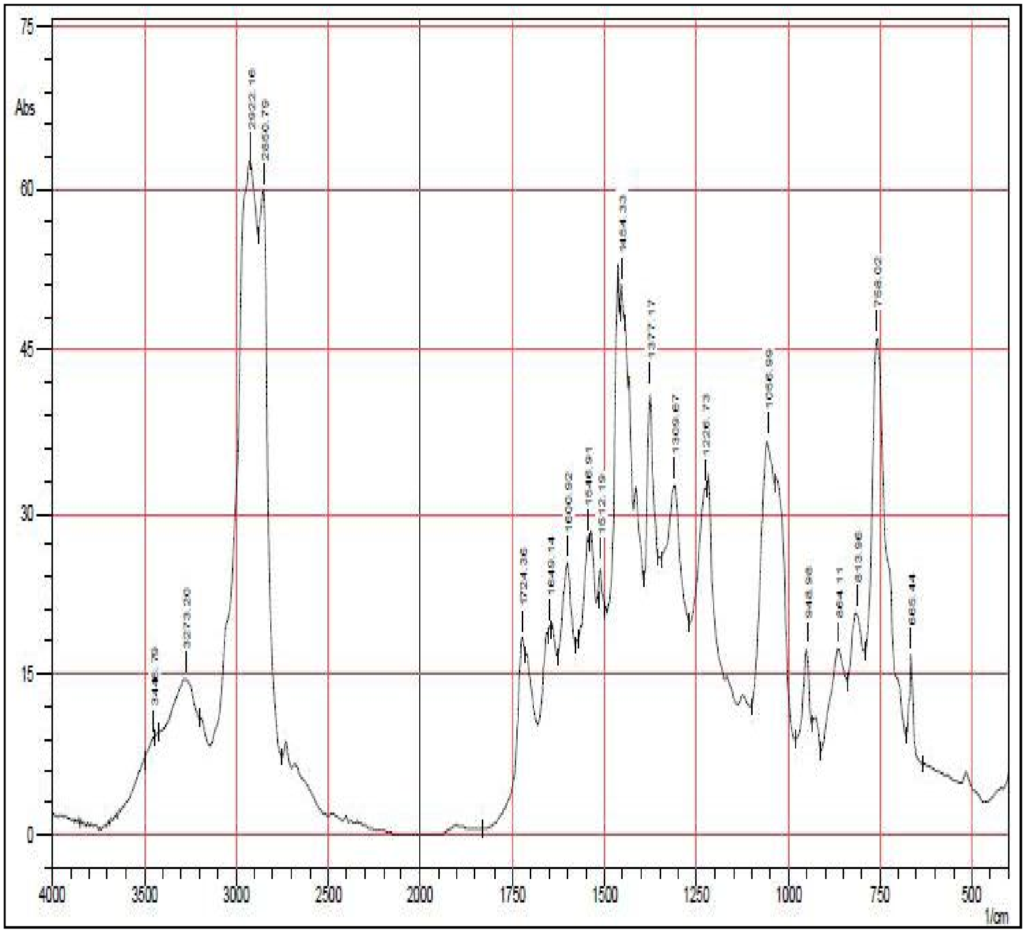

Fig.3.1 BHETA Terephthalamide Derived PMB

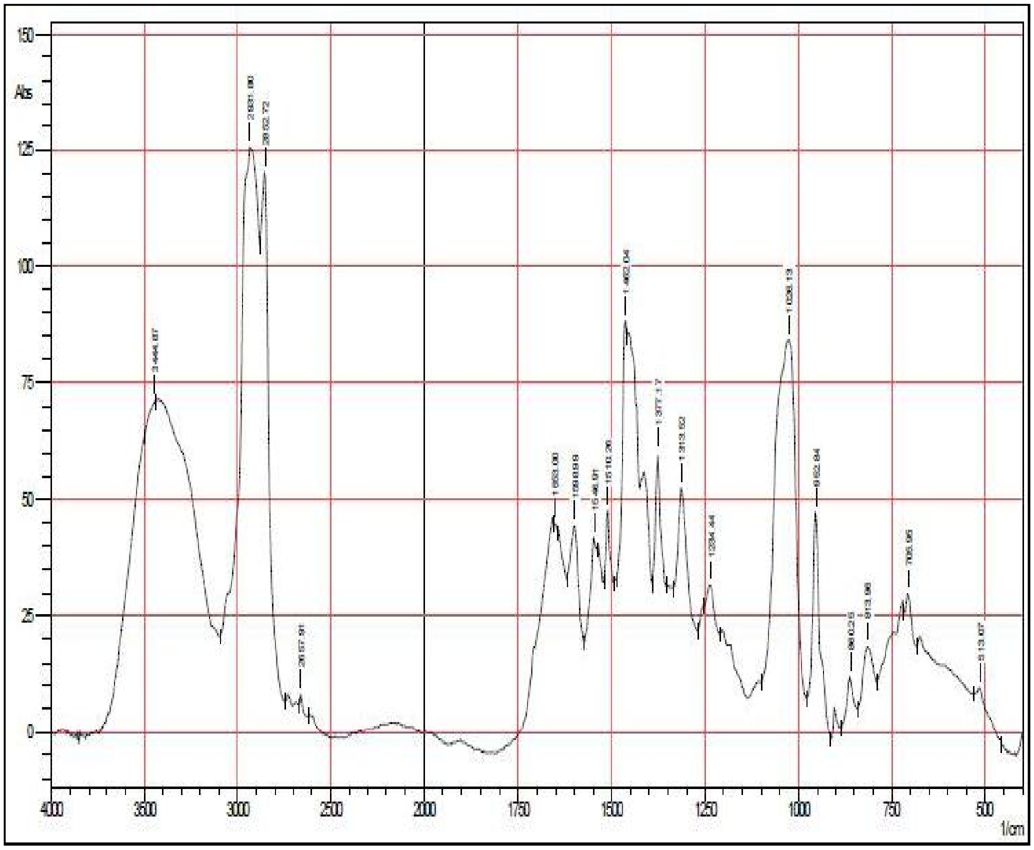

Fig.3.2 TETA terephthalamide derived PMB

3.2.2.3 Evaluation of terephthalamide based PMB

Physical and chemical properties were characterized by FTIR (Spectrum BX Series), Marshall Equipment (ELE International). Dynamic Shear Rheometer (Physica Anton Par 300), Bending Beam Rheometer (Cannon), Penetration (RIGO) Softening Point (Tanaka), Ductility (Koehler), Rotational Viscometer (Thermo Haake).

3.2.2.4 Mixing and compaction temperatures

The bitumen binder was heated at 170 ^{0}C to produce required kinematic viscosity of 170 ± 20 x 10-6 m2/s for mixing and a compaction temperature of 150 ^{0}C were selected for achieving the viscosity 280 ± 30x10-6 m2/s.

3.3 Results and Discussion

Chemical recycling [**33-34**] through aminolysis of PET leads to the formation of monomer which can be used to synthesize the new polymer or some other secondary value added products. However, the commercial applicability of the aminolysed product derived from PET is limited. In the present study, we pursued a new approach for in-situ polymerization of different terephthalamide monomers with polyisocyanate in the body of bitumen. Following this approach, terephthalamide (derived from PET with TETA as per our earlier reported method) [**8**], was reacted with methylene diisocyanate (MDI) in bitumen to prepare a polyurea based novel storage stable PMB. The physic-chemical properties of developed PMBs were evaluated against conventional standard test methods and compared with SBS based PMB (Table 3.2).

Table 3.2 Properties of Neat VG-10 & In-Situ PMB

Properties	VG-10 Bitumen	TETA-terephthalamide Mod. Bitumen	BHETA-terephthalamide Mod. Bitumen	SBS Mod. Bitumen	PMB-grade-3 (IRC:SP:53-2010)
Penetration 25 ^{0}C (100g, 5s), 0.1mm	84	67	66	63	60-120
Softening Point ^{0}C	46	51.5	52	52	50 Min
Ductility at 27 ^{0}C (5 Cm/Min)	100	90+	40		---
Elastic recovery at 15 ^{0}C (%)	-	26	27	65	
Viscosity(at 150 ^{0}C) (Poise)	1.57	2.78	2.95	2.86	1-3 poise
Separation diff.(in Softening Point ^{0}C)	---	2	2.7	0.8	3 Max

3.3.1 Dynamic Shear Rheometer (DSR)

Rheological properties of bitumen are commonly studied through dynamic mechanical methods using oscillatory-type testing. These oscillatory tests are undertaken using a dynamic shear rheometer (DSR), which applies oscillating shear stresses and strains to samples of bitumen sandwiched between parallel plates at different loading frequencies and temperatures. Dynamic Shear Rheometer (DSR) is also the most commonly used methods for measuring the deformation characteristics of modified bitumen for road surface applications. Measurements of the complex shear modulus (G*) can be carried out using a DSR (Physica Anton Par 300 make)), fitted with a circulating water bath for temperature control of the sample. The test procedure measures the G*/Sin(δ), a parameter for interpreting rutting-resistance of both neat bitumen and rotating thin film oven test (RTFO) aged bitumen samples. Greater the G*/Sin(δ), better is the rutting resistance of developed product at high temperature. The Superpave specification states that in alter to provide suitable resistance against rutting at the maximum pavement design temperature of a bituminous product the G*/Sin(δ) value should be at least 1.0 kPa for neat bitumen and 2.2 kPa for RTFOT-aged bitumen samples. DSR studies were done on samples of neat bitumen, TETA-Modified bitumen, BHETA-modified bitumen and SBS based modified bitumen within the temperature range from 58-82 ^{0}C. The results of DSR are shown in Table 3.3. The results indicate that all modified bitumen samples exhibited G*/Sin(δ) values higher than neat bitumen. The Table 3.3 shows that all modified bitumen have G*/Sin(δ) values of 1.23 and 1.16 kPa for unaged and 2.84 and 2.22 kPa at 70 ^{0}C for the RTFO aged TETA-terephthalamide modified bitumen and BHETA- terephthalamide modified bitumen, respectively. Thus, both modified bitumen samples under unaged conditions as well as RTFO aged conditions showed acceptable values up to a temperature of 70 ^{0}C. This indicates that in-situ modified bitumen exhibits improved stiffness values as compared to neat bitumen.

Table 3.3 Dynamic Shear Rheometer Results

Properties	Test Temp. (^{0}C)	VG-10 Bitumen G*/Sin (δ)	TETA-Modified Bitumen G*/Sin (δ)	BHETA-modified bitumen G*/Sin (δ)	SBS based Modified Bitumen G*/Sin (δ)	Passing limit of G*/Sin (δ) (ASTM: D-7175)	PMB-grade-3 (IRC:SP:53-2010)
DSR of (unaged samples)	58 ^{0}C	2.14	5.32	4.93	3.15	1.0	58^{0}C Min Required Temperature
	64 ^{0}C	0.92	2.55	2.35	1.42		
	70 ^{0}C	0.43	1.23	1.16	0.64		
	76 ^{0}C	0.2	0.639	0.519	0.29		
DSR of RTFO aged	58 ^{0}C	3.99	11.34	10.67	6.1	2.20	58^{0}C Minimum Required Temperature
	64 ^{0}C	1.71	5.49	4.96	3.15		
	70 ^{0}C	0.61	2.84	2.22	1.42		
	76 ^{0}C	0.27	1.27	1.01	0.74		

3.3.2 Bending Beam Rheometer (BBR)

In order to examine low temperature thermal cracking properties, thin beams of modified bitumen were tested for creep stiffness using BBR. The maximum stiffness criteria of 300 MPa and the minimum m-value criteria of 0.300 have been recommended as per ASTM: D 6648. In these tests, the bitumen beams (125 mm long, 12.5 mm wide and 6.25 mm thick) are submerged in a constant temperature bath and kept at the test temperature (starting at -18 ^{o}C) for 30 min. A constant load of 100 gram is then applied to the rectangular beam which is supported at both ends by stainless steel half-rounds (102 mm apart), and the deflection of center point is measured continuously. Creep stiffness (S) and creep rate (m) of the binders are determined at several loading times ranging from 8 to 240 s.

A comparative study of BBR test data for neat and modified bitumen samples is given in the Table 3.4. The Table 3.4 showed that the modified bitumen has stiffness 256, 280 & 363 MPa and m-value has 0. 326, 0.292 & 0.269 at -18 ^{0}C for TETA-Modified, BHETA-Modified bitumen and SBS modified bitumen samples, respectively. This means that, except BHETA-modified bitumen, other PMB binder are consistently matched with the desired value limits at -18 ^{0}C and thus these TETA modified bitumen and SBS-Modified binders were found to be more resistant to low temperature cracking.

Table 3.4 Bending Beam Rheometer of Neat and Modified Bitumen

Properties	VG-10 Bitumen		TETA-Modified bitumen		BHETA Modified bitumen		SBS modified bitumen		Specification
Temperature (in ^{0}C)	Stiffness	m-Value	Stiffness	m-Value	Stiffness	m-Value	Stiffness	m-Value	ASTM: D 6648
-6 ^{0}C	74	0.402	41.3	0.495	35.3	0.508	84.6	0.377	Stiffness=300 mPa (max.) & m-value=0.300 (min.)
-12 ^{0}C	147	0.362	93.3	0.432	110	0.381	161	0.34	
-18 ^{0}C	395	0.288	256	0.326	280	0.292	363	0.269	

3.3.3 Marshall Stability Test

Marshall Stability test is used to evaluate theq resistance to plastic deformation of a compacted cylindrical bituminous pavement specimen. The Marshall stability of the bituminous pavement specimen is defined as the maximum load bearing capacity of the compacted cylindrical specimen at a standard test temperature and load. The flow value is the deformation that the test compacted cylindrical bituminous specimen undergoes during loading up to the maximum load. According to Indian Road Congress Specification (IRC: SP-53), the Marshall strength and the flow value for hot climate, is 12KN and 2.5 - 4 mm. For cold climate the Marshall Stability is 10KN and Flow value is 2.5 - 4 mm and for high rainfall areas Marshall Stability is 12KN, flow at 60 ^{0}C is 3.0 - 4.5mm. All modified bitumen samples were found to improved Marshall Stability and flow value as shown in Table 3.5. The result indicates that all formulations meet with Marshall Stability criteria for all types of climatic condition as per IRC: 53-2010.

Table 3.5 Marshall Stability Test

Binder content	**(Marshall Strength KN / Flow in mm) Compaction temp:150 ^{0}C**				**Specification**
	VG-10 Bitumen	**TETA-terephthalamide Modified bitumen**	**BHETA-terephthalamide Modified bitumen**	**SBS modified bitumen**	**IRC:53-2010**
5%	11.9/2.24	14.54/3.66	11.28/2.32	16.5/2.27	Hot Climate: Marshall Stability: 12KN, Flow at 60 ^{0}C = 2.5-4mm
5%	12.30/2.43	13.44/3.75	12.47/2.80		
5%	13.15/2.80	12.55/3.45	10.92/2.12		
Average Value	**12.45/2.49**	**13.51/3.62**	**11.55/2.41**	**16.5/2.27**	
5.5%	13.55/2.39	17.75/3.45	14.09/3.89		Cold Climate: Marshall Stability: 10KN, Flow at 60^{0}C = 3.5-5 mm
5.5%	12.98/2.55	16.25/4.08	14.20/3.46		
5.5%	14.59/2.52	16.8/3.67	13.89/3.21		
Average Value	**13.67/2.48**	**16.93/3.73**	**14.06/3.52**	**19.75/3.16**	
6%	13.55/2.39	20.15/5.08	15.23/5.23		For High Rainfall Marshall Stability: 12KN, Flow at 60 ^{0}C = 3.0-4.5mm
6%	14.58/3.59	17.71/4.35	16.82/5.03		
6%	14.09/3.12	20.48/4.05	14.67/4.87		
Average Value	**14.07/3.**	**19.44/4.49**	**15.57/5.04**	**24.26/3.89**	

3.3.4 Hot Water Stripping Test

The Boiling Water Test (ASTM D 3625-96, Reapproved 2005) is a subjective test for estimating any adverse effects of water ingress on the bituminous mixes. It is used primarily as an initial screening test for moisture resistance of the bituminous mixes. During the study it was observed that the bitumen doped with 2% PMB, generated through in-situ reactions of MDI and a TETA based terephthalamide (derived from PET), shows good anti-strip properties with >90% anti-strip performance in hot water immersion tests (Fig.3.3). However, BHETA based PMB did not show much promising results as compared to TETA based PMB.

VG-10 Bitumen

BHETA – terephthalamide Modified Bitumen

TETA- terephthalamide modified Bitumen

Fig.3.3 Hot water stripping test (ASTM D 3625-96 (Reapproved 2005)

3.4 Conclusions

In order to ensure better dispersion of polymers in bitumen, in the present study, we pursued an innovative approach of in situ polymerization of terephthalamide derivatives (derived from waste PET) in the body of bitumen. The reaction of MDI with terephthalamide derivatives in the body of bitumen led to the development of polymer in bitumen. The developed PMB was chemically characterized by IR analysis, which confirmed in-situ formation of polyurea and polyurethane. The results obtained from the present studied, show the advantages of reactive polymer modified bitumen binder over the conventional bitumen binder. The result also indicates that Marshall Stability of in-situ polymerized PMB was increased and found to meet with all requirements as per IRC: 53-2010. Bending beam rheometer test (BBR) for creep stiffness at lower temperatures reveals that the creep stiffness of modified bitumen was decreased and the m-value was increased. The developed in-situ polymer modified binders showed lower stiffness and satisfies the acceptable criteria up to a temperature of -18 °C. Similarly, dynamic shear rheometer (DSR) shows that for both unaged and RTFO aged polymer modified bitumen, the G*/Sin(δ) was higher than unmodified and SBS based polymer modified bitumen binder. The G*. Sin(δ) also indicates that modified binder has shown desirable values as it is softer and more flexible at lower temperatures. The results of the present study suggest that PET waste derived polymer modified bitumen binder (PMB) may be a suitable product for national highways road construction.

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CHAPTER 4

Surface Modification of Poly (Vinyl Chloride) Using Polyamine to Improve Antistripping Characteristics of Bitumen

This chapter deals with the chemical surface modification of PVC by using polyamines (such as ethylene diamine, diethylene triamine and triethylene tetramine) and their surface modified products used to modified bitumen. The substitution of chlorine from PVC was confirmed by the elemental analysis and Solid State 13C-NMR. It has been observed that bitumen doped with modified PVC improves property of bitumen. Furthermore, the modified bitumen efficacy was examined in terms of its antistripping characteristics and rheological properties.

4.1 Introduction

Petroleum bitumen is commonly used as a binder in flexible pavements. Bituminous materials perform quite satisfactorily for highway, if designed and manufactured properly. However, many special applications, such as where traffic is very heavy and sever climatic change require materials that can improve the cracking, resistance to permanent deformation and stripping of paving mixes. One approach is to modify the bitumen with polymer additives. Polymers are well-known to improve the rheological properties of bitumen [**1-5**]. Commonly used polymers include styrene-butadiene-styrene copolymer (SBS), styrene-butadiene rubber, polyolefin, ethylene vinyl acetate (EVA), Polystyrene and polypropylene. However, most of these polymers are costly for road construction leads to their limited used. PVC is the second most widely used polymer in terms of consumption volume accounting for a global production of over 25 million tons per annum. Polyvinyl chloride (PVC), a thermoplastic material, has found extensively used in various construction works for being cheap, durable, flame retardant properties and also due to its easy workability. Globally, over 50% of PVC manufactured is used in construction industries. In recent years, PVC has been replacing traditional building and construction materials such as concrete, wood and clay in many areas.

Chemical modification of PVC is a facile method to change the surface chemical nature, in order to be suitable for desired properties. The labile chlorine displacement from PVC indicated the possibility of easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes [**6**]. The amination of chlorine containing polymers using alkyl amines has been reported in the literature [**7**]. Ferruti et al [**8-9**] aminated PVC using a concentrated aqueous solution of bis-(2-aminoethyl) amine. Emad Yousif et al [**10**] studied on the optical properties of pure and modified PVC films.

This chapter deals with the chemical surface modification of waste poly (vinyl chloride) (PVC) by using polyamines (such as ethylene diamine, diethylene triamine, and triethylene tetramine). The modified PVC was then used for bitumen modification. During this study, it has been observed that bitumen doped with modified PVC improves antistripping property.

4.2 Experimental

4.2.1 Materials & Methods

4.2.1.1 Chemicals

Triethylene tetramines (TETA), ethylene diamine, diethylene triamine and Distilled water, were of Laboratory Reagent (LR) grade.

4.2.1.2 Aggregates

Aggregates were used from local granite rocks of particle size that 100% passed a 19-mm sieve and were retained on a 13.2-mm sieve. The aggregate was washed in distilled water to remove all fines dried at 105 -110 ^{0}C to constant weight and stored in airtight containers for subsequent use.

4.2.1.3 Bitumen

Bitumen (VG 10 grade) was supplied by IndianOil Mathura refinery meeting BIS specification IS: 73-2006. Typical properties of bitumen used are given in Table 4.1.

4.2.1.4 Polyvinyl Chloride (PVC)

High molecular weight PVC with K-value of 69-71 and density of 1.4 g/ml at 25 °C was purchased from Aldrich Chemical.

4.2.1.5 Surface modification of PVC by Amines

PVC was aminated by treating it with excess of 85% aqueous solution of polyamine and stirred magnetically in an oil bath maintained at 120°C for 2 h. After the completion of the reaction, the product was filtered and washed with plentiful amounts of distilled water to remove amine and then dried in an oven under vacuum up to constant mass. The aminated PVC derived from triethylene tetraamine (TETA), diethylene triamine (DET), ethylene diamine (ED) are named as PVC-TETA, PVC-DET and PVC-ED, respectively.

4.2.1.6 Modification of Bitumen with PVC-NH2

A three necked round bottomed flask equipped with heating mantle, overhead stirrer, nitrogen gas sparging tube and a thermo well pocket containing a thermometer was charged with 1% of PVC-NH2 and 99 % of bitumen respectively to form modified bitumen. The blending was continued for 2h at 150 °C to 160 °C.

4.2.1.7 Spectral Analysis of PVC-NH2

To study the substitution on the PVC surface, spectrochemical analysis of modified PVC was carried out by using solid state C^{13}NMR and elemental analysis techniques.

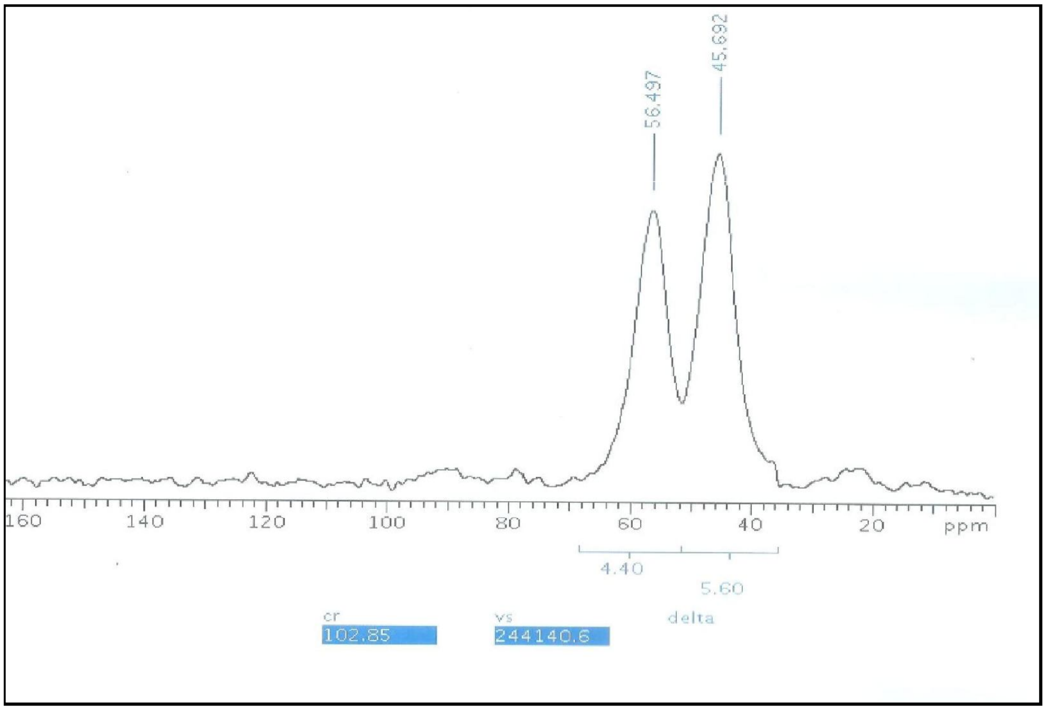


Fig.4.1 Solid State C^{13} NMR spectra of Neat PVC

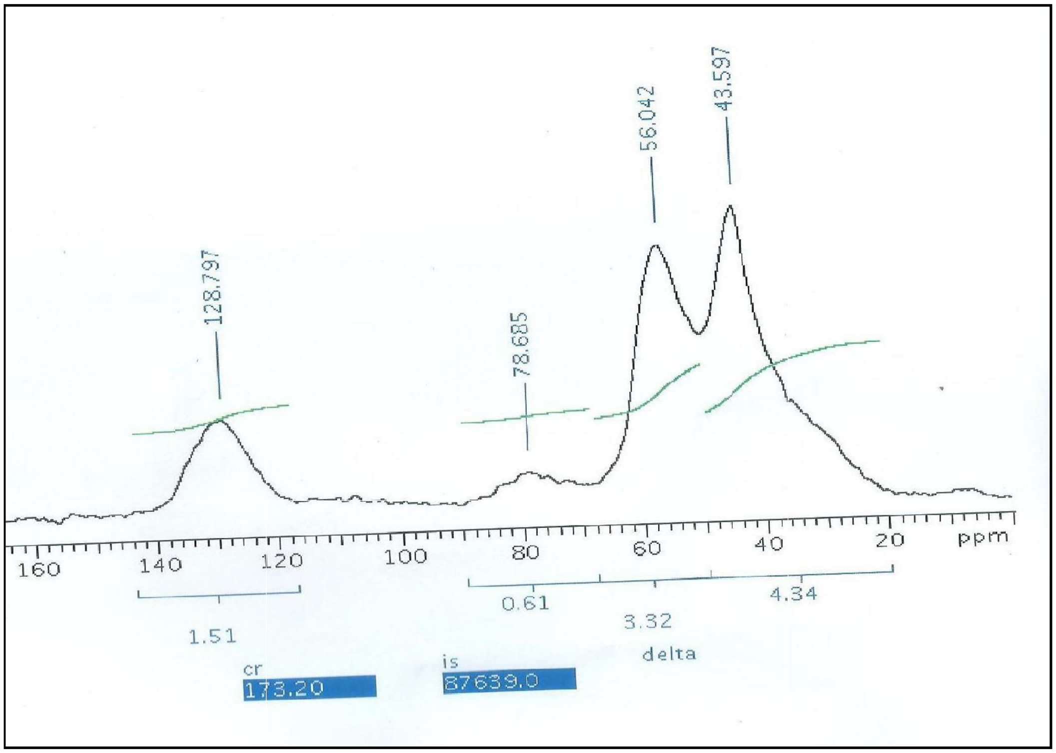


Fig.4.2 Solid State C^{13} NMR spectra of PVC-NH2-TETA

Comparative solid state C^{13}NMR spectra for each transformation and elemental analysis results are shown in Fig.4.1, Fig.4.2, Fig.4.3 and Fig.4.4. Shifting of peak from 56.497 and 45.492 in C^{13}NMR in all cases confirms the modification of PVC by amine. However, solid state C^{13}NMR spectra also showed extra peaks in the higher range. These could possibly arise from elimination reaction. The substitution was also confirmed by the elemental analysis: 10.3 % N, 56.56 % C, and 7.35 % H for TETA modified PVC and 10.77 % N, 59.64 % C, and 7.65 % H for DET modified PVC and 9.93% N, 59.60 % C, and 7.76 % H for ED modified PVC. This corresponds to degree of transformation of PVC substitution by amine degree up to 50 %.

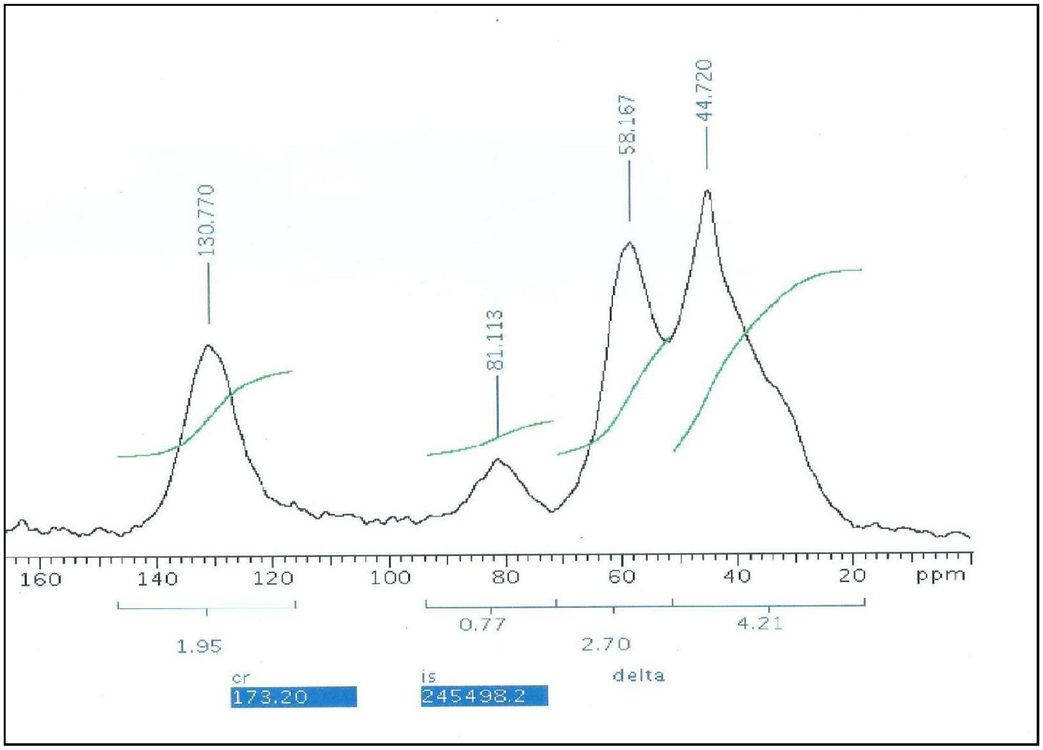


Fig.4.3 Solid State C^{13} NMR spectra of PVC-NH2-DET

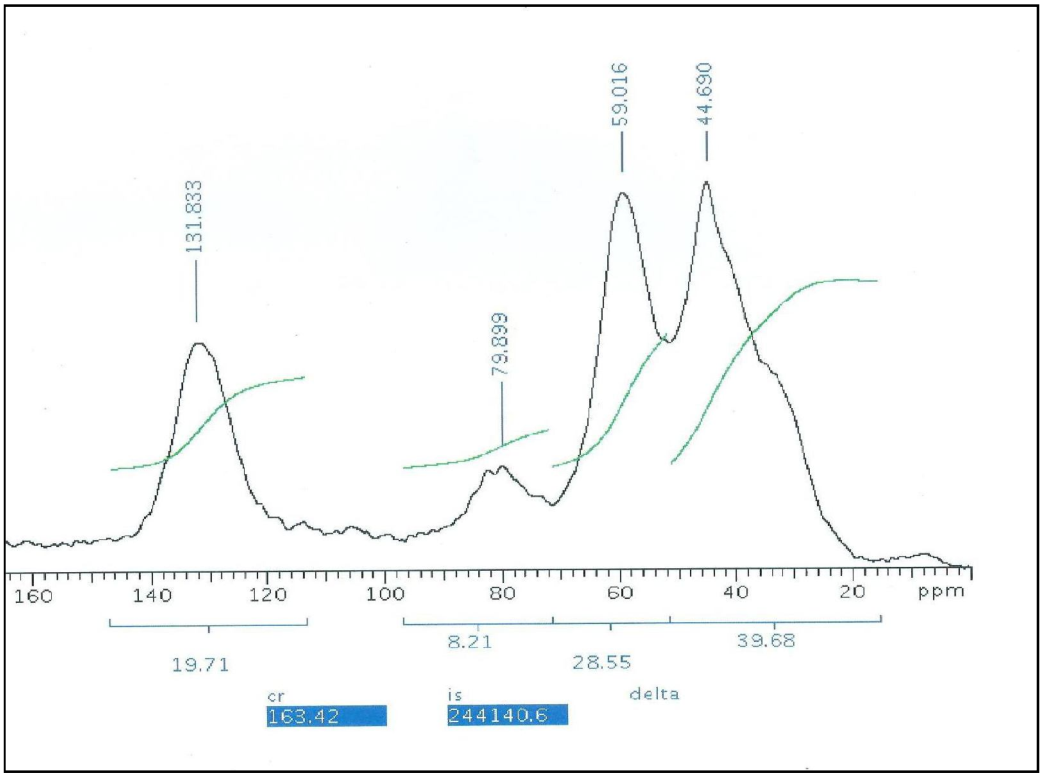


Fig.4.4 Solid State C^{13} NMR spectra of PVC-NH2-ED

4.3 Results and Discussion

4.3.1 Conventional Bitumen Binder Tests

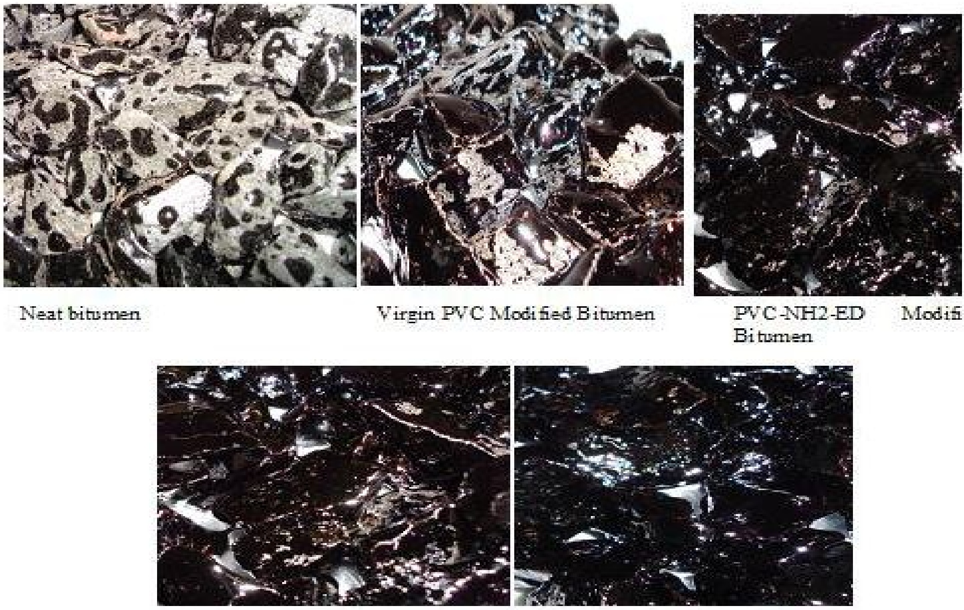
The virgin bitumen, virgin PVC Modified and PVC-NH2 modified bitumen were subjected to penetration test, softening point and ductility test. The results of these tests are listed in Table 4.1. The results showed that in PVC-NH2 modified bitumen binders; there is decrease in penetration value and an increase in the softening point temperature as compared to virgin PVC modified bitumen. The modification also reduces the temperature susceptibility of bitumen, as indicated by a slight higher softening point of the test sample.

Table 4.1 Properties of Neat VG-10 & PVC and PVC-NH2 Modified Bitumen

Properties	VG-10 Bitumen	PVC Modified Bitumen	PVC-ED Modified Bitumen	PVC-DET Modified Bitumen	PVC-TETA Modified Bitumen
Penetration 25 C (100g, 5s),0.1mm	84	75	73	76	75
Softening Point, ^{0}C	46	46.7	48.5	47	48
Ductility at 27 ^{0}C (5 Cm/Min)	100	90	100	95	97

4.3.2 Hot Water Stripping Test

The Boiling Water Test (ASTM D 3625-96, reapproved 2005) is a subjective test for estimating any adverse effects of water ingress on the bituminous mixes. It is used as an initial screening test for moisture resistance of the bituminous mixes. During the study, it was observed that the bitumen doped with 1 % PVC-NH2 polymer, shows good anti-strip properties with >90% anti-strip performance in hot water immersion tests (Fig.4.5). However, virgin PVC based PMB did not show much promising results.



Neat bitumen

Virgin PVC Modified Bitumen

PVC-NH2-ED Modified Bitumen

PVC-NH2-DET Modified Bitumen

PVC-NH2-TETA Modified Bitumen

Fig.4.5 Hot Water immersion tests for neat and PVC modified bitumen

4.3.3 Creep tests using a bending beam rheometer

Low temperature stiffness and relaxation properties of bitumen binder were carried out at different low temperatures (0 TO -18 °C) using bending beam rheometer (BBR, Cannon Instrument Company). According to AASHTO specification, the maximum creeps stiffness allowed to satisfy the low temperature bitumen binder grade is 300 MPa. Fig.4.6 shows that the PVC-NH2 modified bitumen binder met creep stiffness specifications up to −12 °C thereby meeting low temperature performance specifications for −22 °C in terms of creep stiffness and m-values (Fig.4.7). According to AASHTO specification the minimum m-value allowed to meet the low temperature bitumen binder grade is 0.3. The PVC-NH2 modified bitumen binder was found to meet with low temperature specifications for −28 °C with BBR testing temperature of −18 °C. However, the PVC modified bitumen binder met creep stiffness and m-value specifications up to −12 °C there by meeting low temperature performance specifications for −22 °C in terms of creep stiffness and m-value.

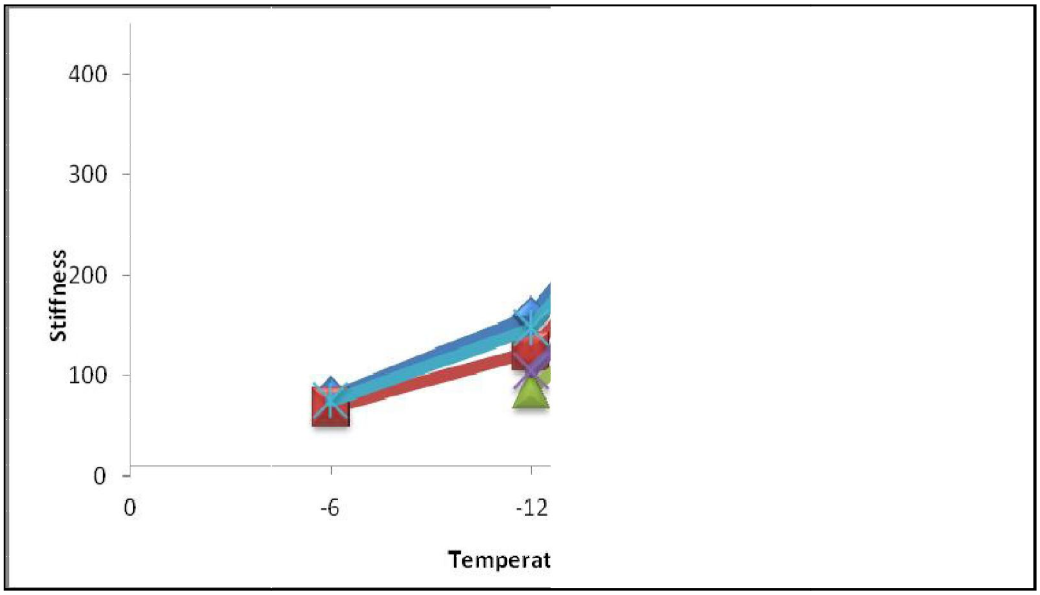


Fig 4.6 Stiffness of neat and modified bitumen

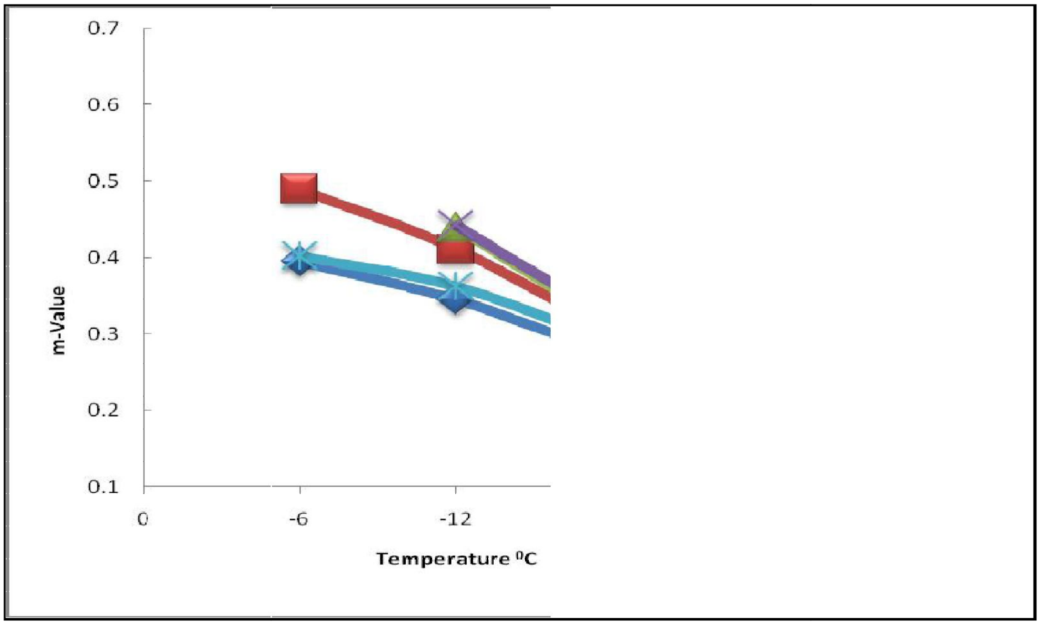


Fig.4.7 m-value of neat and modified bitumen

4.3.4 Dynamic Shear Rheometer

The dynamic shear rheometer (DSR) was conducted to evaluate permanent deformation and fatigue cracking properties of the PVC-NH2 modified bitumen binder, PVC- modified bitumen binder and virgin bitumen binders. Adopted procedures for the DSR are given in AASHTO T315-10. Physical property measurements using the DSR for bitumen binder were made using unaged (Fig.4.8) and rolling thin film oven (RTFO-aged) (Fig.4.9). The 25-mm DSR plate was used to test for all unaged and RTFO-aged bitumen binder. The PVC-NH2 modified bitumen binder showed increase of G*/Sinδ compared to the original virgin binder and virgin PVC modified bitumen binder. The virgin bitumen and virgin PVC modified bitumen showed less thermal susceptibility and elastic response as compared to PVC-NH2 modified bitumen binder as shown in the graph (Fig.4.8 &Fig.4.9).

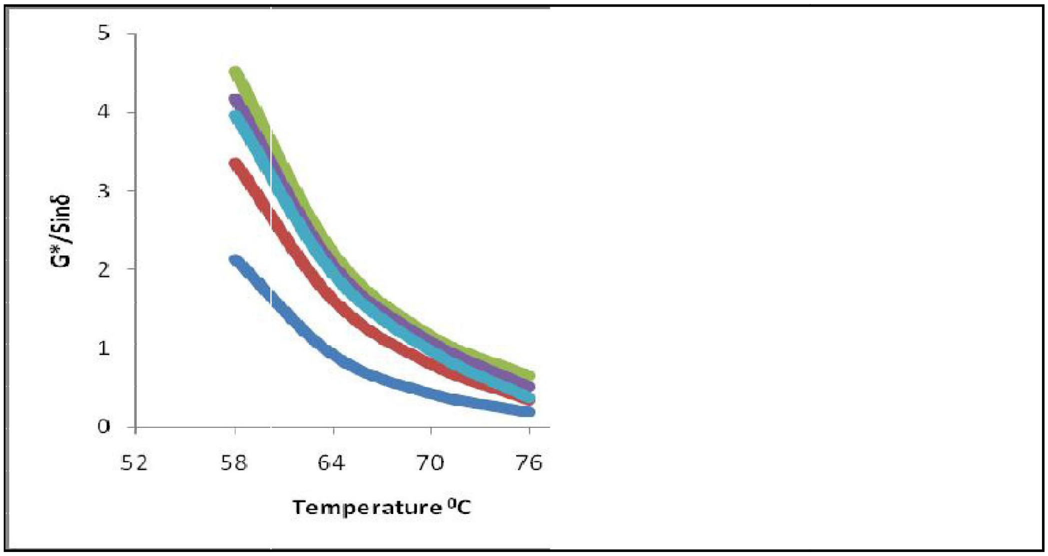


Fig.4.8 G*/Sinδ (kPa) measured as a function of temperature of neat and modified bitumen

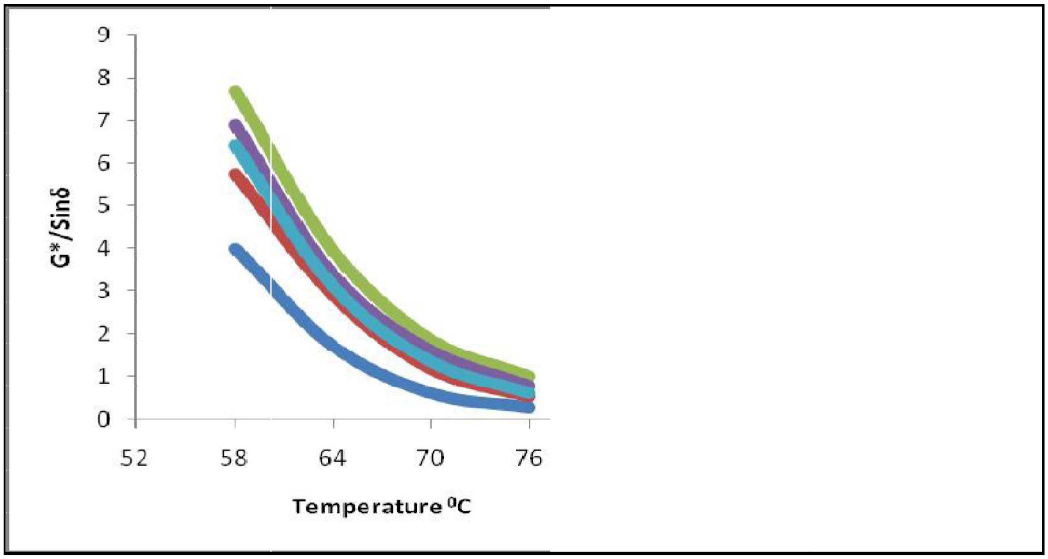


Fig.4.9 G*/Sinδ (kPa) measured as a function of temperature of neat and modified bitumen after RTFO-aged

4.4 Conclusions

Development of bituminous concrete mixture with improved antistripping properties through incorporation of small amount of PVC-NH2 derivative (derived from the reaction of polyamines with PVC polymer) in bitumen is reported for the first time. From the above study, it has been concluded that:

1. It was observed that bitumen doped with 0.5% to 1.5% of PVC-NH2 product shows good anti-strip properties with >90% anti-strip performance in hot water immersion tests. The test result shows that PVC-NH2 derivative also improves the physic-chemical properties of original binder.

2. It was also observed that, the rutting factor (in terms of $G^*/\sin\delta$) and the fatigue resistance values (in terms of $G^*. \sin\delta$) of binder doped with PVC-NH2 were higher than the neat bitumen.

3. The PVC-NH2 modified bitumen binder met creep stiffness and m-value specifications up to −12°C, thereby meeting low temperature performance specifications for −22°C in terms of creep stiffness and m-value.

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CHAPTER 5

Improved Performance of Crumb rubber modified bitumen by addition of Polyoctenamer and sulphur

In this research work, bitumen binders formulated with crumb rubber, polyoctenamer and sulphur additives have been studied. The combination of reactive polyoctenamer along with cross linking agent was also found to promote anchoring of crumb rubber in bitumen to produce storage stable crumb rubber modified bitumen. The use of reactive polyoctenamer polymer to develop storage stable crumb rubber modified bitumen also avoid milling operation which further make the products cost effective and energy efficient.

5.1 Introduction

Petroleum derived bitumen is generally used in most highway pavement, airport pavement and roping applications. However, during the last decade considerable increase in traffic loads, severe climatic conditions and construction failures led to the need for improvement in the properties of the bitumen **[1-3]**. Environmental factors such as variation in temperature, air and rainfall can have adverse effect on the durability of bitumen pavement. The ideal bitumen should be strong enough at high temperatures, to prevent rutting and at the same time soft enough to avoid excessive thermal cracking at low pavement temperatures and fatigue. Properties of bitumen largely depend on the origin of the crude oil and on the refinery processes employed. However, in order to achieve and improve the desired in-service properties of bitumen such as to prevent rutting and thermal cracking, bitumen is usually modified mainly with additives and polymers. For bitumen to be effective in road applications, it should be blended with the polymer to improve its resistance to rutting, fatigue, cracking, aging, stripping, etc. **[4]** at moderate and high temperatures. Addition of virgin polymer materials for bitumen modification tends to increase the cost of the final product. Therefore, from an economic and environmental standpoint, waste rubber from discarded tires can provide an alternative source of elastomeric polymer material for bitumen modification and can be an effective substitute to the virgin polymers **[4-8]**. However, researches on crumb rubber (CR) to improve performance of pavement as an elastic binder additive have been known for more than 50 years **[9-13]**. Crumb rubber modified bitumen known to exhibit improved mechanical performance by reducing fatigue cracking, reflective cracking, and increasing performance of the pavement **[14-17]**. Although crumb rubber has been extensively accepted by its low cost and easy availability as compared to other polymer, but asphalt rubber's low resistance to heat and low storage stability weakens the duration in service life and check the recycling opportunities of end-of-life road pavements [18-19]. Therefore, it is necessary to determine further studies on the utilization of crumb rubber as well as reduction of elastomeric polymer without compromising performance of bitumen from ecological point of view.

Other researchers also investigate the chemically modified crumb rubber asphalt (CMCRA) prepared through chemical treatment with hydrogen peroxide of the crumb rubber show in improved elastic recovery property of the bitumen and showed good performance both in the lab and in the field tests **[18]**. Another article showed that a reactive polyoctenamer plastomer (namely Vestenamer®) chemically reacts with crumb rubber (CR) and bitumen to improve tackiness properties **[20]**. In another article, the authors have studied the effects of polyoctenamer on the rheological properties of CRMB produced from base bitumen and ground tire rubber **[21]**.

In the present research work, bitumen binders formulated with crumb rubber, polyoctenamer and sulphur additives have been studied. The combination of reactive polyoctenamer along with cross linking agent was found to promote anchoring of crumb rubber in bitumen to produce storage stable crumb rubber modified bitumen. The use of reactive polyoctenamer polymer to develop storage stable crumb rubber modified bitumen also avoids milling operation which further makes the products cost effective and energy efficient.

5.2 Experimental

5.2.1 Methods and Materials

5.2.1.1 Virgin bitumen

Experiments were carried out with commercial VG 10 grade bitumen obtained from the Indian Oil Mathura refinery. Typical properties of bitumen used are given in Table 5.1.

Table 5.1 Properties of Virgin bitumen

Properties	Virgin Bitumen	Referral specification
Absolute Viscosity (60^0c), Poise	1140	IS1206 (PART2)
Kinematics Viscosity (135^0C)	301	IS1206 (PART3)
Penetration 25^0C (100g, 5s),0.1mm	86	IS1203/1978
Softening Point ^{0}C	46	IS 1205/1978
Ductility at 27 ^{0}C (5 Cm/Min)	100+	IS 1208 : 1978
Flash Point, ^{O}C	350	IS1209

5.2.1.2 Polyoctenamer

Polyoctenamer was supplied by Micu Traders, Vadodara, India. Typical properties of Polyoctenamer are shown in Table 5.2.

Table 5.2 Properties of Polyoctenamer

Tensile impact strength kJ/m2 23°C	165	ISO 8256
Molecular weight (MW)	90,000	DIN 55672-1 GPC
Tensile Stress Yield	7.5 MPa	ISO 527-2
Glass transition temperature	- 65°C	ISO 11357

5.2.1.3 Crumb rubber

The crumb rubber powder was supplied by Indian Oil (Marketing Division). Typical properties of crumb rubber powder are shown in Table 5.3.

Table 5.3 Properties of Crumb Rubber Powder

Ash contain	5.8%	ASTM D5667-95
Volatile contain	0.59%	ASTM D5668-99
Toluene insoluble	58.78%	
Type of rubber	Isoprene	1SO 4650
Particles size passing through 600 micron	100%	ASTM 5667-95
Moisture contain	0.52%	ASTM D 5668-99

5.2.1.4 Sulphur

Sulphur was supplied from Indian Oil Mathura Refinery. It is a yellow lumpy solid powder of 99.9% purity.

5.2.1.5 Method of Preparation of Modified CRMB

Bitumen was heated at 170 ^{0}C until it became a liquid in a glass container then transferred the sample into the mixer chamber and then slowly added 10 parts crumb rubber powder, based on 100 parts of bitumen. The mixture was stirred by applying high speed shear mixer at 170 to 175 ^{0}C and a stirring rate of 650-800 rpm for 2 hours to produce CRMB-1. Similarly, 0.5%, 1% and 1.5% polyoctenamer added to CRMB-1 and stirrer at 650-800 rpm for 1h at 175 ^{0}C and then 0.1% sulphur was added to form CRMB-2-A, CRMB-3-A and CRMB-4-A, respectively. Similarly, 0.5%, 1% and 1.5% polyoctenamer added to CRMB-1 and stirrer at 650-800 rpm for 1h at 175 ^{0}C and then 0.5% sulphur was added to form CRMB-2-B, CRMB-3-B and CRMB-4-B respectively. The above processing of bitumen was showed to improve performance of crumb rubber modified bitumen.

5.3 Result and Discussion

5.3.1 Conventional bitumen binder tests

The virgin bitumen and CRMB-1, CRMB-2-A, CRMB-2-B, CRMB-3-A, CRMB-3-B, CRMB-4-A, CRMB-4-B were subjected to penetration test, softening point and elastic recovery as per IS & ASTM test method. The results of these tests are listed in Table 5.4.

Table 5.4 Physico-Chemical Properties Modified CRMB

Formulation	Penetration (25°C,100g, 5s)	Softening point (°C)	Elastic recovery (%) at 5°C	Separation test (Diff. of Softening Point)
CRMB-1	46	57.3	65	9
CRMB-2-A	44	59.8	67	6.5
CRMB-3-A	45	59.9	70	5
CRMB-4-A	45	62.5	73	2
CRMB-2-B	41	60	69	6
CRMB-3-B	40	61.7	72	4
CRMB-4-B	40	62	75	8

The results very clearly shows that all the developed formulations were found to have decrease in penetration and an increase in the softening point as compared to reference sample CRMB-1. It was also found that increase in the percentage of polyoctenamer and decrease in crumb rubber content leads to increase in the elastic recovery and softening point of modified binder. Similarly, increase in sulphur percentage also affects the elastic recovery and softening point of developed product.

5.3.2 Storage stability Test

The use of crumb rubber in bitumen without appropriate stirring generally results in compatibility problems, leading to phase separation. Such problems have been more severe with increases of CR content, which otherwise provides good performance. To confirm its compatibility, storage stability was determined according to ASTM D5892 test method. The sample was placed in a tube and put into an oven at 163±5°C oven for 48 h. The tube was then conditioning at room temperature and stored in a freezer. The tube was then cut into three equal parts. Samples from the upper and lower parts of the tube were then melted and poured into the rings for the ring and ball softening point test. The difference in °C between the softening point of respective top and bottom fraction were determined. The results showed that increase in the percentage of polyoctenamer content increases the storage stability of modified CRMB. However, test data of CRMB-4-B (Table 5.4) showed that, increase in the percentage of sulphur leads to decrease in the storage stability.

5.3.3 Viscosity at 150 ^{0}C by Rotational Viscometer

Fig.5.1 shows the results of rotational viscosity of neat bitumen and various developed binders at 150°C. When test data of neat bitumen and CRMB-1, CRMB-2-A, CRMB-2-B, CRMB-3-A, CRMB-3-B, CRMB-4-A and CRMB-4-B was compared it has been found that the viscosities of all the modified bitumen binders are higher than neat bitumen and CRMB-1. Addition of polyoctenamer and sulphur plays an important role in increase in viscosity of modified binder. All the modified CRMB binders were found to meet super pave specifications.

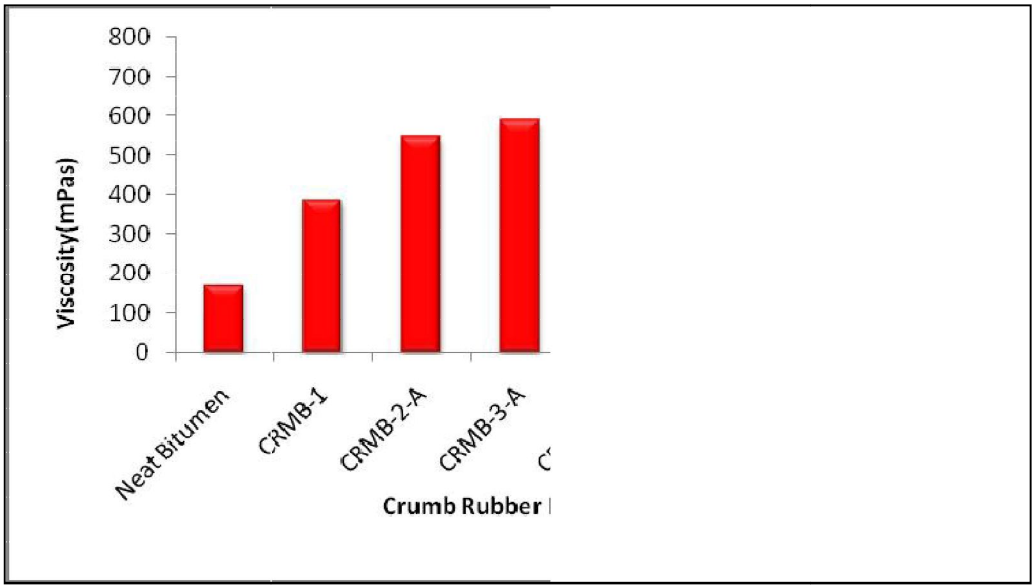

Fig.5.1 Viscosity of virgin bitumen and modified CRMB at 150 ^{0}C

5.3.4 Dynamic Shear Rheometer

The dynamic shear rheometer (DSR) was carried out to evaluate the permanent deformation and fatigue cracking properties of the various developed product in the present work, virgin crumb rubber modified bitumen and virgin bitumen. Adopted procedures for the DSR are given in AASHTO T315-10. Physical property was determined with the help of DSR using unaged (Fig.5.2), rolling thin film oven (RTFO-aged) (Fig.5.3), and pressure aging vessel (PAV-aged) binders (Fig.5.4). 25-mm DSR plate was used to test all unaged and RTFO-aged modified bitumen binder and the 8-mm DSR plate was used to test for all PAV-aged modified bitumen binders. All the polyoctenamer and sulphur doped crumb rubber modified bitumen showed an increase of G*/Sinδ as compared to original virgin bitumen and CRMB-1 binder. The virgin bitumen and CRMB-1 showed less thermal susceptibility and elastic response as compared to polyoctenamer modified CRMB as shown in the graph of G*/Sinδ versus temperature relationship. The graph also showed that increases in the percentage of polyoctenamer and sulphur content in modified binder leads to increases in the G*/Sinδ value.

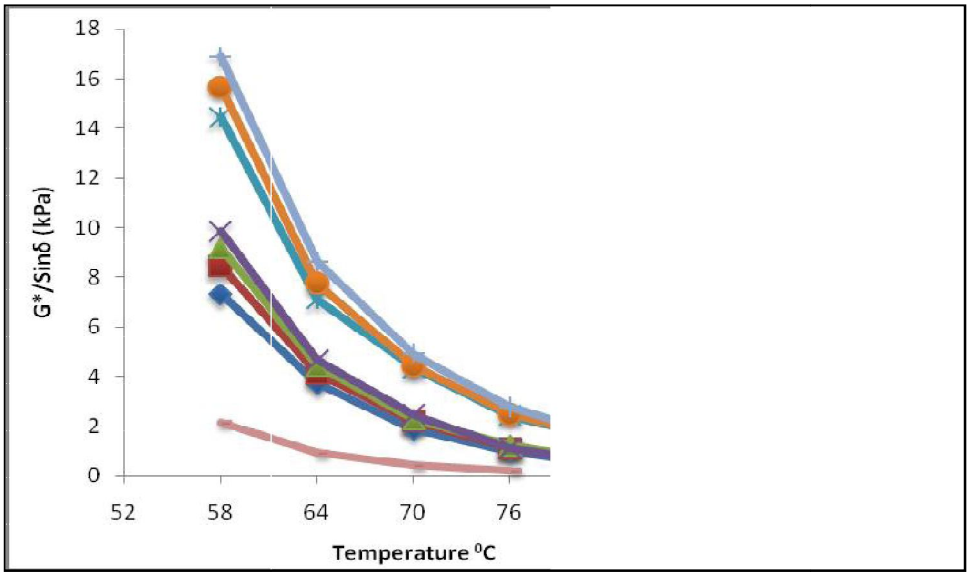

Fig.5.2 G*/Sinδ (kPa) Measured as a function of temperature of unaged binder

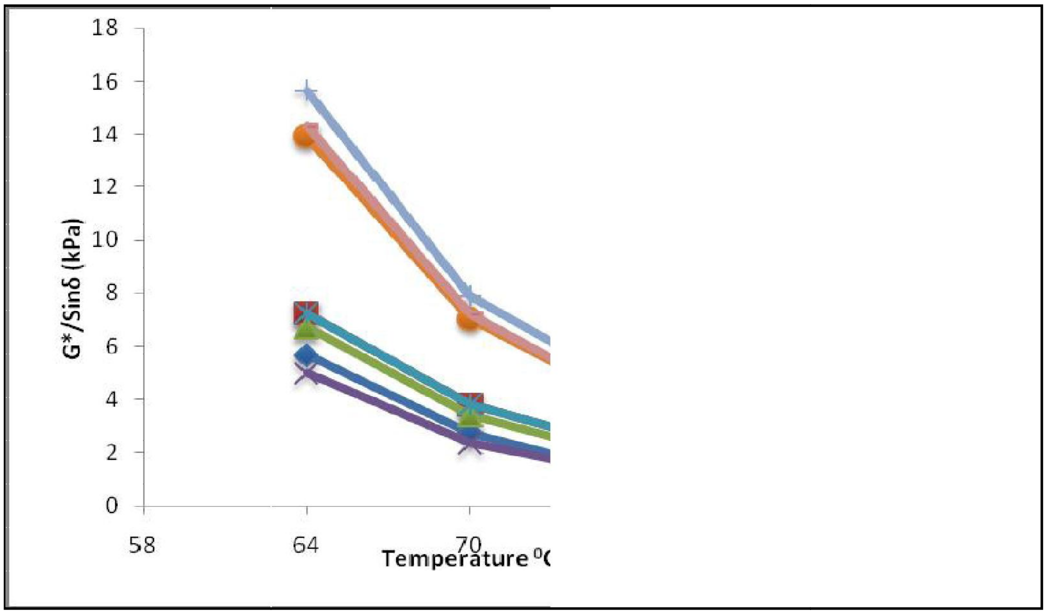

Fig.5.3 G*/Sinδ (kPa) Measured as a function of temperature of RTFO aged binder

5.3.5 Bending Beam Rheometer

The BBR was used to determine the thermal cracking of all binder. In this research work the BBR test was adopted according to the AASHTO T313-10. The low temperature performance of the neat bitumen, CRMB-1, CRMB-2-A, CRMB-2-B, CRMB-3-A, and CRMB-3-B were determined in terms of bitumen binder creep stiffness and m-value over a series of temperatures. According to AASHTO specification, the maximum creeps stiffness allowed to satisfy the low temperature bitumen binder grade is 300 MPa. Fig.5.5 shows that the CRMB-2-A, CRMB-3-A and CRMB-4-A were found to meet with creep stiffness specifications up to −18 °C thereby meeting low temperature performance specifications for −28 °C in terms of creep stiffness. But the CRMB-1, CRMB-2-B, CRMB-3-B and CRMB-4-B were found to meet with creep stiffness specifications up to −12°C their by meeting low temperature performance specifications for −22°C in terms of creep stiffness. From this result, it is interesting to note that by increasing the percentage of polyoctenamer, the temperature susceptibility of bitumen was found to reduce and one AASHTO grade was increased. However, increase in sulphur content did not affect the temperature susceptibility and meets with creep stiffness specifications up to −12°C. According to AASHTO specification the minimum m-value allowed to meet the low temperature bitumen binder grade is 0.3. Similar order was observed in the case of m-value which confirms the above stiffness order with reduced temperature susceptibility by increasing the percentage of polyoctenamer up to 1.5%.

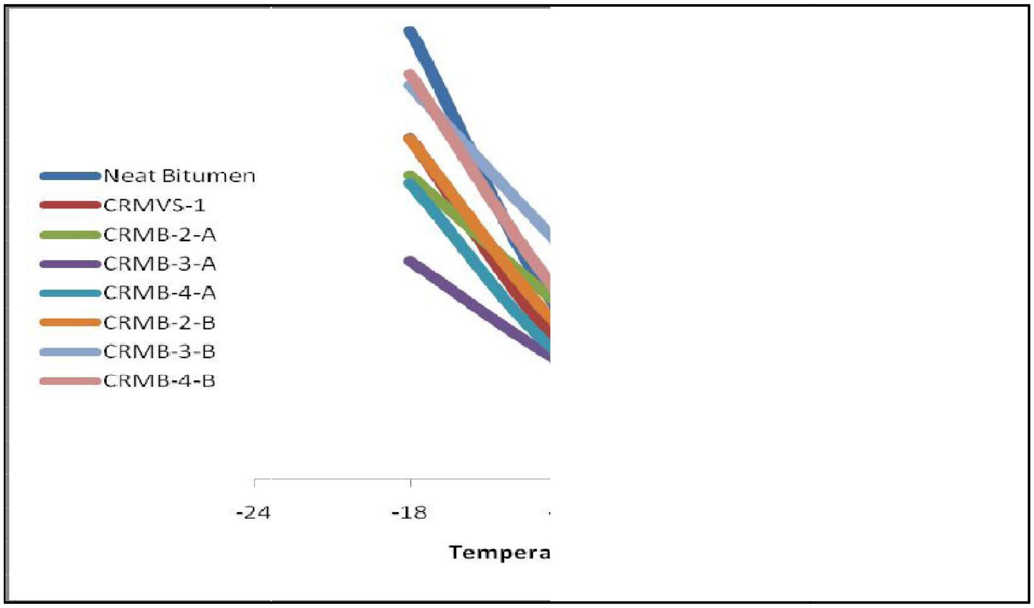

Fig.5.4 Stiffness of bitumen at different temperature

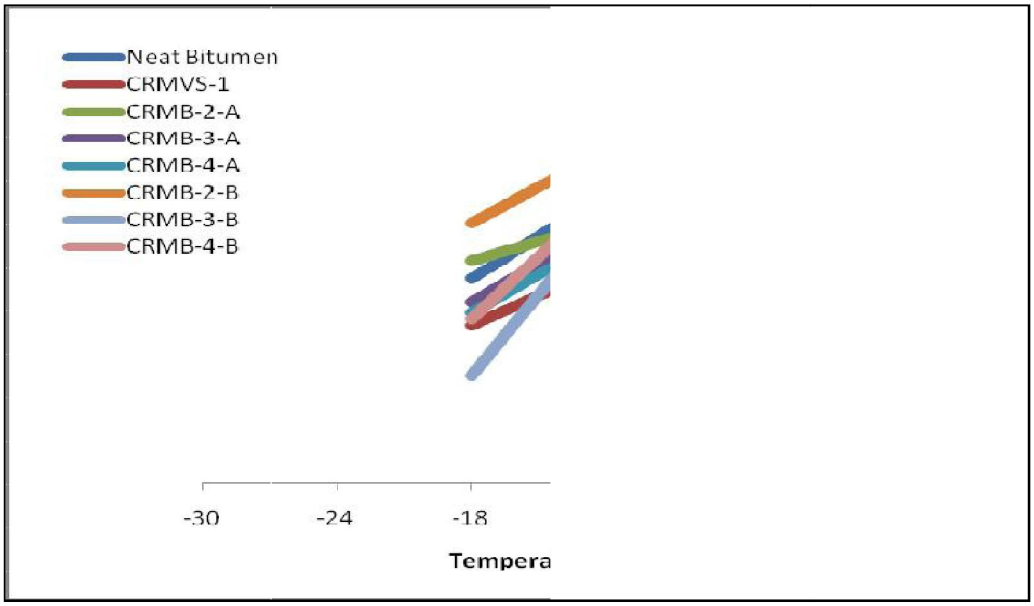

Fig.5.5 m- Value of Bitumen at Different Temperatures

5.4 Conclusions

The combination of reactive polyoctenamer along with cross linking agent was also found to promote anchoring of crumb rubber in bitumen to produce storage stable crumb rubber modified bitumen. The present study also covered various performance tests on CRMB formulations using reactive polyoctenamer polymer and sulphur cross linking agent. From the above study, it has been concluded that:

1. Physical properties of bitumen such as penetration and softening point were improved with the addition of polyoctenamer and sulphur in CRMB indicating better temperature susceptibility of developed product.
2. All the CRMB modified with polyoctenamer and sulphur were found to possess less rutting susceptible as compared to CRMB-1 and virgin bitumen binders. However, by increasing the percentage of polyoctenamer up to 1.5%, the high temperature performance of the modified bitumen increases drastically.
3. By increasing the percentage of polyoctenamer in modified binder the creep stiffness values were also increased. However, with increase in

sulphur content from 0.1% to 0.5%, the temperature susceptible of the modified bitumen was also decreased.

4. The combination of reactive polyoctenamer along with cross linking agent was also found to promote anchoring of crumb rubber in bitumen to produce storage stable crumb rubber modified bitumen.
5. The use of reactive polyoctenamer polymer also avoid milling operation for the production of storage stable crumb rubber modified bitumen which further makes the products cost effective and energy efficient.

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CHAPTER 6

Improved Performance of a Reactive Polymer Based Bituminous Mixes–Effect of Cross Linking Agent.

In the present work, polymer based modified bitumen with enhanced performance was prepared by using reactive polyoctenamer plastomer and cross linking agent such as sulphur. Properties of developed PMB were compared with Styrene Butadiene Styrene (SBS) based Polymer modified bitumen (PMB). The results indicate that developed PMB compares well with SBS elastomer based PMB in all tests including storage stability, rheological properties, Marshal Strength, Stripping properties, rutting characteristics and creep recovery test. The developed PMB in the present work has been developed without milling operation which further make the product cost effective with energy saving.

6.1 Introduction

Polymers have been extensively used for the modification of bitumen in recent days so as to improve the performance of bituminous pavements under severe conditions of service such as extreme climatic conditions, ever increasing axle loads, and ingress of moisture. Currently, the most commonly used polymer for bitumen modification is the styrene-butadiene-styrene (SBS). SBS improves the desired properties like elastic recovery, rutting resistance, resistance against low temperature cracking of bituminous pavements and therefore globally used for bitumen modification in large volume at present. However, it is reported that SBS containing bitumen quite often shows thermodynamically unstable nature and leads to some serious problems such as early phase separations when stored at high temperature, tendency to degrade on exposure to heat, oxygen, and UV light **[1-5]**. These conditions generally may lead to undesirable ageing of bitumen and polymer degradation, thus affecting the overall performance of the blend. Such observation has led to research studies for improving the compatibility & storage stability of modified bitumen through the use of novel additives and other polymers of varying chemistry including reactive polymers **[6-9]**. The reactive functional groups of reactive polymer are usually expected to interact with some components of bitumen in various ways such as forming chemical bonds or hydrogen bonds, which may improve the compatibility of the resulting binder.

For instance, the functionalized SBS copolymers by respectively adding amino and carboxylic acid groups during synthesis and claimed that these functional groups could improve the compatibility of SBS with bitumen without considerable influences on their other physical properties **[10]**. In another article, the authors investigate the rheological property change due to grafting and the effect of grafted eucommia ulmoides gum (EUG) on bitumen **[11]**. Meanwhile, other researchers investigate the chemically modified crumb rubber asphalt (CMCRA) prepared through chemical treatment with hydrogen peroxide of the crumb rubber show in improved elastic recovery property of the bitumen and showed good performance both in the lab and in the field tests **[12]**. Two reactive polymers namely ethylene terpolymer (SRETP) and ethylene terpolymer (ETP) are used improve the performance of bitumen **[13]**. The viscosity functions of bitumen blended with polymers such as styrene-butadiene-styrene (SBS), ethylene vinylacetate (EVA) and reactive polymer "Ethylene terpolymers" (RET) at different temperatures, showed that the first two polymers form a physical network that is swollen by the asphalt, while the latter (which is functionalized with glycidyl methacrylate) is cross linked and/or have formed chemical bonds with the molecules of asphaltenes. In another article showed that a reactive polyoctenamer plastomer, namely Vestenamer® from Evonic-Degussa, reacts chemically with crumb rubber (CR) and bitumen to produce uniform, crumb rubber modified bitumen (CRMB) with relatively low tackiness properties. This chemical bonding has been attributed to the double-bond structure of the polyoctenamer plastomer which may permits cross-linking with the sulphur associated with the bitumen **[14]**. In another article, the author studied the effects of the binder additive polyoctenamer on the rheological properties of CRMB produced from base asphalt and ground tire rubber to see the effects of polyoctenamer in the characterization of the performance of bitumen rubber mixtures **[15]**.

In the present work, polymer modified bitumen (PMB) with enhanced performance properties was developed by using reactive polyoctenamer plastomer and cross linking agent such as sulphur. The developed PMB compares well with SBS based PMB in all performance tests such as storage stability, rheological properties, Marshal Strength, Stripping properties, rutting characteristics, creep recovery test and fatigue damage. The developed PMB in the present work has been developed without milling operation which further make the product cost effective with energy saving.

6.2 Experimental

6.2.1 Materials & Methods

All experiments were carried out with commercial VG 10 grade bitumen meeting IS specification (IS:73-2007), obtained from the IndianOil Mathura refinery. Typical properties of bitumen used in the present work are given in Table 6.1. Sulphur used in this work is also obtained from the Indian Oil Mathura refinery.

Table 6.1 Physio-chemical properties of VG-10 grade neat bitumen

Penetration 25 °C (100 g,5s), (0.1mm)	82	IS:1203/1978
Absolute Viscosity at 60^{0}C/ 30 cm Hg, Poise	1135	IS:1206(PART2)
Kinematic Viscosity at 135^{0}C (cst)	373	IS:1206 (PART3)
Softening Point, ^{0}C	47	IS: 1205/1978
Ductility at 25^{0}C (5 cm/min), cm	100+	IS: 1208 : 1978
Viscosity at 150°C, Pa.s	171	ASTM:D4402
Ductility after TFOT at 25^{0}C, cm	100+	IS: 1208 : 1978

6.2.1.1 Styrene Butadiene Styrene (SBS)

SBS was supplied by LG Chem. Ltd South Korea, whose properties are shown in Table 6.2.

Table 6.2 Properties of SBS Polymer

Density	0.940 g/cm^{3}	ISO2781
Melt Mass-flow rate (200^{0}C/5.0kg)	<0.50 g/10 min	ASTM D1238
Tensile Strength (Yield)	34.3 MPa	ASTM D638

6.2.1.2 Polyoctenamer Polymer

Polyoctenamer plastomer was supplied by Micu Traders, Vadodara, India; its critical properties are shown in Table 6.3.

Table 6.3 Properties of Polyoctenamer

Density	0.91g/cm^{3}	ISO 1183
Tensile Stress Yield	7.5 MPa	ISO 527-2
Glass transition temperature	- 65°C	ISO 11357

6.2.1.3 Aggregate

Properly graded aggregates, as per Ministry of Road Transport and Highways 2000 Specifications were used. The adopted gradation of aggregates used is given in Table 6.4.

Table 6.4 Gradations of aggregate for bituminous concrete

Aggregate Sieve size (mm)	Requirement of MORT&H	Aggregate gradation Adopted, % Passing
26.5	100	100
19.0	100	100
13.2	79-100	93.6
9.5	70-100	87.6
4.75	53-71	70.8
2.36	42-58	54.2
1.18	34-48	36.8
0.600	26-38	29.2
0.300	18-28	25.4
0.150	12-20	16.4
0.075	4-10	5.9

6.2.1.4 Procedure for the Modification of Bitumen

To ensure consistency and homogeneity of polymer dispersion in bitumen, a high shear mixer from ENH Engineering's A/S PMB bitumen pilot plant was used. Four modified bitumen mixes such as RPMB-A, RPMB-B, and PMB-C & PMB-D were produced. The properties of the blended bitumen samples, RPMB-A, RPMB-B, and PMB-C & PMB-D are given in Table 6.5.

6.2.1.5 Procedure for preparing formulation RPMB-A and RPMB-B:

To prepare formulation RPMB-A, a blend of polyoctenamer in Bitumen in the ratio 2:98 was prepared at 600 rpm for 1 hour using the above high shear mixer at 170 ^{0}C. After that sulphur (0.1%) was added in formulation RPMB-A and again mixed for 30 minutes at 170 ^{0}C to get formulation RPMB-B. The developed RPMB in the present work has been developed without milling operation which further make the product cost effective with energy saving.

6.2.1.6 Procedure for preparing formulation PMB-C and PMB-D

To prepare formulation PMB-C, a blend of SBS in Bitumen in the ratio 2:98 was prepared by churning at 600 rpm for 2 hrs using the above high shear mixer at 170 ^{0}C and further milling it for 15 minute. After that sulphur (0.1%) was added in formulation PMB-C separately and again mixed for one more hour at 170 ^{0}C to get formulation PMB-D.

6.3 Results and Discussion

6.3.1 Conventional binder tests

Physicochemical properties (Table 6.5) of the modified bitumen sample indicate that the addition of polymers (both Polyoctenamer and SBS polymer) in bitumen, with and without sulphur additive, showed reduction in the penetration values and an increase in the softening point as well as the viscosities of all formulations. These results indicate that the softening point of PMB get enhanced with addition of polymeric additives. This is an indication of increased temperature susceptibility of binder. With high degree of unsaturation in polyoctenamer polymer, one would expect it to degrade faster under extreme conditions particularly at high temperatures. Therefore, the understanding of the aging behavior of modified bitumen formulation containing this polymer, at high temperatures was considered essential. An accelerated aging test was, therefore, performed in which viscosities (at 150 ^{o}C) for modified bitumen formulations were studied for 30 days at elevated temperature of 140 ^{o}C (Fig.6.1). The results show a continuous trend of increase in viscosity with increase in aging days. However, after 15 days the formulation RPMB-B started showing decrease in viscosity and lumps started forming. This is presumably due to degradation of the polymer-sulphur matrix in bitumen. However, the other formulations (RPMB-A, PMB-C and PMB-D) consistently showed an increase in viscosity. The results suggest that in the unlikely event of storing (Formulation RPMB-B) at 140^0C or higher temperature for more than 15 days, the bitumen mix may have negative effect on performance.

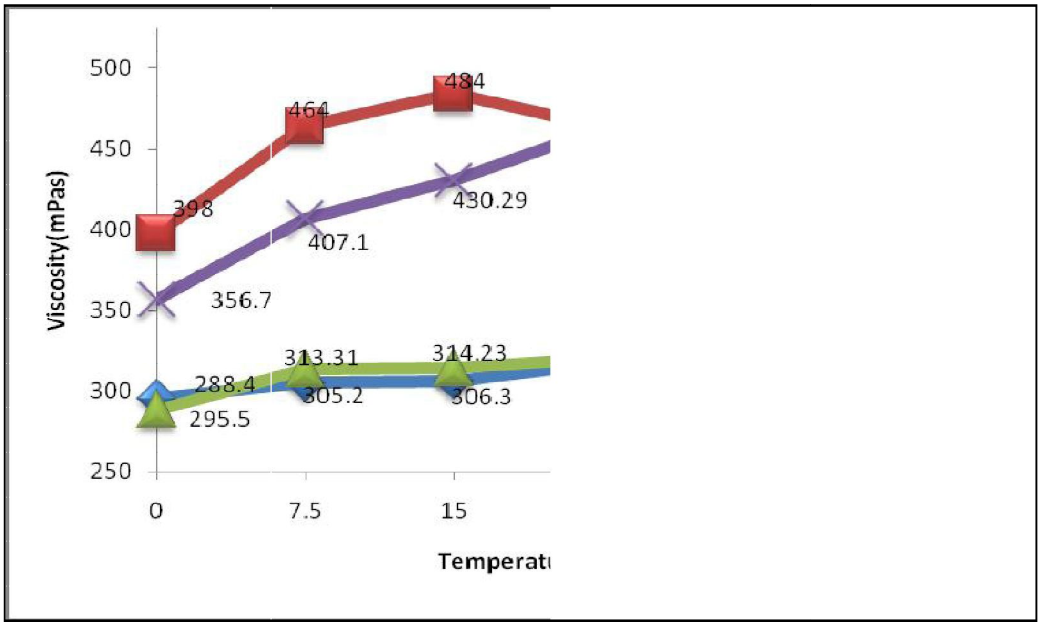

Fig.6.1 Long term aging effect

Table 6.5 Physico-chemical properties of formulated modified bituminous Product

Properties	Bitumen	Formulations			
		RPMB-A	RPMB-B	PMB-C	PMB-D
Penetration, 25℃,100g, 5s	82	68	66	63	62
Softening Point, ℃	47	51	54	52	55
Penetration Index, PI	- 0.773	-0.198	+0.455	-0.15	+1.239
Elastic recovery at 15℃, %	--	38	70	65	70
Viscosity at 150 ℃, Pa.s	171.3	295.5	398	288.4	356.7

Separation Test (Difference of Softening Point, °C)	--	0.5	0.6	0.8	1

6.3.2 Storage stability Test.

Use of high molecular weight polymers, in the absence of appropriate stirring, may result in compatibility problems of polymer in bitumen leading to phase separation. Such problems have been reported even in elastomeric polymers such as SBS, which otherwise provide good performance. To confirm its compatibility, storage stability was determined according to ASTM D5892 test procedure. The sample was placed in a tube and the same is kept into an oven at 163±5°C for 48 hour. The tube was then conditioning in room temperature and then stored in a freezer. The tube was then cut into three equal parts. Samples from the upper and lower parts of the tube were then melted and poured into the rings for the ring and ball softening point test. The difference in °C between the softening point of respective top and bottom samples were determined. The results of separation test for RPMB-A is 0.2 and RPMB-B is 0.3 which is very low value compared to any other PMB formulation such as PMB-C and PMB-D whose value is 0.8 and 1 (Table 6.5). However, all the formulations were within safe limits.

6.3.3 Elastic Recovery

IS: 15462 specifications have classified polymers as plastomer or elastomers based on their chemical structure rather than any specific property. Traditionally, both plastomers and elastomers have been used in making PMBs but bitumen modified with the elastomer type of polymers have been preferred as they recover faster from distortions, on the removal of heavy loads on pavements. The polyoctenamer used in this study belongs to a plastomeric class and like other members of this class, it has poor elastic recovery e.g. polyoctenamer modified bitumen RPMB-A (with 2% Polyoctenamer in bitumen) has only 38% elastic recovery against the required value of 70% (min) (IS: 15462 Spec). However, with the addition of 0.1% of sulphur to this formulation (RPMB-B), elastic recovery value changes to 70%, while SBS modified bitumen (which has about 65% elastic recovery), on addition of sulphur shows only little change in the range 5 to 7 % (Fig.6.2). This remarkable change observed with polyoctenamer based formulation may be due to the reactive nature of polymer which provides a higher degree of cross linking with sulphur and makes the formulation RPMB-B behave like an elastomer modified bitumen.

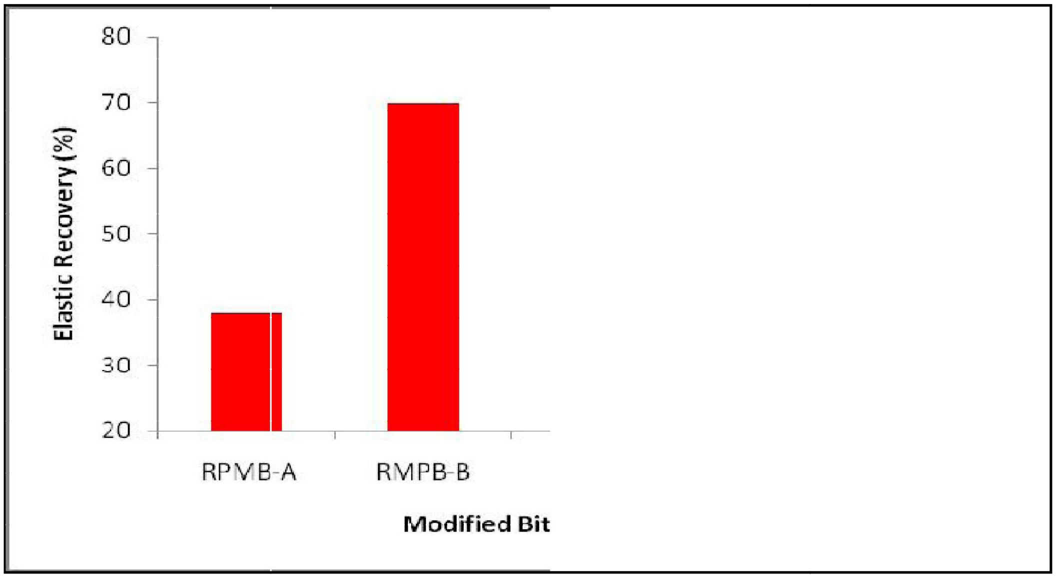

Fig.6.2 Elastic recovery of modified bitumen

6.3.4 Marshall Stability Test

The Marshall Stability and flow value of the pavement was performed on (ELE International). Marshall Stability and flow value represents the maximum load that causes failure of the specimen and total amount of deformation, respectively. To produce compacted bituminous mix specimens of thickness 63.5 ± 0.5 mm, 1150 gm of aggregates was taken. The bituminous mix is placed in a mould and compacted and tested at 150-160 ^{0}C as per ASTM: D 6926 and ASTM: D 6927 methods. The specimen is immersed in a bath of water at a temperature of 60 ± 1°C for a period of 30 minutes. Accordingly, several test specimens were prepared and tested and finally calculated the Marshall Strength and plastic flow values for the three bitumen contents corresponding to maximum mixture density, maximum aggregate density and stability. The results indicate that Marshall Stability increases from 14.82 KN to about 25 KN on three formulations viz. RPMB-A, RPMB-B and PMB-C while it increases to 22.96 KN in formulation PMB-D (Table 6.6).

Table 6.6 Marshall Stability Test

Formulation	Stability (kN)	% of Increase in stability over neat bitumen	Flow (mm)	Marshall quotient (kg/mm)	% of Increase in MQ over neat bitumen	Retained Marshall stability	Flow (mm) in Retained Marshall stability
Neat Bitumen	14.82	-	3.29	4.50	-	10.15	3.66
RPMB_A	25.19	41.16	3.34	7.54	40.31	18.71	3.11
RPMB-B	25.63	42.17	3.59	7.13	36.88	18.15	2.87
PMB-C	25.76	42.46	4.07	6.32	28.77	19.14	4.54
PMB-D	22.96	35.45	4.32	5.31	15.25	19.44	3.19

The Marshall Flow value is lower in formulation RPMB-A and RPMB-B in comparison to SBS based formulations, PMB-C and PMB-D. These results would indicate that formulations RPMB-A and RPMB-B will provide equal or better strength and resistance against the plastic flow when compared to SBS based formulations PMB-C and PMB-D. The retained Marshall Stability test results at 5.5% binder's content showed that the performance of all formulations was nearly equivalent. (IRC: 53-2010)

6.3.5 Antistripping Performance

Besides some other deformations caused due to field conditions, moisture induced damage to flexible pavements, such as raveling or localized bleeding, becomes a critical factor leading to premature failure of bituminous pavements. When water enters the bitumen aggregate interface, it weakens the bond in bituminous mixes and causes bitumen to strip off from the aggregate surfaces. There may be several ways through which moisture may diffuse through bitumen films and cause stripping. Generally, stripping is attributed to variables like bitumen's chemical and rheological properties, aggregate surface chemistry, adsorbed coatings, pH at the interface, traffic, construction practices and presence and nature of anti-stripping additives. There are several tests, such as the hot water boil test and freeze-thaw test for determining anti-strip properties of additives. In this study, we employed the hot water boiling test (ASTM: D 3625) for evaluating the stripping property of bituminous mixes. The adhesion between bitumen and aggregate was determined by visual estimation of the stripped degree of a bituminous film on an aggregate surface after the water boiling test. Fig.6.3 illustrates stripping characteristics of PMB and compared the anti-stripping properties of developed product with SBS based PMB and found that the developed product has equivalent behavior as SBS based PMB.

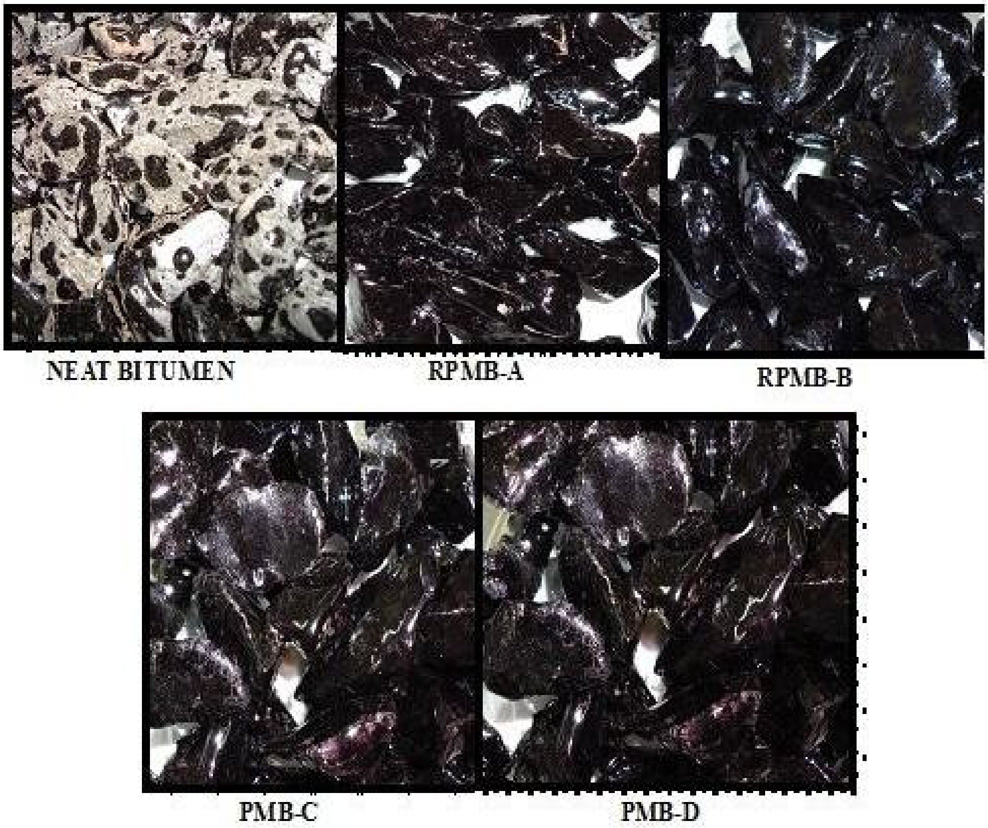

Fig.6.3 Hot water stripping Test

6.3.6 Dynamic Shear Rheometer (DSR)

DSR method has been one of the standard approaches for measuring the short & long term deformation characteristics of bitumen. The test measures the $G^*/\sin(\delta)$ and $G^*\sin(\delta)$, which are parameters of rutting-resistance and fatigue resistance of bituminous products, respectively. The Superpave performance graded binder specification, ASTM: D 6682-06, states that at the maximum pavement design temperature, the G*/Sin(δ) value should be at least 2.2 kPa for RTFOT-aged bitumen to resist rutting. The limit value for neat bitumen is 1.0 kPa. It is seen from the Fig.6.4 and Fig.6.5, that the failure temperature of formulations RPMB-A, RPMB-B, PMB-C, PMB-D is 69.0, 73.8, 68.6 ^{0}C and 70.9 ^{0}C respectively, for original binders and 67.9, 69.3, 66.5 and 68.1 ^{0}C respectively for RTFOT residues. The results show that, for both original and RTFO aged binder, G*/sin(δ) has been marginally higher in formulations RPMB-B and PMB-D than RPMB-A and PMB-C formulations respectively. This suggests that sulphur plays an important role to increase the performance of modifier at higher temperatures. The results also indicate that that the plastomer (polyoctenamer) with 0.1% sulphur could also be a good modifier for bitumen like SBS.

To evaluate the effect of polymer on the binder performance at intermediate service temperatures, the DSR test was performed on the PAV-aged modified bitumen, in a temperature range of 34-16 ^{0}C. The performance graded bitumen (ASTM: D6682) specification states that the fatigue parameter G*Sin (δ) for the PAV aged binder should be less than 5000 kPa at intermediate pavement design temperatures. Fig.6.6 shown that G*Sin (δ) values have been lower than 5000 kPa at 19 ^{0}C for all crumb rubber modified bitumen. For all four formulations namely, RPMB-A, RPMB-B, PMB-C, and PMB-D, the G*Sin (δ) has given acceptable results at 17.6 °C, 16.4 °C, 17.4 °C and 16.9 ^{0}C, respectively. The result thus shows that all the formulations would meet the same performance grading.

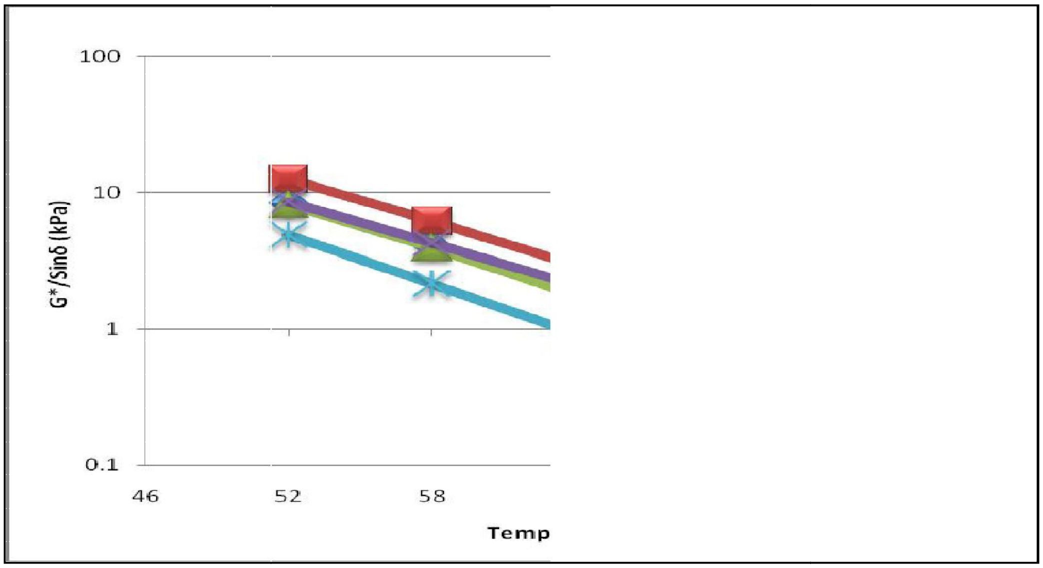

Fig.6.4 G*/Sinδ (kPa) measured as a function of temperature of unaged modified bitumen

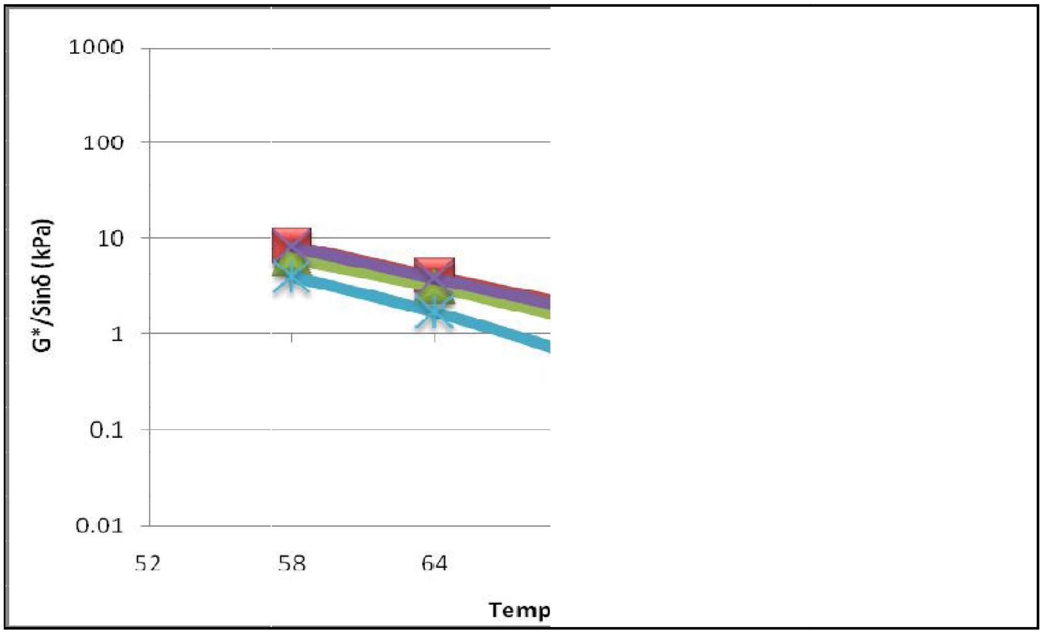

Fig.6.5 G*/Sinδ (kPa) measured as a function of temperature of modified bitumen after RTFO-aged

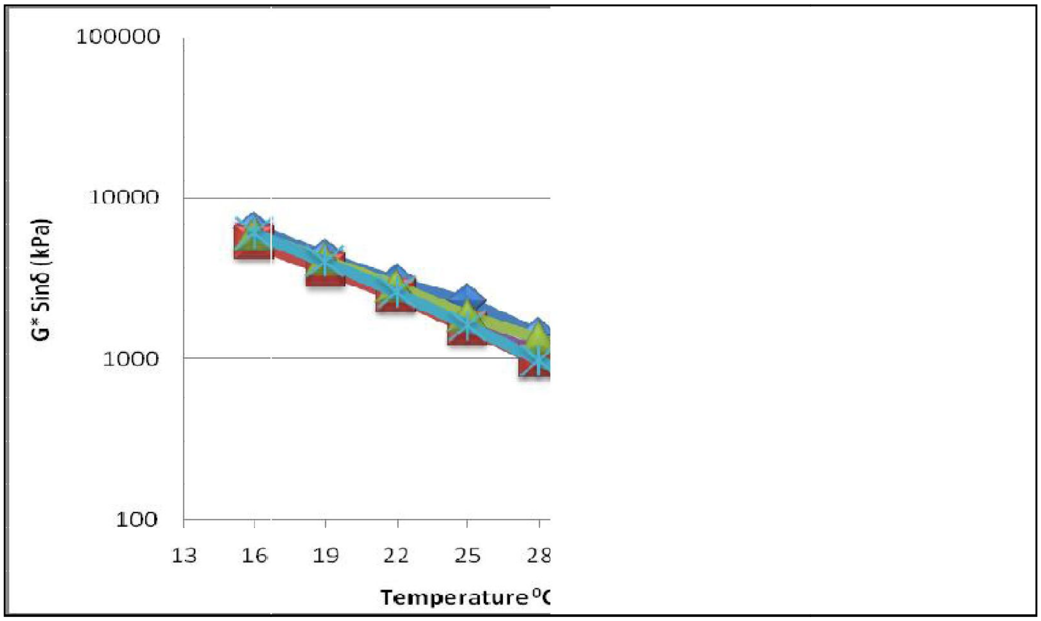

Fig.6.6 G*. Sinδ (kPa) measured as a function of temperature of PAV-aged modified bitumen

6.3.7 Multiple Stress Creep Recovery test (MSCR)

The performance of the binder was also characterized using Multiple Stress Creep Recovery test (MSCR). AASHTO TP70-07 and ASTM D7405 specifications are used to classify the presence of elastic response in the modified bitumen and also the change in elastic response at two shear stress levels at 0.1 and 3.2 kPa. The percent recovery in the MSCR test of modified bitumen is affected by the type of polymer used in the polymer modified bitumen. Non-recoverable creep compliance (Jnr) has been used to explain the resistance of modified bitumen to permanent deformation (rutting) under repeated load. Fig.6.7 & Fig.6.8 show MSCR test results in terms of percent recovery and non-recoverable compliance at different stress levels at two shear stress levels at 0.1 and 3.2 kPa at 64.0 ºC.

The Jnr values for all modified binders increase with the increase in stress level as can be seen in Fig.6.8. For example, the Modified bitumen Binder RPMB-A, RPMB-B, PMB-C and PMB-D have the Jnr values 0.8679, 0.4904, 0.4256, 0.848 kPa-1, respectively at 0.1 kPa but exhibit higher Jnr values i.e. 1.1769, 0.6775, 1.2865 and

0.9287 kPa-1, respectively at 3.2 kPa stress level. From the above data it may be inferred that the binders RPMB-A and PMB-D have Jnr values 1.5 to 2 times larger than RPM-B and PMB-C. This implies that the–sulphur modified reactive polymer based PMB (i.e. RPMB-B) shows greater rutting resistance than SBS based PMB (i.e. PMB-C) at 64 °C. From the Fig.6.7, it can also be observed that Sulphur has significant impact on polyoctenamer modified bitumen and therefore, it is expected to give more flexibility to pavement to recover the deformation under heavy traffic. Higher stress levels did not have a large influence on the behaviour of sulphur modified polyoctenamer bitumen binder when normalized for the effect of stress. It, therefore, proves sulphur has suitability to be used under heavy traffic condition to modify polyoctenamer modified bitumen binders.

The percent recovery observed during the study reflects the elastic response of the binder. The MSCR results (Fig.6.7) showed that at lower stress levels, i.e. 0.1 kPa, RPMB-B and PMB-C formulations exhibit higher elastic response than RPMB-A and PMB-D. However, at lower stress levels, i.e. 3.2 kPa RPMB-B and PMB-D modified binders exhibit higher elastic response compared to RPMB-A and PMB-C. In nut shell, MSCR test results indicate that adding sulphur in case of reactive polyoctenamer and SBS modified bitumen largely increased resistance to rutting. This result is in agreement with wheel tracking rutting test and G*/sin δ values obtained from the Superpave PG grading test.

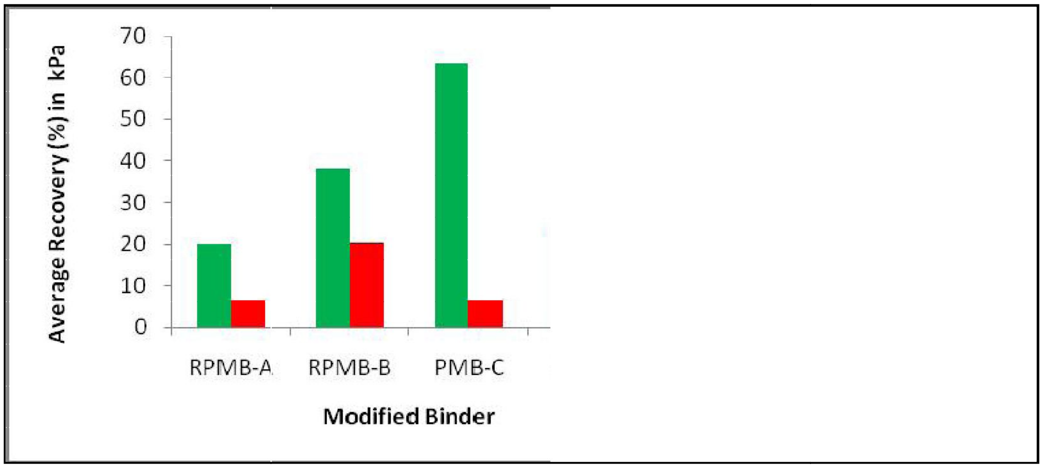

Fig.6.7 MSCR average recovery at 64 ^{0}C (RTFOT residue)

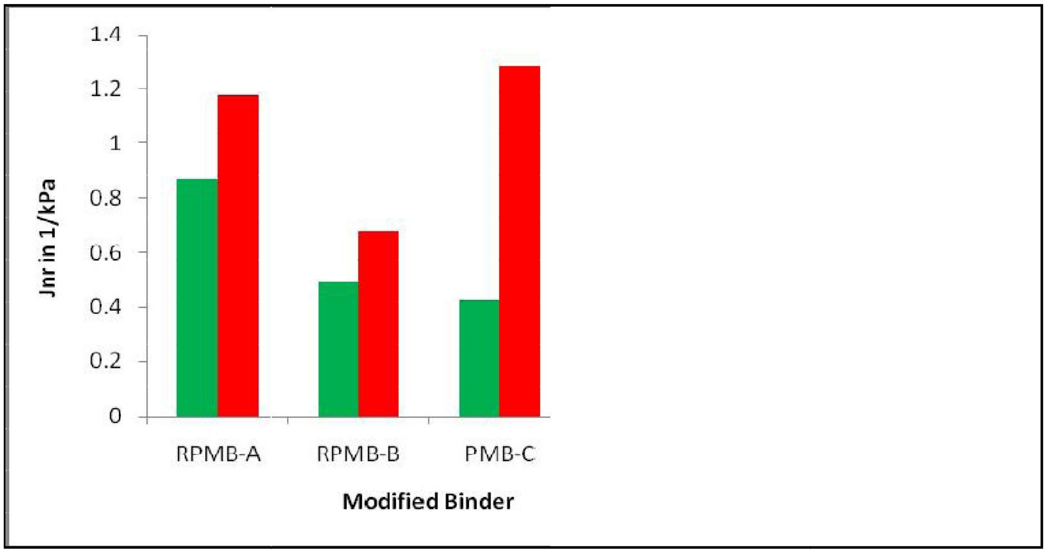

Fig.6.8 Non-recoverable compliance, Jnr, in modified binder

6.3.8 Bending Beam Rheometer Test (BBR)

In order to further examine low temperature cracking properties, thin beams of bitumen were tested for creep stiffness at low temperature using bending beam rheometer. BBR measures the stiffness and m-value. Stiffness is a measure of the thermal stresses developed in the Hot Mix Asphalt (HMA) as a result of thermal contraction. The slope of the stiffness curve, m, is a measure of the rate of stress relaxation. The maximum stiffness criteria of 300 MPa and the minimum m-value criteria of 0.30 has been recommended in performance graded binder specifications (ASTM: D 6682), which is generally an accepted value for mitigating low-temperature cracking. In the present study, we carried out creep tests on PAV aged binders at four different temperatures (-18, -12 and -6 ^{o}C) using bending beam rheometer (TE-BBR, Cannon Instrument Company). The creep stiffness and m-value results are shown in Fig.6.9 & Fig.6.10. These results reveal that the creep stiffness of modified bitumen has decreased while the m-value has increased. According to the results, PMB-C has maximum stiffness followed by RPMB-A, RPMB-B and PMB-D in that order. The minimum stiffness is observed in PMB-D. In terms of m-value, formulation RPMB-A has minimum m-value, followed by RPMB-B, PMB-C and PMB-D. The maximum m-value is shown by formulation PMB-D. Bitumen pavements with high creep moduli and low m-values are more susceptible to low-temperature thermal distress. In view of above, it may be concluded that all formulations, including formulation RPMB-B, satisfy the acceptable performance criteria up to a temperature of -12 °C.

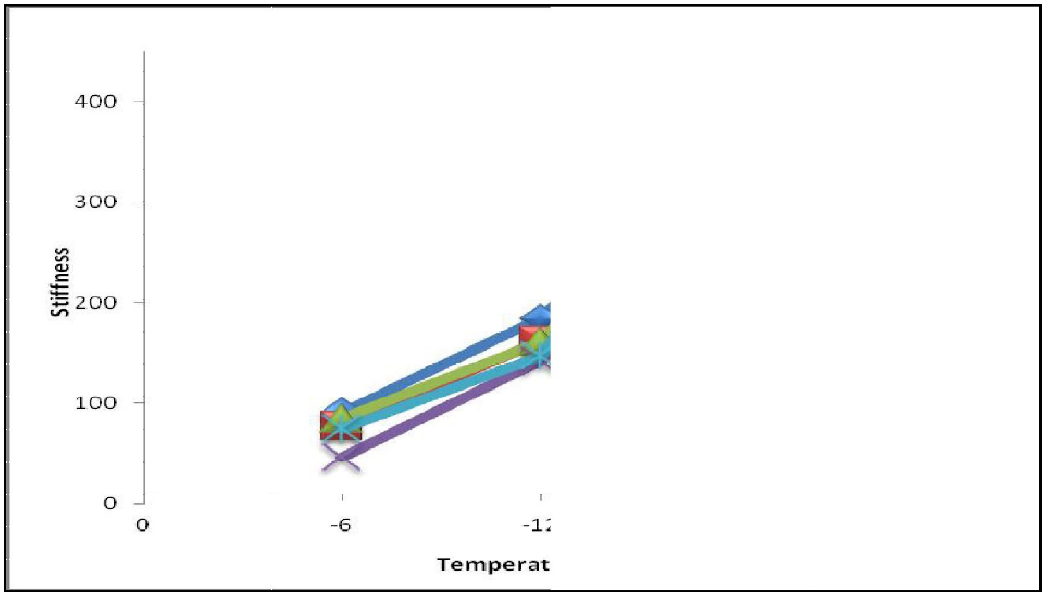

Fig.6.9 Stiffness of modified bitumen

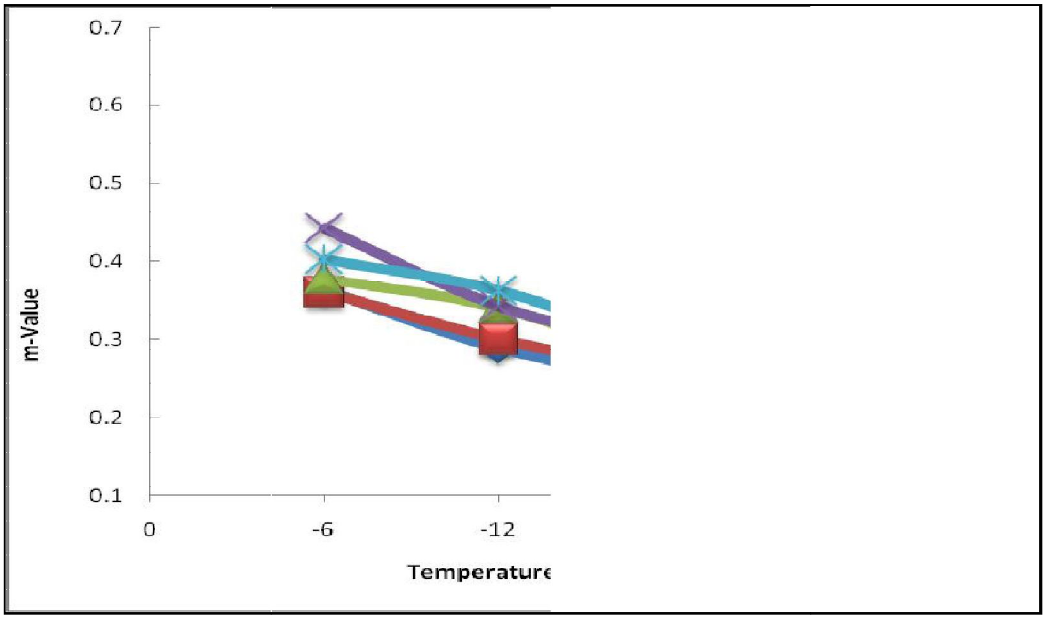

Fig.6.10 m-value of modified bitumen

6.3.9 Rutting Resistance Test

The rutting resistance test was done according to the wheel tracking test (EN12697-22: 2003+A1). In this test, the sample taken was a square slab with the length of 300 mm and width of 300 mm and height 40mm. The mixing conditions of samples RPMB-A, RPMB-B, PMB-A and PMB-B with aggregate were designated such that the percentage of air voids were maintained at 4.5-5.5. The mixes were compacted by compactor at 150 to 160 ^{0}C. The finished slab was allowed to cure at room temperature for 48 h. It was then put into an oven at 60 °C for another 5 h for conditioning before being placed into the wheel tracking device for conducting rutting test at 60 °C. The movement of a wheel was organized at a frequency of 53 passes per minute. During the test, rut depth recorded at various time intervals. Calculation of the rate of the rutting (RR) was based on a time interval between 15 and 30 min. The RR was computed as (d2-d1) /15 with a unit of mm/min. A lower RR means better resistance to rutting. For each of the four kinds of polymer modified bituminous mixes two experiments were conducted and their average was considered to represent the rut resistance for each polymer modified bituminous mix. It was observed (Fig.6.11 & Fig.6.12) that the rutting depth of formulation RPMB-B was lowest under all cycles as also the rate of rutting (0.02mm/minute for RPMB-B against 0.07mm/minute for neat bitumen). This data, therefore, indicates that the rutting characteristic of formulation RPMB-B has an edge over other three formulations w. r. t performance stated.

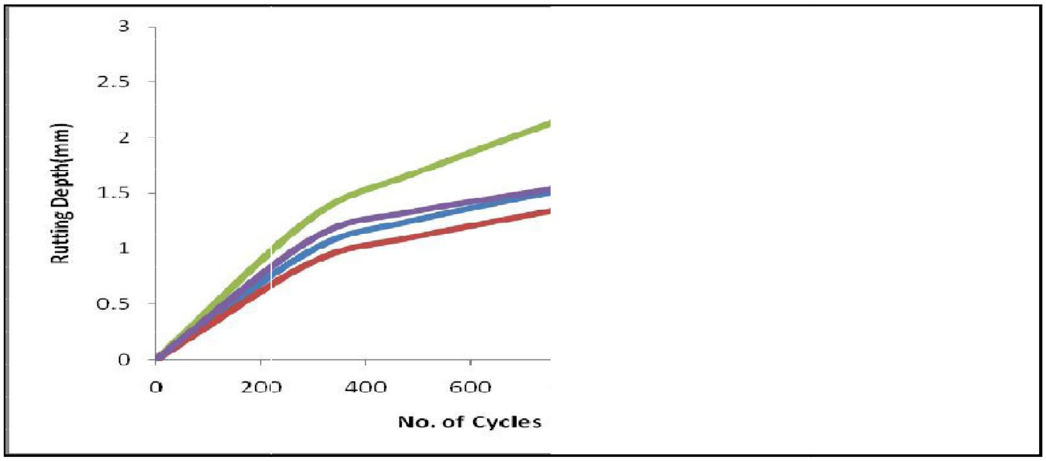

Fig.6.11 Rutting depth of modified bitumen

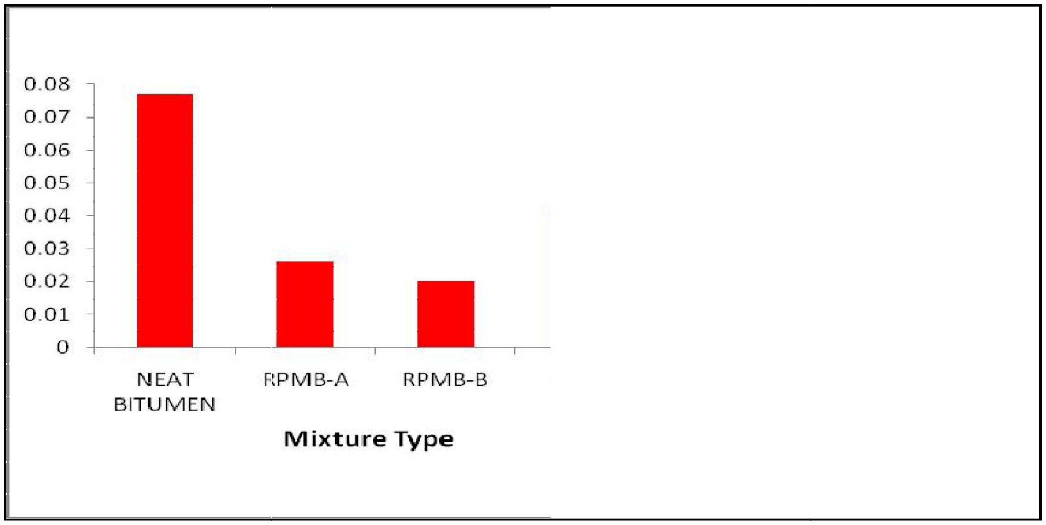

Fig.6.12 Rate of rutting of modified bitumen

6.3.10. Four Point Bending Beam test

The fatigue resistance of the bituminous mixtures was studied in four point bending apparatus (IPC Global, Australia) according to SHRP M-0009 and EN 12697-24:2004 test method. Prepared specimens were subjected to four point bending beam analysis for determining the fatigue life at constant tensile stain of 300µ€. This test is a closed loop, computer controlled system that measures the deflection of the beam specimen, computes the stain in the specimen, and adjust the load such that the specimen experiences a constant level of stain on each load cycle. The test system record load cycles, the applied load, beam deflection, and compute the maximum tensile stress, maximum tensile stain, phase angle, flexural stiffness, dissipated energy, and cumulative dissipated energy at specified interval of load cycles. The test is conducted for 10 lacs cycles. The test specimens were prepared of size 381± 6mm in length, 50.8± 6mm in height and 63.5± 6mm in width at predetermined compaction temperatures at 160 ^{0}C by using Roller Compacter (Dyna-comp Roller Compactor, model 77-B3602, supplied by M/s Controls Testing Equipment Ltd, UK.) using force step mode with 28 cycles passes (4 passes at 7 KN, 4 passes at 9 KN, 6 passes 10KN, 6 passes at 12 KN and 8 passes at 14 KN). The specimens with 100mm diameter, 68 mm height were prepared by using compacted slab followed by cutting with the help of core cutter (model, D75387, type DK-13, supplied by M/s Weka Elektrowerkzeuge, Germany). The prepared specimen was conditioned at 20 ^{0}C at least for 2 hrs before carried out the experiment. The fatigue test data of all test specimen were determined at 20 ^{0}C. The fatigue property of all binder is shown in Table 6.7. Comparable flexural stiffness at 100 for the binders RPMB-A, RPMB-B, PMB-C and PMB-D is given in Table 6.7. However, the sulphur modified PMB (i.e. RPMB-B and PMB-D) passes greater number of cycles to reach half of the initial flexural stiffness. From this observation it has been found that sulphur has significant impact on both SBS and polyoctenamer polymer in bitumen which further expected to enhanced life of pavement.

Table 6.7 Four Point Bending Beam Test for Flexural Stiffness

(Compaction Temperature 155 ^{0}C)

No of Cycles	**Formulation**				
	Neat Bitumen	**RPMB-A**	**RPMB-B**	**PMB-C**	**PMB-D**
Initial Flexural Stiffness (at 100cycles)	2161.62	4156.5	3987.75	4121.89	4269.97
Final Flexural Stiffness (in cycles)	1077.29 (at 389040 Cycles)	2077.69 at 357540 cycles	1986.39 (at 860990 cycles)	2058.75 (At 416860 Cycles)	2129.17(at 662400 Cycles)
Maximum tensile tress (kPa) (at 100cycles)	647.22	1246.43	655.97	1245.55	1285.89
Maximum tensile tress (kPa) (in	323.61(at 389040 Cycles)	624 kPa (at 357540 cycles)	323.18 (At 860990 cycles)	618.61(At 416860 Cycles)	634.91(at 662400 Cycles)

cycles)					
Maximum tensile strain (µ€) (at 100cycles)	299.41	299.88	299.84	302.18	301.67
Maximum tensile strain (µ€) (in cycles)	300.39 (At 389040 Cycles)	300.57 (at 357540 cycles)	303.42 (At 860990 cycles)	300.48 (At 416860 Cycles)	299.67(at 662400 Cycles)

6.4 Conclusions

The present study covered various performance tests on PMB formulations using 2% reactive polyoctenamer polymer and 0.1% sulphur and compared with a SBS based PMB formulation. From the data presented, it has been concluded that:

1. Polyoctenamer modified bitumen formulation RPMB-A, which has no sulphur, does not meet the performance characteristics of polymer modified bitumen on elastic recovery. However, when it is blended with a small percentage (0.1% only) of sulphur, a remarkable change is observed in its properties, particularly the elastic recovery. The product, RPMB-B, eventually becomes comparable in properties and performance to the well established SBS based modified bitumen (PMB-C). Further, The developed RPMB in the present work has been developed without milling operation which further make the product cost effective with energy saving
2. Conventional bitumen testing such as penetration and softening point results showed that the addition of both polyoctenamer and SBS polymers in bitumen increased hardness of the binder residues and reduced their temperature susceptibility.
3. Storage stability characteristics of the all formulations were determined according to ASTM D5892. The result showed that polyoctenamer modified bitumen has comparable stability with SBS modified bitumen. .

4. In terms of Marshall Stability test, the results of all formulations studied indicate that stability increases by about 25%. Similarly the flow value was lower and the Marshall Quotient value (MQ) was higher in comparison to SBS based formulations. These results indicated that formulation RPMB-B is likely will provide equally good resistance against permanent deformations due to their higher stability numbers, lower flow and higher MQ values.
5. The formulation, RPMB-B, also shows significant improvement in antistripping properties and was found to be comparable to SBS based formulation (both showing 100% adherence to aggregate surfaces in boil test). However RPMB-A showed lesser stripping characteristics.
6. The results of Dynamic Shear Rheometer (DSR) show that for both unaged and aged formulation, RPMB-B, the $G^*/\sin(\delta)$ was slightly higher than SBS based formulation. This indicates that sulphur plays an important role to improve the performance of modifier at higher temperatures.
7. According to the BBR results, all formulations showed lower stiffness and satisfies the acceptable criteria up to the test temperature of -12°C.
8. The MSCR test results indicate that adding sulphur in the formulation increases the resistance to rutting in both cases of polyoctenamer and SBS modified bitumen.
9. The wheel tracking test was done to check the Rutting resistance of the formulations. It was observed that the rutting depth of formulation RPMB-B was the lowest under all cycles tested as also the rate of rutting (0.02mm/minute for RPMB-B against 0.07mm/minute for neat bitumen). This data also indicated that the rutting performance of formulation RPMB-B is better compared to other three formulations tested under similar conditions.
10. The Four Point Bending Beam test results indicate that all formulations have comparable flexural stiffness at 100 Cycles. However, sulphur modified based PMB (i.e. RPMB-B and PMB-D) passes greater number of cycles to reach half of the initial flexural stiffness.

6.5 References

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CHAPTER 7

Conclusions & Recommendation

7.1 Conclusions

The present thesis is directed to chemically conversion of waste plastic (such as PET and PVC) into useful polymeric compounds which in turn leads to several bituminous applications. Thus this research not only utilizes waste non-degradable PET but also provides a new platform to use these additives for in-situ polymerization in the body of bitumen. This research also provides a new approach to develop polymer modified bitumen & crumb rubber modified bitumen using reactive polymers to avoid milling operation which further make the products cost effective and energy efficient. The present research work also provides an alternate way for the disposal of waste plastics and waste tires keeping the environment free of pollution. This may contribute a important role in **Swachh Bharat Abhiyan** which is a national level campaign by the Government of India.

Following conclusions can be drawn from the present thesis:

- Utilization of waste PET derived products for industrial use has seen in literature, only for limited applications. The present study explores the use of aminolysis process employing green chemistry approach for conversion of environmentally hazardous waste PET into industrially useful anti-stripping compounds and their use in various bituminous applications. It has been observed that bitumen doped with PET derivatives improves 100 % anti-stripping property of bitumen. Pavement researchers have also found that bitumen doped with amine base antistripping additives deteriorates original properties of bitumen but the test results of present research work shows that bitumen doped with synthesized terephthalamide derivatives do not affect the properties of original binder.

- In order to ensure better dispersion of polymers in bitumen, the present thesis also describes the innovative approach for in-situ polymerization of terephthalamide derivatives (derived from waste PET) with methylene diphenyl diisocyanate (MDI) in the body of bitumen to synthesize polyurea and polyurethane. Insitu polymerized polymer modified bitumen was found to enhance the rheological properties of bitumen.

- Bituminous concrete mixture with improved antistripping properties is reported for the first time through incorporation of PVC-NH2 derivative (derived from the reaction of polyamines with PVC polymer) in bitumen. It was also observed that PVC-NH2 product with 0.5 to 1.5% dosages in bitumen shows good anti-striping properties.

- In the present thesis, polymer modified bitumen with enhanced performance properties was prepared by using reactive polyoctenamer plastomer and cross linking agent such as sulphur in bitumen. The results of the developed PMB were found to be compare well with SBS elastomer based PMB in all tests methods including storage stability, rheological properties, Marshal Strength, Stripping properties, rutting characteristics and creep recovery test. The PMB in the present work was developed without milling operation which further makes the product cost effective with energy efficient.

- PMB modified with CR/polyoctenamer/sulphur was found to have improvement in penetration, softening point, elastic recovery, viscosity and storage stability as compare to virgin bitumen and conventional crumb rubber modified bitumen. BBR studies also showed that by increasing the percentage of polyoctenamer in crumb rubber modified bitumen, creep stiffness were also increased. However, with the increase in sulphur content from 0.1% to 0.5%, creep stiffness of the modified CRMB was decreased.

7.2. Recommendation

However, it is recommended that more research regarding reactive polymers, in-situ polymerization of different polymers, anchoring of crumb rubber using waste PET, should be commence. In addition to this, field trial sections should also be laid and their performance should be studied.

LIST OF PATENTS & PUBLICATIONS

PATENTS

- ✓ **Rabindra K Padhan**, A.Krishna, A.A.Gupta, and A.K.Bhatnagar Process for conversion of polyethylene terephthalate (PET) polymers to anti-stripping compounds for bitumen and a process for improving anti-stripping properties of bitumen" **(European Patent) Patent No. EP:13716382.0**

- ✓ **Rabindra K Padhan**, A.Krishna, A.A.Gupta, and A.K.Bhatnagar Process for conversion of polyethylene terephthalate (PET) polymers to anti-stripping compounds for bitumen and a process for improving anti-stripping properties of bitumen" **Sri Lankan Patent, Patent No. 17819.**

- ✓ **Rabindra K Padhan**, A.Krishna, A.A.Gupta, and A.K.Bhatnagar Process for conversion of polyethylene terephthalate (PET) polymers to anti-stripping compounds for bitumen and a process for improving anti-stripping properties of bitumen" Indian patent, **Patent No. 140/KOL/20112, PCT File No: PCT/IB2013/050974.**

- ✓ **Rabindra K Padhan**, A.A.Gupta, and A.K.Bhatnagar "A Process for Manufacturing Reactive Polymer Modified Bitumen with Enhanced Elastic Recovery" **Indian patent, Patent No. 2235/MUM/2013**

- ✓ **Rabindra K Padhan**, A.A.Gupta, and A.K.Bhatnagar Modified Polyethylene Terephthalate (PET) Derived Polymer Modified Bitumen (PMB), **Indian Patent, Patent No.1049/MUM/2014**

PUBLICATIONS

- ✓ **Rabindra K Padhan**, A.A.Gupta, R.P.Badoni and A.K.Bhatnagar, PET Polymer derived chemicals as antistripping additive for bitumen- An Environment Friendly Approach for Disposal of environmentally hazardous material, **Journal of Polymer Degradation & Stability, Vol-98, Issue 12, 2013, pp 2592–2601.**

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- ✓ **Rabindra K Padhan**, A.A.Gupta, R.P.Badoni and A.K.Bhatnagar. Surface Modification of Poly (Vinyl Chloride) Using Polyamine to Improve Antistripping Characteristics of Bitumen. Journal of Applied Polymer Science. **(Communicated Date, Nov.15).**

- ✓ **Rabindra K Padhan**, A.A.Gupta, R.P.Badoni and A.K.Bhatnagar, Investigation of the rheological properties and storage stability of CR/polyoctenamer/sulphur modified bitumen. International Journal of Pavement Engineering **(Communicated Date, Nov.22).**

SEMINAR/POSTER PRESENTATIONS

- ✓ **Rabindra Kumar Padhan, Invited talk** on Third International Conference on Recycling and Reuse of Materials (ICRM 2014) Kerala Environment friendly approach for the recycle of Poly(ethylene terephthalate) waste

- ✓ **Rabindra Kumar Padhan**, Veena Yadav, A.A.Gupta, N.S.Raman, A.K.Bhatnagar, "Production of Plastomeric Bitumen by Using Waste Plastic, **9th** International Symposium on Fuels and Lubricants, Paper Presentation held at India Habitat Centre, New Delhi, India. **(Best Poster Award)**

- ✓ **Rabindra K Padhan**, A.A.Gupta, R.P.Badoni and A.K.Bhatnagar, 2012 "An environment friendly synthesis of BHETA from Polyethylene Terpthalate(PET)" **8th International Symposium on Fuels and Lubricants**, Paper Presentation held at India Habitat Centre, New Delhi, India.
- ✓ Workshop on Analytical Techniques in Petroleum Analysis, IndianOil R&D Centre, Faridabad held during August 08-12, 2011.
- ✓ Workshop on Chromatography, Indian Analytical Scientist Delhi Chapter at Manav Rachna International University, Faridabad held during January 11 – 16, 2011

AWARDS/ HONOURS

- ✓ **Best Poster Award** in 9th International Symposium on Fuels and Lubricants **(ISFL)** 2014**.**
- ✓ **IPR Incentive Award** for creation of IP Wealth for IndianOil in 2013.
- ✓ **Invited Talk** in the Third International Conference on Recycling and Reuse of Materials **(ICRM 2014)** to be held on 11, 12 and 13 April 2014, Kottayam, Kerala, India.
- ✓ Qualify National **Eligibility Test (NET) 2010 & 2011**, conducted by Council of Scientific and Industrial Research (CSIR), New Delhi.
- ✓ Qualify Graduated Engineering Aptitude Test **(GATE) 2013,** conducted by IIT Mumbai.
- ✓ Qualify DL-101 Course on **Intellectual Properties Right** by WIPO academy 2013.