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POLYMER MODIFIED BITUMEN PREPARED USING ABS POLYMER-CHARACTERIZATION AND APPLICATION IN FLEXIBLE PAVEMENT

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ABSTRACT

The modification of bitumen using polymers in road paving applications is gaining momentum day to day over the past few years. The need for the modification is raised due to the need in the improved performance of the flexible pavements. Developing countries like India whose transportation mainly depends upon the road, need a vast research in this field. Presently the commonly used modifier for the modification of bitumen is the styrene butadiene styrene polymer which is elastomeric in nature. Polymers like styrene butadiene rubber, natural rubber and CRMB are also used for the modification of bitumen. Many scientists are experimenting on the use of waste polymers for the bitumen modification. The present paper is to study the modification of the bitumen using an elastomeric polymer Acrylo Nitrile Butadiene Styrene. Samples of ABS modified bitumen were prepared by mixing different percentages of ABS with neat bitumen of PG 80/100. The prepared PMB was subjected to various studies starting from empirical tests, Infra Red Spectroscopy and the thermal analysis. The results of IR investigations indicate that the mixed ABS modifies the chemical nature of the bitumen chain with some increased butadiene concentration in the mix. The nitrile group present in ABS also alters the structure of the bitumen mix. The thermal investigation indicates the various distinct decomposition stages of the modified bitumen and it shows an increase in the thermal stability of the polymer modified bitumen. The ageing characteristics of the modified bitumen were also studied and the results obtained are discussed in this research paper. The polymer modified bitumen aggregate mix was also prepared to study the mix properties. Properties like stripping test and extraction test was carried to study the binding nature of ABS PMB with the aggregate. The stability nature of the mix was carried using the Marshal Stability test and the voids parameters were also measured. The results obtained shows improved characteristics of the mix properties. With the results obtained for the ABS PMB and its mix shows that the prepared sample can be very well used for flexible pavement applications.

Keywords: polymer modified bitumen, thermal analysis, FTIR, ABS, ageing.

Abbreviations

ABS = Acrylo Nitrile Butadiene Styrene
FTIR = Fourier Transformation Infra Red Spectroscopy
PMB = Polymer Modified Bitumen
MSV = Marshal Stability Value
ASTM = American Society for Testing and Materials

1. INTRODUCTION

The Development of polymer modified bitumen composites gain momentum due to its vast application in the field of flexible pavements (Airey GD., 2002). The performance of asphalt concrete pavement depends on the bitumen properties, asphalt concrete mixtures volumetric properties and external factors such as traffic volume and environment. Bitumen is a visco-elastic material where temperature and rate of load application have a great influence on its behavior. Conventional flexible pavement is exposed to a wide range of loading and weather conditions; it is soft in a hot environment and brittle under low temperature. Higher traffic volume produces high stress within pavement layer, which is one of the main causes for pavement distress. Fatigue cracking and permanent deformation are considered as most serious distresses associated with flexible pavements. These distresses reduce the service life of the pavement and increase the maintenance cost. To reduce the pavement distresses there are different solutions such as by adopting new mix design or by using asphalt additives. Using of asphalt additives in highway construction is known to give the conventional bitumen better engineering properties as well as it is helpful to extend the life span of asphalt concrete pavement.

Considerable research in recent years is going on in the polymer modified bitumen to improve the performance of the bitumen in the flexible pavements. Modified bitumen provides the diversified properties needed to build better performing roads. Addition of polymer to asphalt cement is the most important form of modification due to its wide range of application and potential for use. Nowadays, polymer technology is considered as a permanent part of the highway construction (Topal A., 2010; González V *et al*., 2010; Pena JJ., 2002; Airey GD., 2003). On the other hand, using crumb rubber from scrap tiers, waste plastics, e waste and other waste related to polymers as asphalt modifier helps to solve serious environmental problems too and to improve the pavement performance. The main advantage of using polymer technology is to improve the adhesion properties between the binder and aggregate. The properties of modified bitumen depend on the modifier type with respect to modifier content and bitumen type. The main advantage of elastomers such as (SBR) and (SBS) (Feng Zhang *et al*., 2011) is that they can provide a higher strength to the modified bitumen or

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mixtures (King *et al*., 1999). The use of ABS is a recent research in the field of polymer modified bitumen. The ABS is also a tri block copolymer (elastomer) which contains styrene molecule and nitrile compound at both the ends and co blocked with diene compound. It is believed that the use of ABS will result in some physical change with the asphaltenes present in the bitumen. ABS polymer is used to modify the bitumen and the modified bitumen is subjected to various studies and the results are discussed in detail in this paper.

2. EXPERIMENTAL PROGRAM

2.1 Materials

Base bitumen is collected from Indian Oil Corporation an Indian bitumen manufacturing company. The basic properties of the bitumen was tested and reported in Table-1. The ABS polymer was supplied by RANBAXY chemicals. The polymer size was measured and found to be >600microns

2.2 Sample preparation

The bitumen was heated to 165.deg.C and it was stirred at a speed of 3000 rpm and then the ABS polymer was added to it. The stirring was continued for six hours. Two bitumen samples were prepared using different percentages of ABS. The polymer content of ABS PMB was ranged as 5% and 7%. All these PMBS were prepared in a mechanical shear mixer, the modified bitumen was named as ABS5 and ABS7 and the plain bitumen was named as Plain B. The polymer modified bitumen were prepared using a shear mechanical stirrer REMI Model

2.3 Methods of testing

2.3.1. Empirical tests

The plain bitumen and the ABS PMB were subjected to the following conventional binder tests: Penetration tests to study the penetration value of the bitumen at 25^0C; Ductility test to study the ductile/elastic recovery of the bitumen at 25^0C; Softening point test to study the softening temperature range of the bitumen; separation test to find the homogeneity of the PMBs formed under this process. All the tests were carried out under the procedure adopted by ASTM standards

2.3.2. Ageing characteristics

The Ageing is the process of inducing/simulating the field performance of the binder in the laboratory (Durrieu F *et al*., 2007; Mouillet V *et al*., 2008). Ageing study on the ABS PMB was done using RTFOT. The process of ageing is to make the bitumen harder by thermally oxidizing the bitumen in the presence of hot air. The standard procedure was heating the bitumen to 160^0C and maintaining the bitumen at that temperature for 75min.

2.3.3. Thermal studies

TGA- Thermal decomposition

The thermal decomposition studies of the Plain B and ABS PMB was done. The study was carried by taking 5mg of the sample in an aluminum holder and heating the sample from 30^0C to 600^0C at a standard heating rate of 10^0C per minute. The samples were run in air atmosphere. The study was done to find out the thermal stability of the bitumen (Feng Zhang *et al*., 2011). The DTG is also obtained using the TGA curve. The study was carried out using Shimadzu TGA- 50 instrument.

2.3.4. FTIR studies

The FTIR spectra of the ABS PMB and the base bitumen were measured using Shimadzu IR Prestige-21. The spectra were analyzed by dissolving bitumen in decaline and then the solution is placed over a KBR discs and subsequently dried using an IR lamp. The study was done to observe the structural modification made by the polymer. All the samples were analyzed in the wavelength range from 400 cm^{-1} to 4600cm^{-1}

2.3.5. Stripping studies

It is the process of studying the binding nature of the bitumen with the aggregate. The study was carried as per the ASTM standard D3625. A known amount of aggregate is coated with calculated amount of PMB and the mix is then immersed in a container with water. The container is then placed over a water bath at 60.deg.C for 8 hrs. The container is then removed from the water bath and the peeling out of bitumen layer from the aggregate is observed visually and the percentage of stripping is noted.

2.3.6. Extraction test ASTM D2172

The polymer modified bitumen coated aggregate mix was also submitted to bitumen extraction using trichloroethylene. The mixture is immersed in trichloroethylene for 3hrs and then it is placed in a centrifugate extractor and the binder is extracted. The difference in weight from the mix and the extracted aggregate will give us the percentage of binder. Here in the extraction test, different percentage of PMB was prepared and it was subjected to extraction and the extraction ability was noted. The extraction with time dependent is noted for the mix

2.3.7. Marshall stability ASTM: D 1559 - 1979

Marshall Stability value is the basic study on the stability of the mix with application of load. The standard mixture was prepared as per the IRC specification. The aggregate mix was coated with Polymer modified bitumen as described above. The mixture was then transferred to the mould. It was compacted with 75 blows on either side. The specimens (64 mm height and 10.2 mm diameter) were prepared by 1. Varying the percentage of plastics waste and 2. by varying bitumen quantity. These specimens were tested. The voids present in the mix also play an important role in deciding the performance of the mix as pavement. The Marshall Mix block is subjected to different types of tests to find out the following properties,

a) Voids filled with mineral aggregate
b) Air voids
c) Voids filled with bitumen
d) Bulk density
e) Specific gravity
f) Voids in mix

The results of the Marshall stability value is shown.

Marshal Stability Value is indicative of load with standing property of the flexible pavement. The minimum value is fixed as 1000Kg by IRC with 5% of bitumen and 95% of stone aggregate.

3. DISCUSSIONS OF RESULTS

3.1. Empirical tests

Table-1 gives the comparison results of the empirical values of the Plain B and ABS PMB. The softening point of the modified bitumen increases with increase in polymer content. The increase in softening point of the ABS PMB is a favorable result; it is observed that as higher the softening point of the bitumen better the resistant to permanent deformation properties like stripping, bleeding and rutting.

The ductility value is responsible for the elasticity of the bitumen samples at low temperature range (25^{0}C), It is observed that the ABS PMB has a low difference in ductility value when compared with the Plain B. This decrease in ductility value of the PMBs is due to the chemical chain alteration inside the asphaltene compounds of the Plain B. The ABS polymer added to the bitumen interacts with the asphaltene molecules and may form a chemical bond, resulting in restricting the change in elasticity of the bitumen at low temperature. The advantage that was found with this property is that the modified bitumen can perform very well in low temperature and high temperature areas and it may also with stand the fatigue cracking.

Penetration point is another important parameter which indicates the temperature susceptibility of the bitumen. From the softening point results, it was found that the polymer modification of bitumen will reduce the temperature related deformation of the binder. The decrease in the penetration point of the PMB shows that it can withstand high temperature environments and by this property deformation of the binder mixture at higher temperature can be avoided.

Table-1. Empirical test results.

Name of the modifier	% of Additive	Ductility	Penetration	Softening
	0	**75**	**67**	**41**
ABS	3%	68	64	58
	5%	64	59	62
	7%	60	51	68

3.2. Thermal analysis

The thermal studies TG/DTG of the base binder and the ABS PMB binder (Chen JH., 1985) were studied Table-2. Figure-1 shows the thermal curves of the Plain B, suggesting a decomposition stage starts from 285^{0}C and it ends on 515^{0}C and also shows a weight loss of 65. The Figure-2 shows the TG of 5% and 7% ABS PMB respectively. The thermal curves show three stages of decomposition as mention in the Table-2, these three stagse shows a maximum decomposition temperature at 382^{0}C, 462^{0}C and 524^{0}C for 5% modified bitumen and 382^{0}C, 463^{0}C and 520^{0}C for the 7% modified bitumen. From the above values the initial decomposition temperature and the final temperature of the modified bitumen are higher than the Plain B. The rate of decomposition of the modified bitumen is also slow due to its three stages when compared with plain B. When analyzing the percentage of decomposition of the modified bitumen, the graph values show that there is a difference in the percentage of loss between the modified bitumen. This is due to the strong bonding of the nitrile and the diene molecules from the polymer over the bitumen. The above results are the confirmation of the increase in the thermal stability of the modified bitumen. The three stage decomposition we have obtained from the TG of PMB also validates that the mixed polymer had formed a chemical bonding with the asphaltene compounds present in the bitumen. Thus it changes the thermal stability of the PMB (Wen-qian Luo *et al*., 2011).

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Table-2. TGA Results of plain and ABS modified bitumen.

S. No.	Modifier	Stage	Onset Tem (°C)	Maximum temp (°C)	End temp (°C)	% of Weight loss
1	Plain Bitumen	I	285	460	550	67%
2	5% ABS	I	294	382	416	24%
		II	416	462	516	37%
		III	516	524	550	13%
3	7% ABS	I	296	382	410	23%
		II	410	463	490	32%
		III	490	520	550	20%

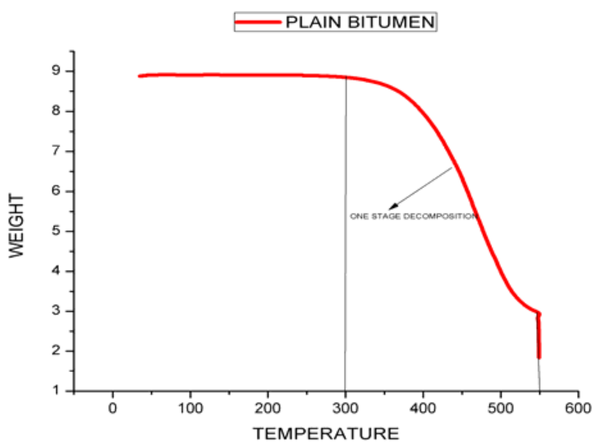

Figure-1. Thermo gravimetric of plain bitumen.

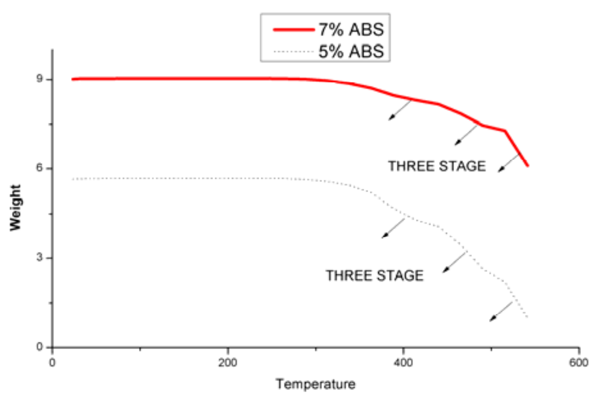

Figure-2. Thermo gravimetry of 5% and 7% ABS modified bitumen.

3.4. FTIR studies

The ABS PMB was subjected to the FTIR spectroscopic studies. The FTIR spectrums of the samples are shown in Fig. 3-5. From the graphs obtained, the modified bitumen shows the following properties.

a) The presence of the ABS in the bitumen structure is confirmed by the appearance of the Nitrile group in the spectra at a wavelength of 2200 - 2300cm$^{-1.}$ This was found by comparing the spectra of plain B and the modified binder. The strength of the peak also differs from 5% and 7% which also shows the increment in the amount of modifier used.
b) The butadiene peak is observed at the wavelength range 1000 - 960 cm^{-1}
c) The peaks at 2853 and 2920 cm^{-1} are the peak of the aliphatic C-H stretching of the bitumen polymer mix respectively.
d) The carbonyl c=o peak was observed in the wavelength 1683cm^{-1}
e) The Main chain of the bitumen is modified with the polymer added- this needs further studies.

The spectroscopic study suggests that the modifier namely ABS used has a good tendency to mix with the bitumen. This also confirms the uniform mixing of the modifier with bitumen.

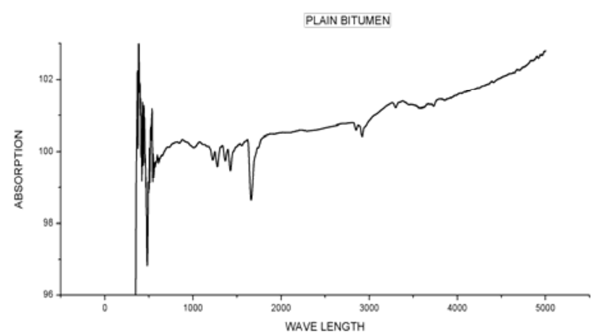

Figure-3. Ftir of plain bitumen.

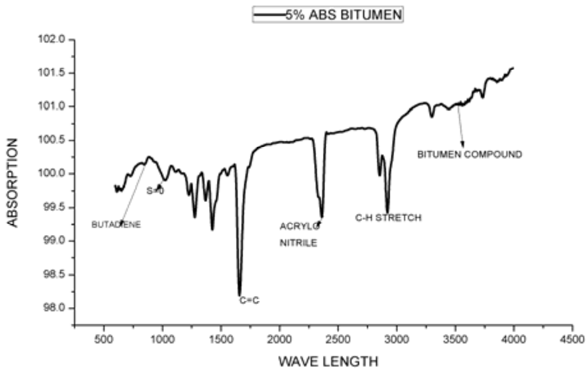

Figure-4. Ftir of 5% abs modified bitumen.

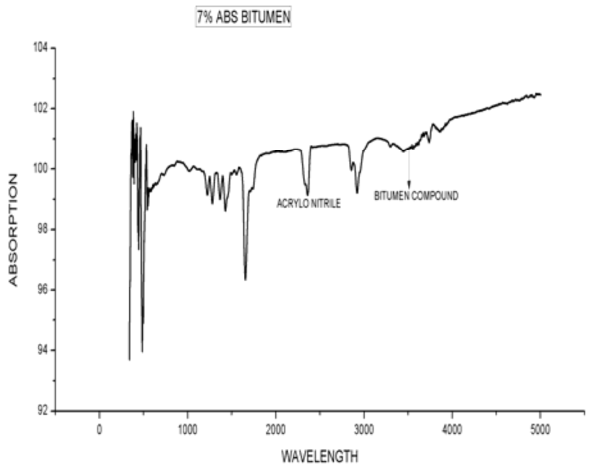

Figure-5. Ftir of 7% modified bitumen.

3.5. Stripping studies

The stripping study was carried out to study the nature of the binding capacity of the PMB over the aggregate. As per the IRC coding a minimum of 5% stripping is allowed for flexible pavements. The study on the ABS PMB with aggregate mix shows that there is no stripping even after 72hrs at 40.deg.c Table-3. The peeling out of the bitumen from the aggregate is called as the stripping value. When bitumen coated aggregate is immersed in water, the water penetrates in between the stone and bitumen resulting in the peeling of the bitumen. This in turn results in the loosening of the aggregate and forms potholes. It shows that if pores and voids are present in aggregate it results in the poor binding of the aggregate with the bitumen. In the case of polymer modified bitumen coated aggregates, there is no pore. So it shows poor stripping value. The PMB binds very well with the aggregate due to the reason that both polymer and bitumen are hydrocarbons, they mix very well to form a newer visco elastic material which can resist the flow of water from the surface to the aggregate. Hence peeling out of bitumen from the aggregate is very low. The striping of bitumen from the aggregate will results in the formation of pothole and cracks which is permanent deformation problem for a pavement, but in the use of ABS PMB the stripping is nil and it shows that there will be no pothole formations and crack formation during stagnation water over the road surface. This is an important finding, since this property improves the performance of the pavement by reducing the permanent deformations caused due to peeling out of bitumen layer from the aggregate.

Table-3. Results of stripping tests for plain and ABS modified bitumen.

S. No.	Percentage of ABS polymer	Percentage of stripping
1.	NIL	7%
2.	5%	NIL
3.	7%	NIL

3.6. Extraction test

The extraction tests is the process of removal bonded bitumen from the aggregate using a solvent. The mix prepared using ABS PMB was subjected to extraction tests and the results are shown in Table-4. The extraction results show that the removal of bitumen from the ABS PMB mix was very difficult when compared with plain bitumen mix. This was due to the reason that the ABS PMB has a tendency to form a strong bonding with aggregate due to its improvement in the sticking / binding nature after the addition of the polymer. The ABS which is mixed with the bitumen strongly interacts with the bitumen and form a new binder with improved binding capability. This results in the difficult removal of bitumen from the mix. This result also suggests that the pavement mix formed with the ABS PMB shows better binding and no permanent deformations.

Table-4. Results of extraction studies for plain and ABS modified bitumen.

ABS content (% by weight)	Bitumen extracted after 5 min %	Bitumen extracted after 10 min %	Bitumen extracted after 15 min %
0	96.0	98.0	100.0
5	63.5	88.7	92.3
7	63.2	86.7	90.7

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3.7. Marshall stability test

The old test to study the stability nature of a bituminous mixes is the Marshal Stability test. The test provides results about the stability (load withstanding capacity) of the mix, voids present, flow property and to determine the mix ratio for pavement construction. The ABS PMB mix was subjected to the MSV test and the results obtained is fairly high when compared with plain bitumen mix Table-5. The other properties also show good results. This improvement is due to the following reasons; both polymer and bitumen are similar in chemical nature. The polymer molecule interact with the constituents of bitumen namely asphaltene and other similar compounds and results in a three-dimensional internal cross-linked network. The cross-linking results in strong bonding with improved elastic structure. This will also add its suitability as a blend for asphalt pavement. This is supported by the high Marshall Stability values. Thus the ABS PMB mix helps in increasing the stability of the mix and makes the mix to perform well even at higher load movements over the road surface.

Table-5. Results of Marshall Stability Value for plain and ABS modified bitumen.

Percentage of Bitumen	**Percentage of ABS with respect to total weight**	**M.V** (Kg)	**F.V** (x 0.25mm)	**Void percentage**	**M.Q Kg/mm**
4.5	0	1100	3.3	62	515
4.5	5	1800	3.4	66	529
4.5	7	1700	3.5	62	486

4. CONCLUSIONS

- The basic empirical tests namely softening point, ductility and penetration point are within the tolerance limit for the ABS PMB used for flexible pavement. This results help us is concluding that the PMB shows higher temperature susceptibility and lower deformation due to cracking.
- It is observed from our thermal studies that ABS PMB has better temperature withstanding property with an increased binding property. The ABS PMB shows lower thermal deformation. This will help to reduce rutting and fatigue cracking during performance.
- The FTIR studies throw more light on the interaction between the polymer and bitumen as it suggests a change in chemical structure, a unique observation. Further studies on the structural characterization will throw more light on the interaction of the ABS polymer with the bitumen constituents namely asphaltenes and maltenes.
- The studies on the mix properties like stripping and extraction shows improved results, indicating the performance of the ABS PMB mix is good with increased binding property and it concludes that the mix may perform better in all condition without any deformations. This can be confirmed by conducting further performance studies on the prepared samples.
- The MSV studies concludes that the mix prepared using ABS PMB can perform in heavy load moving areas and can be used in pavement surfaces where different load vehicle move.
- In our findings the ageing due to oxidative heating is also shows a small influence in the modified bitumen.

The ABS PMB prepared can be very well used for flexible pavement application.

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