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PREPARATION AND CHARACTERIZATION OF POLYESTER POLYOL MODIFIED BITUMEN FOR PAVEMENT APPLICATIONS

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ABSTRACT

In this study, polymer modified bitumen (PMB) from polyester polyols was prepared by bis(2-hydroxyethyl terephthalate) (BHET) which was obtained by glycolysis of Polyethylene terephthalate (PET) waste. The effect of polyester polyol structure on the rheological properties of PMB was investigated. Polyester polyols obtained by the reaction of various polyols and polycarboxylic acids. POL1, synthesized from BHET and adipic acid (AA), were blended with the bitumen resulting in improved stiffness, rutting resistance and fatigue performance with respect to neat bitumen. Also, the synergistic effects of the polyester polyol addition into styrene-butadiene-styrene modified bitumen (SBS-Bitumen) were investigated where this reference mixture contains SBS loading of 3 % according to the weight of bitumen. Although the addition of POL1(1.3:1) into SBS:Bitumen mixture at 3:3:94 weight ratio didn't alter the high temperature performance grade of PMB, POL1:SBS:Bitumen exhibited higher softening point, elastic recovery and rutting parameter than reference mixture. The early stage promising results of this study indicated the potential benefits of polyester polyol as bitumen modifier. Also, this study showed that the use of BHET obtained by PET waste as a starting material for polyester polyol synthesis could be an alternative way to utilize plastic waste.

Keywords: PET waste, Polymer modified bitumen, Polyester polyol

1. INTRODUCTION

The global demand for bitumen used in pavement industry has continued to increase caused by the growing population and industrialization. The amount of asphalt used in pavement industry is 278 million tonnes in 2015 in Europe [1]. The amount of bitumen within the asphalt mixtures varies between 4-7% wt. Although bitumen as a binder for road pavement construction exhibits unique properties, such as adhesivity, ductility, resistance to the effect of weathering and chemicals [2], increased traffic load, growing traffic volume and dramatic changes of temperature lead to road distresses [3]. The main distresses of road pavement are: (i) rutting or permanent deformation at high temperature; (b) thermal cracking at the low temperature due to lack of flexibility and (c) fatigue cracking arising from failure of the surface layer due to the repetitive traffic loading. These distresses of bituminous pavement have to be improved to meet the growing needs. To improve the pavement performance, the use of polymers as modifier has been investigated for a long time. Polymeric modifiers for bitumen can be divided into two categories; passive and active [4]. Passive polymers (e.g. thermoplastics, elastomers, plastomers) form a physical network inside bitumen [5]. Aromatic components of bitumen swell polymer, consequently, swollen polymer contributes to rutting resistance and elastic properties of binder.

Various PMBs were developed after 1950s. Researchers reported that the addition of polymers into bitumen improved bitumen properties; such as higher rutting resistance at high temperature, better resistance to thermal fracture at low temperature, better elastic recovery or longer fatigue life. Despite of these improvements, PMBs have still had some challenges including high cost, poor storage stability, low ageing resistance and the limited improvement in elasticity [6]. Researchers have attempted to develop new PMB formulations.

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Before a road construction, the required performance of bitumen binder should be known. The cost and the final performance of PMB are strongly influenced by the structure and content of polymer. Popular polymers used for bitumen modification are thermoplastic elastomers (styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), styrene-ethylene/butylene-styrene (SEBS), styrene-butadiene rubber (SBR), ethylene-propylene-diene monomer rubber (EPDM)) and plastomers (polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA). Thermoplastic elastomers generally provide greater enhancement in bitumen performance than plastomers. SBS is the most popular thermoplastic elastomer to PMB applications because of its good dispersibility in bitumen and its excellent properties [6-8]. Polystyrene (PS) and polybutadiene (PB) blocks inside SBS provide the strength and the elasticity of SBS, respectively. PS swollen in the light components of bitumen and PB interacting with positively charged groups in bitumen [9] constitute a network in the bitumen. Thus, the addition of SBS to bitumen results in better elastic recovery, higher complex modulus and better cracking resistance compared to neat bitumen.

Sengoz and Isikyakar investigated the fundamental properties of SBS based PMBs [10]. They reported that the addition of SBS caused decreasing in penetration, increasing in softening point and viscosity. These results showed increased stiffness and low sensitive to permanent deformation. However, SBS modified bitumen has several disadvantages. Low storage stability is one of the main problems. The compatibility between SBS and bitumen depends on the aromatic content of bitumen, in case of incompatibility the storage stability of bitumen decreases. Also, SBS-PMBs exhibit low resistance to heat, oxidation and ultraviolet due to double bonds in the PB chain [11, 12]. To achieve the desired bitumen performance, the amount of SBS should be determined. In case using of large amount of SBS is required, the cost rises. As known, SBS price have risen for the last few years because of the surging price of butadiene (BD) and BD price continues rising due to tight supply, strong demand and other factors. To overcome these drawbacks, studies about developing the new polymeric modifier for bitumen have been still undertaken in industry as well as in academia. Zhong et.al synthesized binder modified by SBR-Weathered coal (WC)/Carbon black to overcome the poor compatibility between polymer and bitumen [13]. They reported that additives improved complex modulus, elastic response and viscosity at high temperature. From stability tests, they observed that SBR-WC had significant compatibility with pure bitumen, thus, the storage stability of binder was improved. In another study, Polacco et al. prepared bitumen modified with SEBS obtained by hydrogenation of SBS in order to improve the resistance to heat and UV [14]. They found that storage stability was obtained below about 4 wt % of SEBS despite of poor compatibility between polymer and bitumen. Also, the viscoelastic properties of PMB weren't improved.

Poly(ethylene terephthalate) (PET) is the most consumed plastic, therefore, the effective use of PET waste and recycling of PET is very important in terms of environmental protection. In the last two decades, the usage of PET waste have been investigated by both the plastic industry and the pavement industry [15-17]. For PMB applications, PET waste can be directly used as additive or new materials derived chemically from PET waste can be added to bitumen mixture. Recently, Karahrodi et. al proposed use of waste PET/GTR (ground tire rubber) blends as low-cost and environmental-friendly bitumen modifiers. They reported that this blend enhanced the performance properties (viscosity, thermal stability), stiffness and resistance against rutting at high temperature [15]. In another study, Gürü et. al synthesized two new materials chemically derived from waste PET and used as additive for the roadway pavement application. They reported that the addition of their new materials improved the low temperature performance, fatigue and stripping resistance of hot mix asphalt [18]. Chemical recycling of PET is carried out by different method like hydrolysis, aminolysis, alcoholysis, ammonolysis and glycolsis [19]. Chemical glycolysis method is the most attractive method for recycling waste PET [20]. The main product obtained by depolymerization of PET waste with ethylene glycol is bis(2-hydroxyethyl terephthalate) (BHET). BHET is widely used to produce various polymeric materials. In this study, polyester polyols were synthesized by polyesterification reaction of BHET obtained by glycolysis of PET waste with dicarboxylic acids. The produced polyester polyols used as bitumen modifier. Up to our best knowledge, the use of polyester polyol as bitumen modifier hasn't been investigated and reported yet. In this study, we attempted to improve the bitumen conventional properties (penetration, softening point, elastic recovery, etc.) by modification with polyester polyols. Based on this consideration, firstly, PET waste was depolymerized by glycolysis reaction and the obtained BHET was used for the synthesis of polyester. The effect of polyester polyol structure on the PMB's characteristics was investigated. The results showed that the developed polyester polyol from BHET and adipic acid is promising to obtain low cost PMBs. Also, especially the use of BHET obtained by PET waste as a starting material for polyester polyol synthesis can be an alternative way to utilize plastic waste.

2. MATERIAL AND METHOD

Bitumen with penetration grade of 50/70 was supplied by Turkish Petroleum Refineries Corporation TÜPRAŞ (İzmit, Turkey). PET waste obtained from post-consumer soft drink bottles was procured from local company. For glycolysis of PET, ethylene glycol (EG) and zinc acetate (ZnAc, catalyst) were obtained commercially. Pentaerythritol (PE) and glycerol (G) were obtained from MKS Marmara Entegre Kimya San. A.Ş. (Turkey). Adipic acid (99%) and sebacic acid (99%) were supplied by Aldrich Chemical Co. and used without further purification. p-Toluen sulphonic acid (p-TSA) was purchased from Aldrich Co. and used as polyesterification catalyst. Styrene-butadiene-styrene (SBS) used was Kraton D1192A supplied by Dolder Kimya (Turkey). Kraton D1192A is a clear linear block copolymer based on styrene and butadiene with bound styrene of 30% mass.

2.1. Glycolysis of PET Waste

PET waste was depolymerized by glycolysis reaction. PET chips, EG and zinc acetate were charged in a 500 ml, three necked glass reactor. The glycolysis reaction was carried out in the presence of 0.5 % w/w ZnAc, based on the weight PET, under reflux in nitrogen atmosphere, at 195-205°C for 3 h. The reaction product was cooled to -5°C and then, 100 ml of boiling water was added to the reactor. The insoluble oligomeric product was separated by filtration and the filtrate containing BHET was stored in a refrigerator at 2°C. After 24 h, the precipitated BHET was filtered and washed with cooled water. BHET was dried at 60°C. BHET was characterized by hydroxyl value, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography (GPC) analysis.

2.2. Synthesis of Polyester Polyol

For polyesterification reaction, BHET obtained from glycolysis of PET waste was used as hydroxyl functional monomer. Also, two multifunctional hydroxyl compounds (PE and G) were used to study the effect of chain structure of polyester polyol on the polymer modified bitumen characteristics. As a difunctional acid, AA or SA was used. The reaction was carried out in a 500 ml reactor fitted with a stirrer, thermometer, nitrogen purge and a dean-stark apparatus. Calculated amount of BHET was charged into reactor and heated 110°C in 30 min so that BHET could melt. Then, AA or SA and p-TSA were added into reactor and the mixture was heated to 170°C in 30 min and held at this temperature for 3 h. Subsequently, the reaction mixture was heated to 200°C and the reaction was kept at this temperature until the acid value of reaction mixture decreased to 20 mg KOH/g. The codes of the synthesized polyester polyols are presented in Table 1. Polyester polyols were characterized by FTIR, DSC, GPC, acid value, hydroxyl value and water content.

2.3. Preparation of Polymer Modified Bitumen (PMB)

Blends of bitumen with the different Polyester Polyols were prepared by melt-blending method. The PMB mixture was prepared by mixing the polyester polyol in a 3% by the weight of bitumen content at temperatures of 180-190°C under vigorous stirring. After 2 h, heating and stirring were stopped, then, the hot mix was transferred to penetration container and left to cool. In addition, PMB samples with a commercial thermoplastic elastomer SBS (3% by weight) were prepared in order to compare. To study the synergistic effects of additives in PMB products, polyester poliols with SBS having three different weight ratios were prepared (POL1:SBS:Bitumen=0:3:97; 3:1:96 and 3:3:94 weight ratio). Properties of the prepared PMBs were determined by penetration, softening, elastic recovery and viscosity tests and dynamic shear rheometer (DSR).

Table 1. Designation of the synthesized polyester polyols

Code	Monomers	Molar ratio	Code	Monomers	Molar ratio
POL1	BHET:AA	1:1	POL2	BHET:SA	1:1
		1.1:1			1.3:1
		1.2:1	POL3	BHET:G:AA	1:0.5:1
		1.3:1			
		1.4:1	POL4	BHET:PE:AA	1:0.5:1
		1.5:1			

2.4. Characterization

FTIR spectra were obtained with a Perkin Elmer Spectrum One FTIR with attenuated total reflectance (ATR) unit and in a wavenumber range of 600-4000 cm^{-1}.

DSC analysis (Mettler Toledo) was performed in order to determine the melting point (T_m) of the obtained BHET and the glass transition-temperature (T_g) of the prepared polyester polyols. To determine Tg, the polyester polyols were heated at a rate of 10 °C min^{-1} from -75°C to 250°C under nitrogen atmosphere. The T_m of BHET was determined in the temperature range of 25-200°C.

The average molecular weight (Mw) of the BHET and obtained polyester polyols were determined by Agilent Model (1200 series) GPC with PLgel Mixed Bed colum. Tetrahydrofuran (THF) was used as solvent and all samples dissolved in THF at constant concentration (0.1 wt %). The flow rate of carrier solvent was 1.00 ml min^{-1}. Polystyrene standards were used for the calibration.

The hydroxyl values of BHET and the polyester polyols were analyzed according to ASTM D4274 method. The acid values were determined according to ASTM D4662 method. Water content of the prepared polyester polyols were evaluated in accordance with ASTM D4672 method.

For the prepared PMB, all tests were carried out in accordance with TS EN standards. The penetration and softening tests of unmodified bitumen and PMBs were performed according to TS EN 1426 (at 25°C) (Anton Paar, PNR12) and TS EN 1427 (at a rate of 5°C/min) (ISL, RB 36 5G), respectively. Determination of the elastic recovery and viscosity of all samples were performed according to TS EN 13398 (at 25°C and a rate of 5°C/min) (Petrotest DDA3 Ductility Tester) and TS EN 12595 (at 135°C) (Brookfield RVDV-II-PX), respectively. To evaluate the rutting potential of PMB, DSR test was carried out according to TS EN 14770 (Anton Paar SmartPave 92). The critical temperature before formation of permanent deformation was determined. From the DSR software, the critical temperature was automatically determined as temperature at which G*/sin δ is equal to 1kPa.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of Glycolyzed PET

After PET waste glycolysis, the purity of the obtained BHET was controlled by DSC and GPC, the structural analysis was characterized by FTIR. The DSC thermogram (Figure 1) exhibiting a sharp endothermic peak at 110 °C was indicated that pure monomer BHET was successfully obtained by glycolysis of PET waste. This peak agrees with the melting of BHET reported in the literature. [21]. The average molecular masses (M_n and M_w) of BHET were measured by GPC. The Mw was found to be 254 g mol^{-1}indicating that the obtained BHET was pure. In addition, the FTIR spectra of the obtained BHET showing –OH band at 3300 cm^{-1}, C=O stretching at 1705 cm^{-1} and aryl group at 1506 cm^{-1} confirmed presence of hydroxyl, ester and aryl groups in BHET (Figure 2). Hydroxyl value for the BHET was observed 447 mg KOH/g in agreement with the theoretical hydroxyl value of pure BHET, about 440 mg KOH/g [21].

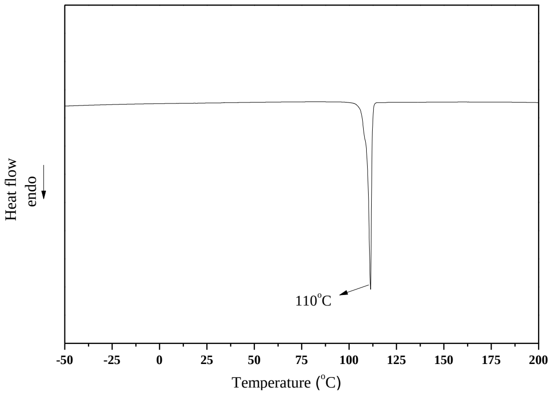

Figure 1: DSC thermogram of the obtained BHET

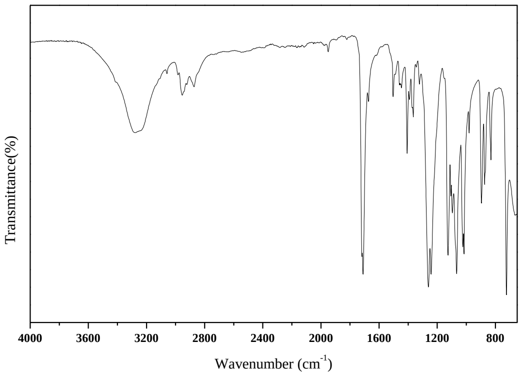

Figure 2. FTIR Spectra of the obtained BHET

3.2. Characterization of Polyesterpolyol

Polyester polyols were synthesized via polyesterification reaction of BHET and BHET/G or PE mix with AA or SA. The hydroxyl to acid ratio was changed in the range of 1:1 to 1.5:1 by molar ratio. The hydroxyl values (HV), average molecular weights (M_n and M_w), polydispersity index (PDI) and water content of the prepared polyester polyols were given in Table 2. In all sample, the HV values increased with increasing di-ol (tri- or tetra-ol) /diacid ratio, expectedly. The BHET:AA polyester polyols have exhibited the similar polydispersity although they had different average molecular weights arising from changes in molar ratio of diol to diacid. All polyester polyols had narrow molecular weight distribution. The POL2 samples, prepared with SA having longer alkyl chain length than AA, exhibited higher polydispersity than POL1 samples. POL3 had the highest PDI value. This was attributed to the use of both diol and triol for polyesterification. The BHET:PE:AA polyester polyol cannot be dissolved in THF and its molecular weight couldn’t determined by GPC. Water content of the polyester polyols varied from 0.04 to 1.70 %. It is known that the water content in hot mixture can cause stripping of aggregate [22]. All of the obtained polyester polyols had too low water content to lead stripping, considering the polyester polyol content (% 3) in the PMB formulation.

Table 2. Properties of the synthesized polyester polyols

Sample	**Molar ratio (polyl/diacid)**	**HV (mgKOH/g)**	**M_n ($gmol^{-1}$)**	**M_w ($gmol^{-1}$)**	**PDI**	**Water content (%)**
BHET:AA (POL1)	1:1	8	5550	7880	1.42	0.60
	1.1:1	19	5940	8200	1.38	0.04
	1.2:1	56	3950	5370	1.36	0.50
	1.3:1	79	4320	5970	1.38	0.10
	1.4:1	143	4700	6640	1.41	0.70
	1.5:1	168	3750	4920	1.31	1.40
BHET:SA (POL2)	1:1	11	4800	9020	1.87	0.30
	1.3:1	61	4040	7480	1.85	0.20
BHET:G:AA (POL3)	1:0.5:1	62	1260	4480	3.55	1.70
BHET:PE:AA (POL4)	1:0.5:1	131	n.d.	n.d.	n.d.	0.40

n.d: not determined

The FTIR spectra (Figure 3-A) for POL1 showed transmission band at 3450, 2900, 1715, 1580 and 1250 cm^{-1} due to -OH, C–H, C=O, C=C and stretching, respectively. IR spectra of products clearly indicates formation of polyester polyol by the presence of the C=O and –OH frequency. The absorption peaks of POL1 and POL2, including SA instead of AA, is almost similar because SA and AA have the same functional group in spite of different alkyl chain length. Similarly, polyester polyols including PE or G showed the same absorption peaks. The thermal behavior of polyester polyols was investigated by DSC. DSC thermograms of the synthesized polyester polyols showed a glass transition in all cases (Figure 4).When comparing the glass transition temperature (T_g) of polyester polyols, it was observed that POL 2, 3 and 4 exhibited lower Tg values than POL1. T_g of POL1 slightly increased with the molecular weight of polyester polyol. POL1 (1.0:1) and (1.3:1) exhibited the highest T_g values among the synthesized polyester polyols.

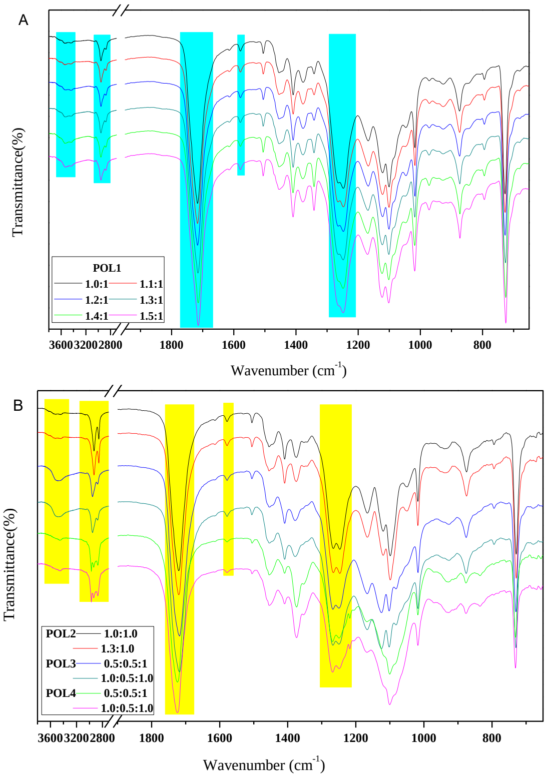

Figure 3. FTIR spectra of polyester polyols (A: POL1 and B: POL2, POL3 and POL4)

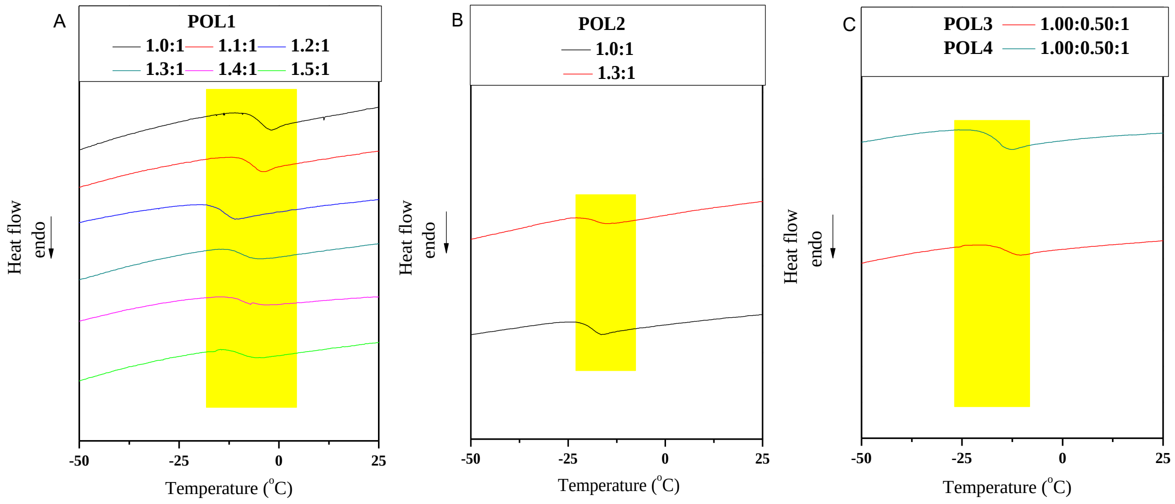

Figure 4. DSC thermograms of polyester polyols

3.3. Properties of Polyester Polyol Modified Bitumen

The modified bitumen was obtained by adding 3 wt.% of polyester polyol to bitumen. The binder behaviors were evaluated depending on polymeric modifier structure. The test results for all modified bitumens are summarized in table 3. The penetration, softening point and viscosity tests were conducted to evaluate the effects of a modifier. Penetration grade of all modified bitumen was decreased with respect to neat bitumen. As it is well known, the decrease in penetration shows the increase in the hardness of binder providing an improved stiffness. The lowest value of penetration was achieved for bitumen samples modified with POL3 (38.3), and, this value is even lower than the penetration of SBS modified bitumen. POL3 had the lowest average molecular weights and the highest PDI among the synthesized polyester polyols. These results indicated that POL3 was composed of non-uniform chain lengths and its chain lengths were smaller than the other synthesized polyester polyols. As to penetration values, bitumen modified with small polymer chain length could exhibit higher dispersion and greater interaction in bitumen and this situation could result in hardening of binder. It is known that bituminous binder having high softening point exhibits enhancement in pavement performance. The softening points of all obtained PMB were slightly higher than that of neat bitumen. This result showed that polymer addition had little effect on the softening point of bitumen and the extent of changes varied as a function of the polymer type. POL1 (1.0:1) and (1.3:1) modified bitumen exhibited the highest softening point among the polyester polyols modified bitumens. This result was in conform with DSC results, namely, POL1 (1.0:1) and (1.3:1) were the highest T_g value and contributed more to increasing in softening point. For 3% polymer modified binder, the addition of SBS even raised the softening point only 3.6 °C. PMBs including POL1 (1.3:1) and the mixture of POL1 (1.3:1) with SBS had the highest softening point of 51.1 and 53.7°C, respectively. Moreover, the softening point of POL1-SBS-Bitumen at 3/3/94 weight ratio was higher than that of SBS-Bitumen, 51.8°C. It can be concluded that the addition of polyester polyols into bitumen improved the performance characteristics such as rutting, fatigue and temperature susceptibility [23].

The penetration index (PI) is beneficial to understand the thermal sensitivity of binders. The PI values are calculated using penetration value and Softening temperature of binders [24]. For road bitumen Pfeiffer and Doormaal developed an equation in order to determinate of PI [24] and PI was calculated according to the following equations;

$$A = \frac{(\log 800 - logP_{25})}{(T_{sp} - 25)} \tag{1}$$

$$PI = \frac{(20 - 500A)}{(1 + 50A)} \tag{2}$$

where P_{25}; penetration of binder at 25°C and T_{sp}; softening point temperature of binder.

The PI value changes from -3 to 7 suggesting that the low PI value indicates high temperature susceptibility, that's binder with low PI becomes brittle at low temperature and are very prone to low-temperature cracking in cold climates. Therefore, bitumen with low PI are preferred to use in hot climates [13, 25]. The calculated PI values of all prepared PMB were given in Table 3. As can be seen the results, the modification with polyester polyols increased the PI of PMB except POL1(1:1) and POL2(1.3:1), which implies that improvement in bitumen thermal susceptibility. While PI value of SBS modified bitumen was -1.30, the addition of polyester polyol into SBS-Bitumen mixture caused to increasing in PI value (-0.86) and decreasing in the thermal susceptibility.

The viscosity of bitumen binder is very important in evaluating its workability during mixing and compaction process. The viscosity at 135°C must be lower than 3000 mPa.s according to Superpave binder specification limits [13]. It is reported in the literature that the addition of polymer into bitumen increases the viscosity of binder [23]. Polymer modified bitumen viscosity changes depending on polymer structure and the interactions between polymer and bitumen [13]. As can be seen in Table 3, the viscosity of binder increased with the modification of bitumen for all formulations. Despite the increase in viscosity, all prepared PMBs met the requirement of the specification.

The results of DSR provide evaluation of the rutting characteristics of bitumen. From DSR test, complex shear modulus (G*) and phase angle (δ) as rheological parameters are determined. For different temperatures, the rutting parameter (G*/sin δ) are calculated. According to Strategic Highway Research Program (SHRP) test, the temperature at which G*/sin δ is equal to 1kPa is the critical temperature before permanent deformation on the pavement [5]. The rutting parameter (G*/sin δ) is also defined as the stiffness indicator [26]. When the critical temperature is high, rutting resistance and stiffness of the pavement will be improved. From Table 3 it can be seen that the rutting parameter value varied with the addition of polyester polyols. Among the polyester polyol modified bitumen, the highest rise in DSR results was obtained by addition of POL1 (1:1) and POL1 (1.3:1), 68.3°C and 68°C, respectively. In case of mixing with SBS of 1%, the critical temperature (at G*/sin δ= 1kPa) reached 69˚C with the addition of POL1 (1.3:1) of 3%. Also, POL1(1.3:1):SBS:Bitumen mixture at 3:3:94 weight ratio, exhibited the highest critical temperature, 72.3˚C, namely, the highest rutting resistance and stiffness among the all prepared bitumen mixture. These results showed that POL1 and SBS had synergistic effects on rutting characteristics of bitumen.

Elastic recovery is important to evaluate the fatigue performance of the binders. A binder having higher elastic recovery exhibits better rutting resistance [27]. Non-reactive polymers are swollen by bitumen fractions (e.g light aromatic component) and constitute a physical network between bitumen and polymer [5]. This formation contributes to improvement in elastic properties of binders. In general elastomers such as SBS improve the degree of elastic recovery [27, 28]. As seen from Table 3, POL1 (1:1) and (1.3:1) showed the better elastic recovery in comparison with other polyester polyol modifiers used in investigation, 21 and 30 %, respectively. Also, the addition of 3 wt % of POL1 (1.3:1) into SBS-Bitumen showed the highest elastic recovery of 60 % compare to the other Polyester Polyol-PMBs and SBS-PMB.

Table 3. Properties of all synthesized PMBs

Sample	Molar ratio in POL (polyol/diacid)	Mixing ratio, (wt. %)	Penetration at 25°C, (dm)	Softening Point, (°C)	PI	Elastic recovery at 25°C, (%)	DSR at $G^*/\sin\delta$=1kPa, (°C)	Viscosity at 135°C, (mPa.s)
Bitumen		100	58.0	48.2	-1.32	5.4	66.0	383
POL1-Bitumen	1:1	3:97	49.0	50.2	-1.22	21.0	68.3	412
	1.1:1	3:97	48.7	48.5	-1.66	17.5	66.2	404
	1.2:1	3:97	48.0	48.6	-1.64	10.0	66.8	395
	1.3:1	3:97	42.3	51.1	-1.36	30.0	68.0	566
	1.4:1	3:97	51.0	48.3	-1.61	5.5	66.4	403
	1.5:1	3:97	47.7	48.7	-1.63	6.5	66.8	423
POL2-Bitumen	1:1	3:97	43.0	49	-1.77	13.5	66.8	419
	1.3:1	3:97	48.0	50.2	-1.24	5	66.8	443
POL3-Bitumen	1:0.5:1	3:97	38.3	49.9	-1.78	16	66.5	413
POL4-Bitumen	1:0.5:1	3:97	45.7	48.8	-1.69	10	67.1	423
SBS-Bitumen		3:97	39.0	51.8	-1.30	47.3	70.1	729
SBS-POL1-Bitumen		1:3:96	43.0	50.5	-1.40	25.8	69.0	566
SBS-POL1-Bitumen		3:3:94	39.2	53.7	-0.86	60.0	72.3	882

4. CONCLUSIONS

In this study, the effect of polyester polyols derived from PET decomposition product on the properties of bituminous binder was investigated. BHET obtained from glycolysis of PET waste were polymerized with different dicarboxylic acids and polyols. All prepared polyester polyols were used as binder modifier. The enhancement in hardness and stiffness of all Polyester Polyol-PMBs were demonstrated using penetration and softening point test. The extent of polymer modification had varied depending on the obtained polyester polyol structure. The addition of Polyester polyol had generally improved the thermal susceptibility of binder according to PI values. The viscosity of binder increased with modification, however, Polyester Polyol-PMBs met the requirement of the Superpave binder specification. The elastic recovery degree of PMBs were varied depend on the polyester polyol structure. The recovery percentage of Polyester Polyol-PMBs could increased up to 30 %. Bitumen performance at high temperature was evaluated from the rutting parameter ($G^*/\sin\delta$) obtained from DSR test result. The rutting parameter value varied with the addition of polyester polyols. The highest rise in the critical temperature (at $G^*/\sin\delta$= 1kPa) was obtained by addition of POL1 (1:1) and POL1 (1.3:1), 68.3°C and 68°C, respectively. It showed that the rutting resistance of POL1(1:1) and POL1(1.3:1)-PMBs were better than that of pure bitumen, 66°C. High temperature Performance Grade of the used bitumen was PG-64. Although the modification of bitumen with Polyester Polyols couldn't promote their Performance Grade, the rutting resistance and stiffness were enhanced. The addition of POL1(1.3:1) into SBS:Bitumen mixture at 3:3:94 weight ratio were able to achieve the critical temperature of 72.2°C. This indicated that POL1:SBS:Bitumen had the higher rutting resistance than SBS:Bitumen despite of having the same high temperature performance grade (PG of 70). Considering the all results, it is seen that Polyester Polyol-POL1(1.3:1) modified bitumen binder exhibits better hardness, stiffness, elastic recovery and rutting resistance than base bitumen even if it doesn't promote its high performance grade. Consequently, these initial results show the potential benefits of polyester polyol as bitumen modifier. We suggest that the new polyester polyols obtained from PET waste should be developed to attain PMBs with high pavement performance.

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