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Preparation and evaluation of waste PET derived polyurethane polymer modified bitumen through in situ polymerization reaction

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HIGHLIGHTS

- New polyurethane polymer is synthesis in situ in bitumen by BHETA with MDI.
- The chemical evolution of polyurethane formation in bitumen is examined through FTIR.
- The FT-IR study confirms that the developed new polymer is polyurethane.
- Better dispersion of polymer in bitumen was attributed by in situ polymerization.
- BHETA-PU improved the low temperature, high temperature and fatigue property of bitumen.

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ABSTRACT

Polymer modified bitumen (PMB) pavement have gained significant importance in the twentieth century and they now play a very crucial role in the field of road construction in every part of world. However, due to well-known difficulties related to the poor solubility of polymers, high temperature stability, sever manufacturing condition and high polymer cost restricts the use of polymer for bitumen modification. To overcome all these difficulties the present study has attempted to demonstrate a new approach where in situ polymerization of monomers bis(2-hydroxyethyl) terephthalamide (BHETA) (which is synthesized from aminolysis reaction of waste Poly Ethylene Terephthalate (PET)) with diphenylmethane-diisocyanate (MDI) in the body of bitumen for the development of polyurethane based Polymer modified bitumen (BHETA-PU). The resulting BHETA-PU product is comparable performance under laboratory condition with conventional styrene butadiene styrene (SBS) based PMB. To investigate the modified bitumen properties and mixture properties, conventional binder tests (Penetration, Softening Point, Marshall Stability, Hot water Stripping & short-term aging test) and Superpave binder tests (Rotational Viscosity, Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR) were carried out. The result reveals that BHETA-PU show significant improvement of antistripping as well as other physico-chemical properties and Marshall Stabilities. This research studies, therefore, suggests not only a new method for making PMB based on PET but also opens a new chapter for the recycling of waste PET in bitumen concrete roads which may help in easy disposal of waste PET polymer.

1. Introduction

India has one of the largest bituminous road networks and aggregating to about 2.1 million miles at present. The roads in India are mainly petroleum 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 heavy axle load, have already additional demands on the highway system. This has led to the need of enhancing the properties of existing bituminous material. Bitumen modification by different additives offers an important solution to overcome the existence deficiencies of bitumen and thereby improve the overall properties and performance of bituminous mixtures [1–3]. One of the most importantly used

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polymeric additives for modification of bitumen is styrene butadiene styrene (SBS). SBS improves the bitumen properties such as elastic responses, rutting resistance, low-temperature cracking resistance and therefore SBS accepted globally for modification of bitumen binder. However, it has been reported that SBS modified bitumen often shows thermodynamically unstable nature when stored at high temperature which leads to early phase separation. Further, SBS modified bitumen have a tendency to degrade long polymeric chain to small molecules on exposure to heat, oxygen and UV light [4–7].

The above mention limitation may lead to unwanted aging of bitumen and degradation of polymer, thus affecting the overall binder performance of the PMB blend. Further, price and production capacity of the SBS polymer relies very much on the petroleum crude oil; The effectiveness substitute of SBS by any materials can not only reduce this dependency and cost but also contribute great extent to the sustainability development. Such an observation has led to research studies for improving various properties such as storage stability and the compatibility of bitumen modified through the use of new sets of additives and various polymers with varying chemistry. The majority of polymeric modifiers other than styrene–butadiene–styrene (SBS) can be categorized as polymers such as, styrene–butadiene rubber, ethyl vinyl acetate, polyvinyl chloride, polyethylene, polyoctenamer, Poly Ethylene Terephthalate (PET) and the others [8–11]. Since PET recycling has not been carried out in the same amount as its production [12,13]. It would be worthwhile to find out new application areas for wastes PET bottle to maximize their end-of service life management effectiveness. The usage of waste PET as an additive for bitumen road pavement material can be a research area to maximize end-of service life is still in its early stage. In the prior studies, PET waste was commonly added to the bituminous mixture with dry process i.e. used as aggregate in the bituminous mixture in order to improve the performance of road pavement. Bitumen researchers have shown that permanent deformation, stiffness, fatigue life and Marshall Stability of the bitumen mixes were increased when PET waste has been used as bitumen modified [9,14–18]. Different from the mentioned studies above, bitumen binder was modified with additive derived from PET waste by aminolysis and glycolysis reaction and found to improve the Marshall Stability and moisture resistance depending on the bitumen and additive contents [8,19]. However, there was few research carried out in past for production of PMB in situ in the body of bitumen. The reviews of these research studies are as follows:

Sang-Yum Lee and his co-workers [20] introduce a new method that could modify neat bitumen by in situ polymerization of dimethyl phenol (DMP). A monomer, dimethyl phenol (DMP), adding to base bitumen in the presence of air occurs 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 [21] disclosed a method for synthesizing a homopolymer or copolymer (with bituminous component less than 50 wt% 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 homogeneous polymer generated is less than 100,000. However, there is no study carried out on in situ polymerization of waste PET based additives in the body of bitumen.

The present study has attempted to demonstrate a new approach where in situ polymerization of bis(2-hydroxyethyl) terephthalamide (BHETA) with diphenylmethane-diisocyanate (MDI) in the body of bitumen to produced polymer modified bitumen. The resulting PMB product is comparable performance under laboratory condition with conventional SBS based PMB. This research work, therefore, suggests not only a new technique for making PMB 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.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Ethanolamine, 4,4-Diphenylmethane Diisocyanate (MDI) and Xylene were of Laboratory Reagent (LR) grade.

2.1.2. Bitumen

Bitumen was supplied by IndianOil Mathura refinery. Typical properties of bitumen used are given in Table 2.

2.1.3. Poly(ethylene terephthalate) (PET)

The waste PET bottles were collected after proper identification. The PET bottles were stripped caps and labels and 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 small pieces about up to 5 cm and dried at 80 °C temperature for 4 h.

2.1.4. Aggregate gradation adopted

Locally available siliceous aggregates were used in this study. The grading of aggregates for bituminous mixes selected for this research were done as per Ministry of Road transport and highways (MORTH: 2000) Specifications and is given in Table 1.

2.2. Methods

2.2.1. Synthesis of BHETA

Experimental procedure for waste PET aminolysis reaction was carried out according to standard developed methods by many researchers [8,22–24]. A three necked 500 ml round bottomed flask equipped with a heating mantle, condenser, inert nitrogen gas sparging tube and a thermometer was charged with 50 grams of waste PET flakes and 100 grams of Ethanol Amine chemicals (1:2, wt/wt). The mixture of waste PET flakes and ethanol amines were refluxed for 8-h. As the PET degradation completed, the reactant mixtures turned homogeneous (i.e., Flakes disappeared entirely). The product was then crystallized in hot water and can then be filtered out. A white crystalline powder named BHETA was produced. The complete conversion of PET into BHETA was confirmed by the FTIR spectra which showed the disappearances of the ester group peak at 1735 cm^{-1} and appearance of new amide peaks at 1637 cm^{-1} and 1547 cm^{-1} (Fig. 1). The white crystal has been used for further chemical reaction.

Table 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