

# Bitumen as a Binder in Flexible Pavement Through New Additives and in Situ Polymerization

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**ABSTRACT-** Bitumen is a black non-crystalline thermoplastic viscous substance used for millennia as an adhesive, sealant and water proofing agent. Bitumen is modified with a number of additives and broadly classified polymeric and other chemical modifiers. Heavy loads, greater tyre pressure and increasing traffic are stressing roadways, triggering early breakdowns. Severe climate and an increasing focus on safety have motivated research into roadway paving materials. To solve these issues highway engineers and researchers have sorted to bespoke pavement materials. It has been shown that polymer modifiers may enhance the binder's ageing properties, delaying the detrimental effects of the process, which results in an improved pavement. Our findings suggest that waste PET-derived (polyethylene terephthalate) compounds, antistripping characteristics are on par with those of commercially available antistripping chemicals. A huge environmental pollution issue may be alleviated as a result of the latest research into the recycling of waste PET (polyethylene terephthalate) in bituminous concrete.

**KEYWORDS-** Bitumen, Polymerization, Binder, Flexible.

## I. INTRODUCTION

Bitumen, a black or dark brown non-crystalline thermoplastic viscous material, which has been used for centuries as a building material, sealant, adhesive and water proofing agent [1]. A tarry fluid with a characteristic smell, oozing out rocks or floating in like waters is well known to man from time immemorial. As early as 3500 B.C, the Sumerians used asphalt as an adhesive for bricks and sealant for water crafts. In 2000 B.C 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 B.C 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 covered from Dead Sea [2]. 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 is derived from crude oil, which in turn originates from 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 enormous weight of the 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 layer's 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].

## II. LITERATURE REVIEW

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 of heat, oxygen and UV light etc. [4-7]. 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 [8], while reviewing the PPA's use in the bitumen, concluded that PPA cannot dissociate and react with bitumen unless enclaves of high dielectric constant exist in the bitumen. The PPA, when used in the appropriate ratio, helps blended bitumen in improving its high temperature characteristics. As per Yudollahi G et al [9] 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 [10] studied the rheological behavior of the 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 [11] 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 [12] 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 behavior Giovanni Polacco [12] studied the viscosity functions of bitumen blended with polymers such as styrene-butadiene-styrene (SBS), ethylene vinyl acetate (EVA) and reactive polymer. "Ethylene terpolymers" (RET) at different temperatures in steady-state rate sweep tests.

### III. PROBLEM FORMULATION AND OBJECTIVES

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 non-toxic 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.

### IV. OBJECTIVES

- To study different flexible pavement additive used in previous research.
- To propose efficient composition of flexible material in pavement.
- To apply different tests on proposed composition of pavements.

## V. METHODS

### A. Synthesis of Terephthalamide Derivative

Experimental procedure for aminolysis reaction of PET waste was carried out according to our earlier described method [13]. 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., Tri ethylene 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.

### B. 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 were heated under vigorous stirring under nitrogen atmosphere at a temperature of about 90-130°C for 4 hours. The formation of polymer (generated in-situ) was confirmed from IR spectra (Fig.1 and Fig.2). A typical FTIR spectrum of segmented polyurethane would display two carbonyl peaks: one at 1724 cm<sup>-1</sup> assigned to bond C=O groups, and a second at 1712 cm<sup>-1</sup> 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<sup>-1</sup>. IR spectra of all the polyurea are similar in almost all aspects and assessment of all the spectra reveals that the spectra compromise of urea linkages. The IR bends at 1663 – 1609 cm<sup>-1</sup> and 1234 – 1220 cm<sup>-1</sup> confirm the urea linkage.

### C. Temperatures Required for Mixing and Compacting

A novel method for in-situ polymerization of Terephthalamide monomers with Poly isocyanate in bitumen has been developed in this work. Terephthalamide (made from PET using TETA as per our previously described process) was reacted with methylene diisocyanate (MDI) in bitumen to produce a poly-urea based new storage - stable PMB. Conventional test techniques were used to assess the physical and chemical characteristics of newly generated PMBs and compared to SBS - based PMBs (Table 1).

### D. Dynamic Shear Rheometer

Oscillatory-type testing is a common method for analyzing bitumen rheology. Samples of bitumen sandwiched between parallel plates are exposed to oscillating shear stresses and strains at varying frequencies and temperatures. The Dynamic shear rheometer is used to assess modified bitumen deformation characteristics for road surfaces (DSR). A DSR (Physica anton par 300 model) with a temperature-controlled water bath may be used to test the complex shear modulus ( $G^*$ ). Use  $G^*/\sin(\delta)$  to compare the performance of neat and RTFO – aged bitumen samples. High temperatures  $G^*(\delta)$  increases rutting resistance. The superpave standard requires  $G^*/\sin(\delta)$  values of at least 1.0 kPa for clean bitumen and 2.2 kPa for RTFO – aged bitumen samples at the pavement design temperature.

Table 1: Marshall stability test

Binder content	( Marshall strength KN/Flow in mm)		
	Neat Bitumen	PET-B	PET-A
Marshall value of 5% dosage	13.45/3.49	13.76/3.01	13.95/3.35
Marshall value of 6% dosage	14.07/3.48	15.79/3.54	14.11/3.53
Marshall value of 6.5% dosage	11.68/4.08	13.05/3.79	11.34/3.10
Retained Marshall Strength	74.37	84.35%	87.31%

Table 2: physical and chemical properties of newly generated PMBs compared to SBS based PMBs

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

## VI. MARSHALL STABILITY TEST

At 60 degrees Celsius, the Marshall stability test was carried out to determine how well the mix held up under a certain amount of stress and how well it resisted deformation. At their optimal binder concentration of 6 percent, Marshall specimens were soaked in the water bath for 34 hours at 60o C, while other specimens were immersed in the water bath for 30 minutes at 60o C. Table 2 displays the findings of Marshall strength at its optimal bitumen concentration. Clean and well-developed bitumen mixtures were used for Marshall stability testing. A more water resistant, better binding bitumen mix has been discovered using Terephthalamide as a chemical modifier. Comparing Terephthalamide modified mixes to plain bitumen modified mixes, it was found that the stability values rose considerably, rising from 14.07 K.N to 15.79 K.N and 14.11 K.N respectively. Thus, the current study

will not only improve road building, but will also extend the life of the road and reduce pollutants in the environment.

## VII. CONCLUSION

In-situ polymerization of waste PET Terephthalamide derivatives in bitumen was pursued in this work to guarantee greater dispersion of polymers in the bitumen. Bitumen polymer was created via the reaction of MDI with bitumen derived Terephthalamide derivatives. The IR examination of the generated PMB revealed the in-situ synthesis of poly urea and poly urethane in the PMB. Results from this study reveal that reactive polymer modified bitumen binder is superior than standard bitumen binder. According to the findings of this investigation, the Marshall stability of in-situ polymerized PMB was also improved, and the material was determined to meet all the requirements of IRC: 53-2010 standards. By conducting a bending beam rheometer test (BBR) on modified bitumen at lower temperatures, it was possible to minimize the creep

stiffness of the material while increasing the  $m$  value. The novel binding agents exhibit reduces stiffness at temperatures as low as  $-180^{\circ}\text{C}$  and fulfill the requirements for in-situ polymer modification binding at these temperatures. It was that that the  $G^*/\text{Sin}(\omega)$  of unmodified and SBS based polymer modified bitumen binder was larger for unaged polymer modified bitumen that it was for aged polymer modified bitumen. It is possible to observe using,  $G^*/\text{Sin}(\omega)$ , that the modified binder is softer and more flexible at lower temperatures. According to the results of this study, polymer modified bitumen binder (PMB) derived from PET waste maybe suitable for use in national highway construction.

### VIII. DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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