Primljen / Received: 21.9.2021. Ispravljen / Corrected: 16.12.2020. Prihvaćen / Accepted: 15.1.2022. Dostupno online / Available online: 10.3.2022.

Effects of recycled PET and TEOA on performance characteristics of bitumen

Authors:



Ceren Beyza İnce, PhD. CE Inonu University, Malatya, Turkey Faculty of Engineering Department of Civil Engineering c.beyzaince@gmail.com Corresponding author



Assoc.Prof. Tacettin Geçkil, PhD. CE Inonu University, Malatya, Turkey Faculty of Engineering Department of Civil Engineering tacettin.geckil@inonu.edu.tr

Ceren Beyza İnce, Tacettin Geçkil

Effects of recycled PET and TEOA on performance characteristics of bitumen

In this study, the recycled PET is used in bitumen modification by applying a different process in order to eliminate the phase separation problem. For this purpose, modified bitumens are obtained by adding the triethanolamine (TEOA) chemical (wt. 2.5 %) and PET (wt. 2, 4, 6, 8, 10 %) to pure bitumen. The properties of modified bitumens are determined by chemical, physical, and rheological tests. According to the test results, bitumen reacts with PET, and 6 % PET ratio is a critical value. At this ratio, the resistance of bitumen to deformations at high and low temperatures increases significantly.

Key words:

bitumen, recycled PET, TEOA, modification, rheological property, characterization

Prethodno priopćenje

Research Paper

Ceren Beyza İnce, Tacettin Geçkil

Utjecaj recikliranog PET-a i TEOA-e na svojstva bitumena

Ovo istraživanje usmjereno je na upotrebu recikliranog PET-a u modifikaciji bitumena primjenom različitih procesa kako bi se uklonio problem faznog razdvajanja. U tu svrhu, modificirani bitumeni dobili su se dodavanjem kemijskog trietanolamina - TEOA (2,5 % mase) i polietilen tereftalata - PET (2, 4, 6, 8, 10 % mase) čistom bitumenu. Svojstva modificiranih bitumena odredila su se na temelju kemijskih, fizikalnih i reoloških ispitivanja. Rezultati istraživanja pokazali su da bitumen reagira s PET-om i da je 6 % udjela PET-a kritična vrijednost, te da se pri tom udjelu značajno povećava otpornost bitumena na deformacije pri visokim i niskim temperaturama.

Ključne riječi:

bitumen, reciklirani PET, TEOA, modifikacija, reološko svojstvo, karakterizacija

1. Introduction

The increasing number of consumer societies in all countries of the world causes an increase in the demand for single-use plastics and, therefore, results in formation of large amounts of plastic piles that need to be managed [1, 2]. While worldwide plastic production has increased by 500 % over the past thirty years, plastic consumption has increased by 50 % in the last decade. According to research conducted in this area, the global plastic production is expected to reach 850 million tons per year in 2050 [3]. Since approximately 79 % of these plastic piles do not degrade in nature and are consequently disposed in the environment as waste, all living things in the ecosystem are negatively affected by this situation. In addition, the fact that plastic stacks occupy large areas is seen as a separate disadvantage of these materials. For this reason, the issue of reusing these materials is considered to be of great importance [1, 2, 4, 5].

Plastics are a compound of a wide variety of materials and allow development of various types of products by mixing these materials in different proportions. Plastics are generally divided into two categories: thermoplastics and thermosets [3, 5]. Thermoplastics are materials that melt when heated and harden when cooled. Due to these properties, thermoplastics can be heated and reshaped repeatedly. Polyethylene terephthalate (PET), low density polyethylene (LDPE), high density polyethylene (HDPE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS) are thermoplastic materials [3, 6]. Thermosets are materials that change chemically when heated and cannot be reshaped. Phenol, melamine, unsaturated polyesters, epoxies, and polyurethanes are known as thermoset materials [3, 6, 7]. In recent years, waste or natural thermoplastics such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP) and polyvinyl chloride (PVC) have been extensively used in bitumen modification [8-12]. The use of plastics has been preferred because they are less sensitive to temperature and exhibit a stable structure when combined with bitumen. However, the emergence of the phase separation problem in the use of plastics or polymers has led researchers to different process applications [11].

Engineering properties of modified bitumens prepared using triethanolamine (TEOA) are examined in this study in order to establish a chemical interaction between the recycled PET and

bitumen. Waste PET constitutes 8 % by weight and 12 % by volume of the overall quantity of solid waste in the world, while also constituting the majority of municipal solid waste (MSW) [13, 14]. This material is a semi-crystalline thermoplastic polymer and is considered a polyester [15]. In addition, it has been listed among significant plastic material groups over the last two decades since it exhibits good chemical resistance and outstanding thermal properties. It is also lightweight and cheap, and can be dyed. Today, PET has many practical applications, including its use for bottles, fibres, and storage boxes [13, 16].

According to results obtained in studies in which PET was used in bitumen modification, the penetration values of binders with PET additive decreased, the softening point value increased, and the rheological properties improved [17-21]. In the studies where PET was used for hot mix asphalt (HMA) pavements, it was observed that the fatigue properties of pavement improved [22, 23], the stability value increased [20, 21, 24], and the resistance to permanent deformations improved [14], all thanks to the use of PET additive. Despite these advantages, it was established that polymeric materials used in the modification, such as PET, show only physical distribution in the bitumen and do not react with bitumen [25, 26]. It was observed that this situation produced adverse results in terms of storage stability of modified binders under high temperatures. The polymers in the modified bitumen blend either sink or rise to the surface of the mixture, due to their different specific weights, which causes deterioration of the homogeneous structure. This result has directed researchers toward production of polymers that can enter into chemical reaction with bitumen (such as reactive polymers) or toward the use of various additives that can create chemical reaction between polymer and bitumen [13, 25, 26]. For this purpose, various chemicals, such as triethylenetetramine and ethanolamine, were used in some studies for bitumen modification with polymer [27].

The main aim of this study is to examine the change in the performance properties of modified bitumens obtained through chemical interaction between the recycled PET, TEOA, and bitumen. These properties were determined using the X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy, penetration, softening point, ductility, rotational viscometer (RV), dynamic shear rheometer (DSR) and bending beam rheometer (BBR) tests.

Properties	Standard	Limits	Result	
Penetration, 0.1 mm	ASTM D5	70 - 100	88	
Softening point [°C]	ASTM D36	43 - 51	46.75	
Ductility [cm]	ASTM D113	min. 100	117	
Flash point [°C]	ASTM D92	min. 230	238	
Specific weight [g/cm ³]	ASTM D70	1.0 - 1.1	1.038	
Penetration index (PI)	-	-	-0.64	
Mass loss [%]	ASTM D2872	max. 0.8	0.23	

Table 1. Physical properties of bitumen



Figure 1. Chemical reaction between bitumen, TEOA, and PET

2. Materials and methods

2.1. Materials

In this study, B 70/100 penetration class bitumen, recycled PET, and triethanolamine (TEOA) were used for modification. Properties of pure B 70/100 bitumen are given in Table 1. The recycled PET, used as the modifier, was supplied by the company called Meltem Chemistry Ltd.Sti. PET properties are given in Table 2. The TEOA chemical was used to create a chemical bond between bitumen and PET. TEOA properties are given in Table 3.

Table 2. Properties of PET [15]					
Properties	PET				
Specific weight [g/cm ³]	1.33 - 1.38				
Form / colour	Granular/light				
Melting temperature [°C]	250				
Usable temperature [°C]	60				
Available size [mm]	max. 0.3				

Properties	TEOA				
Chemical formula	C ₆ H ₁₅ NO ₃				
Molar mass [g/mol]	149.19				
Boiling point [°C]	335.4				
Density [g/cm³]	1.12				
Structure	Alkaline				

Table 3. Chemical properties of TEOA [13]

TEOA binds to a structure easily through its amine group, while at the same time it has a very good solubilization ability thanks to its strong solvent feature (solubility parameter; PET δ_{p} :18.2, TEOA δ_{p} : 17.3, Bitumen δ_{p} : 17.5 - Hansen) [28-30].

In this study, upon adding TEOA and PET to the bituminous binder, a chain chemical bond is formed among these three materials as can be seen in Figure 1. This chemical interaction is thought to have positive effects on performance properties of PET modified bitumens.

2.2. Preparation of samples

Modified bitumens were prepared by mixing in a mixer at 160°C for a total of 40 minutes. TEOA was added to pure bitumen at the rate of 2.5 % by weight, and the mixing continued for 10 minutes at the rotational speed of 500 rpm. This TEOA ratio was determined by examining the effect on the chemical structure of bitumen during preliminary studies in laboratory. When PET (2 %, 4 %, 6 %, 8 %, and 10 % by weight) was added to the bitumen

+ TEOA blend, the rotational speed was increased to 1000 rpm and the mixing continued for another 30 minutes. In this study, pure and modified bitumens were named as B, B+2P, B+4P, B+6P, B+8P and B+10P, respectively.

2.3. Microstructural properties of bitumens

XRD, SEM and FT-IR Spectroscopy tests were conducted to evaluate chemical and microstructural properties of the binders. XRD patterns and SEM images of the binders are given in Figure 2, and FT-IR Spectroscopy results are shown in Figure 3.





Table 2. Dreparties of DET [12]

The peak value of approximately $2\theta \cong 20^\circ$ was obtained by examining the XRD pattern of pure bitumen (Figure 2). This value illustrates a characteristic property of the bitumen. The material generally consists of a single amorphous macromolecular structure. Furthermore, the SEM image of the bitumen also indicates that the structure is homogenous and single phase. By examining Figure 2b, it can be seen that there is a significant decrease in the peak intensity even though a typical bitumen peak of approximately $2\theta \cong 20^\circ$ was obtained in the XRD pattern of the 2 % PET additive binder. It is considered that this decrease is due to the semi-crystalline and largely amorphous macromolecular structure of PET [31]. However, it was observed that the SEM image of this binder has homogeneous boundaries, which confirms the decrease in peak intensity in the XRD pattern. XRD peak intensities of the binders (especially 6 % PET) increased with an increase in the additive rate (Figure 2c-f). It can be stated that this is due to the high peak intensity of PET [32] and, when PET is added to the bitumen + TEOA blend, the best chemical interaction occurs at the rate of 6P %.

When SEM image of the binder added at this rate is examined, the fact that the structure is smooth and homogenous compared to the other ratios actually confirmed this situation. For that reason, it is thought that modified binders with 6 % of PET have better performance. However, it was established that the peak intensity decreases at the ratios of 8 %PET and 10 % PET binders, which reach at approximately the same values as pure bitumen. This situation can possibly be explained by the fact that a certain amount of PET sinks, since PET density is higher compared to bitumen density. Hence, upon examination of SEM images of these binders, the creation of limits in the structure at these ratios confirms this situation. In conclusion, it was established that a weak chemical bond was constituted between the bitumen and PET when low-content additives were used; however, this bond became stronger when the rate of PET increased and the best result was obtained when 6 %PET was used while, at higher ratios, PET did not react with bitumen any more.



Figure 3. FT-IR spectroscopy of bituminous binders

By examining FT-IR analyses of B+6P binder, pure and the most appropriate rate (Figure 3), it can be observed that the peak of pure bitumen was very low at 1032 cm⁻¹. However, two peaks at 1034 cm⁻¹ and 1065 cm⁻¹ appeared when PET was added at the rate of 6 %PET. At both binder contents, aliphatic C-H peaks can

clearly be seen at 2921 cm⁻¹ and 2852 cm⁻¹ peaks. The carbonyl peak can explicitly be seen at 1700 cm⁻¹ with PET additive. At the B+6P binder content, peaks with low intensity appeared at 1275 cm⁻¹. Furthermore, large but not broad peaks belonging to hydroxyl (-OH) in PET appeared at 3328 cm⁻¹ at this binder content. Consequently, the fact that there is no change in peaks at 3248 cm⁻¹ and 3254 cm⁻¹ with TEOA additive indicates that TEOA created a chemical reaction by combining with bitumen and PET.

2.4 Methods

2.4.1. Conventional bitumen tests

Physical properties of pure and modified bitumens were determined through penetration, softening point, and ductility tests conducted according to ASTM D5, ASTM D36, and ASTM D113, respectively. In addition, the penetration index (PI), which is considered to be an indicator of bitumen sensitivity to temperature effects, was calculated for all binders using the following equation (1).

$$PI = \frac{1952 - 500 \cdot \log(P_{25}) - 20 \cdot SP}{50 \cdot \log(P_{25}) - SP - 120}$$
(1)

In the above equation, P_{25} refers to the penetration value at 25°C and *SP* refers to the softening point value. The increase of PI value of the bitumen shows that temperature sensitivity decreases and the hardness of binder increases. When a bitumen with a high PI value was used in the asphalt mixture, it was established that the mixture was more resistant to cracking, and temperature sensitivity decreased [33].

2.4.2. Aging methods for bituminous binders

Bituminous binders are subject to aging for a short period of time in pre-service processes such as mixing, compaction, transportation and storage, and also to long-term aging due to various environmental conditions during service life (8-10 years) on the road. The short-term aging of binders is determined by the rolling thin film oven test (RTFOT) according to ASTM D2872, while the long-term aging is determined by the pressure aging vessel (PAV) test according to ASTM D 6521 [33].

2.4.3. Rotational viscosity (RV) tests

The fluidity properties of bituminous binders at high temperatures are determined by the RV test according to ASTM D 4402. The high temperature viscosity values of binders are determined in order to establish whether binders are sufficiently fluid during the pumping, mixing and compaction. In order to determine the mixing and compaction temperatures of binders, it is recommended by the Asphalt Institute to determine viscosity values of binders at 135°C and 165°C.

However, viscosity values of binders at 135 °C must not exceed 3000 cP. As a result of the RV test, the mixing and compaction temperature ranges of HMA are also determined my means of the viscosity-temperature chart drawn for binders. It is recommended to use temperature ranges corresponding to the 170 \pm 20 and 280 \pm 30 cP viscosity limits, respectively, to determine the mixing and compaction temperatures [33–35].

2.4.4. Dynamic shear rheometer (DSR) tests

Bituminous binders are materials that exhibit viscoelastic and thermoplastic behaviour under various temperature and loading conditions. Their rheological properties (complex shear modulus, phase angle) at high and intermediate temperatures are characterized by examining these behaviours of binders with the DSR experiment. Fatigue and rutting performances of binders at intermediate and high temperatures can be determined based on these rheological properties. The performance grade (PG) of binders is also determined by this test. The test is performed on the unaged, RTFOT and PAV aged samples [34]. The complex shear modulus (G*) and phase angle (δ) values of the binders are determined as a result of the experiment. G* is defined as a measure of the total resistance of binder to deformation when subjected to shear stress. δ is an indicator of relative viscous and elastic deformations of the binder. The permanent deformation parameter ($G^* \cdot sin\delta$) and performance level of binders at high temperatures, and the fatigue parameter (G* $\cdot \sin \delta$) at intermediate temperatures, are obtained as a result of the experiment. According to the Superpave specification, the minimum $G^*\cdot \mbox{sin}\delta$ value is suggested to be 1.00 kPa for unaged binders, minimum 2.2 kPa for RTFOT-aged binders, and maximum 5000 kPa for $\mathsf{G}^* \cdot \mathsf{sin}\,\delta$ value for PAV-aged binders. It is expected that binders with high G^* and low δ values will be more resistant to permanent deformations, while binders with low G^* and high δ values are expected to be more resistant to

Table 4. Physical properties of binders

fatigue cracks [33-35].

2.4.5. Bending beam rheometer (BBR) tests

Bituminous binders, being viscoelastic materials, harden under cold climate conditions and become more rigid, which causes HMA pavements to harden. As a result, HMA pavements with a high hardness modulus become sensitive to thermal cracking, and the cracking potential increases. For this reason, the BBR tester was developed as a means to determine hardness of bituminous binders, and hence to evaluate the cracking potential of HMA pavements. With the BBR test, the creep hardness (S) and the creep rate (m-value) values of binders are determined. S is the resistance of the binder to creep stress, while the m-value refers to the change in binder hardness during loading. In the BBR test, a constant singular force $(100 \pm 5 \text{ g})$ is applied to the beam shaped bitumen sample of standard dimensions (12.5 x 125 x 6.25 mm). The deflection in the middle of the beam during the 240 second test period is measured by the system at different times (8, 15, 30, 60, 120, 240 s.) and the S value and m-value are calculated. The loading during the testing represents thermal stresses that the HMA pavement is subjected to at very low temperatures. According to the Superpave specification (ASTM D 6648), the S value should not exceed 300MPa, and the m-value should not be lower than 0.300 [33-35].

3. Results

3.1. Conventional bitumen tests results

Physical properties of pure binders and PET modified binders, before and after the aging process, are determined in this study by means of conventional bitumen tests. PI values, which are a measure of temperature sensitivity of all binders, are also calculated (Table 4).

Drenerties	Binder types						
Properties	В	B+2P	B+4P	B+6P	B+8P	B+10P	
Penetration, 0.1 mm	88	75	73	64	73	81	
Softening point [°C]	46.8	50.8	51.1	52.2	50.3	48.4	
Ductility [cm]	117	109	105	101	107	112	
PI	-0.64	0.026	0.027	-0.06	-0.20	-0.41	
After RTFOT							
Mass loss [%]	0.23	0.18	0.24	0.28	0.25	0.21	
Penetration, 0.1 mm	53.0	51.6	47.0	46.6	47.1	49.5	
Retained penetration [%]	60.2	68.8	64.4	72.8	64.5	61.1	
Softening point [°C]	52.85	54.0	54.65	54.90	54.35	54.25	
Change in softening point [°C]	6.1	3.2	3.6	2.7	4.1	5.9	
PI	-0.37	-0.17	-0.25	-0.21	-0.31	-0.22	

As can be seen in Table 4, penetration values of PET modified bitumens decreased by 14.8 %, 17 %, 27.3 %, 17 %, and 8 %, respectively, compared to pure bitumen. As a natural result of this hardening caused by the addition of PET, the softening point values of the binders increased by 8.7 %, 9.3 %, 11.7 %, 7.5 %, and 3.5 %, respectively. However, the ductility values of the binders also decreased by 6.8 %, 10.3 %, 13.7 %, 8.5 %, and 4.3 %, respectively. It can be seen that the increase and decrease rates in all these results peaked at 6 % PET, and that the changes decreased after this rate. Because of this ratio, it is considered that the reason for changes in the penetration, ductility, and softening point values is that PET, which cannot react with bitumen and has a higher specific weight, settles to the bottom of the mixture. According to physical test results, the consistency of the binders hardened with the addition of PET and, as a result of this hardening, the binder containing 6 % of PET became B 50/70 penetration class bitumen of harder consistency. It can therefore be stated that binders obtained with 6 % of PET additive can be used against permanent deformations in warmer regions. In addition, as can be seen in Table 4, an increase in PI values with the addition of PET indicates that the binders are more resistant to permanent deformations and low temperature cracking [33]. Moreover, it can be observed that PET does not have a negative effect on the aging of binders, making the binders more resistant to high temperature and oxidation.

3.2. RV test results

In this study, viscosity values of pure binders and PET modified binders were determined at high temperatures (135°C and 165°C) by means of the Brookfield DV-III rotational viscometer device. Using the temperature-viscosity graph shown in Figure 4, which was created based on these viscosity values, the mixing temperatures in the plant and the compaction temperatures on the road were determined for all binders. In addition, the modification index (η) values (modified bitumen viscosity value/pure bitumen viscosity value) were calculated for all binders, and are given in Table 5 together with the mixing and compaction temperatures.



Figure 4. Viscosity-temperature relationship of binders

RV test results show that the mixing and compaction temperatures of PET modified bitumens exhibit partial changes compared to pure bitumen. However, considering that 6 % PET rate is a critical value according to microstructural and physical test results, it can be seen that, at this rate, temperature values remain approximately at the same level when compared to pure bitumen.

Considering that bitumen modified at this rate is a harder B 50/70 class bitumen, it can be stated that the mixing and compaction temperatures obtained are lower compared to pure bitumen. It can be observed that modified bitumen has a more elastic consistency despite hardening, and it has different thermal properties. This shows that the use of PET modified bitumen in road pavements would result in a lower energy consumption.

3.3. DSR test results

In the study, rheological properties of pure binders and PET modified binders, before and after aging at high and intermediate temperatures, were determined by means of the DSR test. The test was carried out in a stress-controlled manner at a frequency of 10 rad/sec according to ASTM D7175, using the Bohlin DSR-II rheometer. In order to determine performance properties of PET modified binders at high temperatures, the experiments were carried out on unaged binders and RTFOT-aged binders. The experiment was

Binder types	Rotational V	Rotational Viscosity (cP)		ղ Modified/ ղ pure		Temperature range [°C]	
	135 °C	165 °C	135 °C	165 °C	Mixing	Compaction	
В	487.5	150.0	1.0	1.0	159 - 165	147 - 152	
B+2P	395.8	125.0	0.81	0.83	154 - 160	142 - 147	
B+4P	491.7	129.2	1.01	0.86	157 - 162	146 - 151	
B+6P	525	145.8	1.08	0.97	159 - 163	148 - 153	
B+8P	529.2	145.8	1.09	0.97	160 - 165	148 - 152	
B+10P	545.8	129.2	1.12	0.86	157 - 162	148 - 153	

Table 5. Viscosity values and mixing-compaction temperature ranges of binders



Figure 5. Complex modulus (G*) and phase angle (δ) temperature relationships of binders

carried out on samples 1.0 mm in thickness and 25.0 mm in diameter at elevated temperatures ranging from 52 to 76°C. In order to determine the fatigue performance of the binders at intermediate temperatures, PAV-aged binders 2.0 mm in thickness and 8.0 mm in diameter were prepared and tested at 25°C and 28°C. As a result of the tests, the changes of binder parameters G*, δ , G* / sin δ and G* \cdot sin δ with the change in temperature are given in figures 5 to 7.

As can be seen in Figure 5, the G* values of the unaged and RTFOT-aged binders increased significantly at all temperatures with an increase in the quantity PET. However, with an increase in PET content, δ values decreased compared to pure bitumen. These results show that PET-modified binders behave like an elastic solid. Increases in the G* values of the binders indicate that their resistance to shear stresses increases, and decreases in δ values indicate that the resistance of the binders to permanent deformations increases. Therefore, high G* and low δ values indicate that PET-added binders can be more resistant to permanent deformations.



Figure 6. The G*/sin δ temperature relationship of binders

It can be seen in Figure 6 that the G*/sin δ value, which is the rutting parameter of binders modified with PET, increases

compared to pure bitumen at the same temperature. This shows that binders containing PET additive become more resistant to permanent deformation at high temperatures. When the high temperature performance grades of the binders are examined, it can be seen that the pure and modified bitumens provide the rutting parameter up to the temperatures of 65.2, 66.4, 66.7, 70.0, 67.0, and 65.9°C, respectively. Performance levels of all binders according to the Superpave specification limits were determined as PG 64-Y, PG 64-Y, PG 64-Y, PG 70-Y, PG 64-Y, and PG 64-Y, respectively. According to these results, the performance grade of the 6 % PET added binder increased by 6°C compared to pure binder. This shows that pavements can be more resistant to permanent deformations with the use of PET in regions with much higher temperatures.



Figure 7. G*- sin δ temperature relationship of binders

When Figure 7 is examined, it can be seen that the values of G^{*} \cdot sin δ , which is the fatigue resistance parameter of all binders, remain within the Superpave specification limit (max. 5000 kPa). This indicates that, although the hardness of the binders increases due to an increase in the PET additive ratio, they can be resistant to fatigue cracks under repeated traffic loads.

According to the DSR test results, the hardness of bituminous binders increases with the PET additive, their temperature

Binder types	HT [°C]	LT [°C]	HT [°C] Improvement	LT [°C] Improvement	Performance grading (PG)
В	65.2	-25.7	-	-	PG 64-22
B+2P	66.4	-27.3	1.2	-1.6	PG 64-22
B+4P	66.7	-27.8	1.5	-2.1	PG 64-22
B+6P	70.0	-32.0	4.8	-6.3	PG 70-28
B+8P	67.0	-28.6	1.8	-2.9	PG 64-28
B+10P	65.9	-26.3	0.7	-0.6	PG 64-22

Table 6. Effects of recycled PET on performance grade of bitumen

sensitivity decreases, and the binders behave like an elastic solid. As a result, it was established that PET added bitumens exhibit a higher resistance to permanent deformations at high temperatures, and to fatigue cracking at intermediate temperatures.

3.4. BBR test results

PAV-aged binders were subjected to the BBR test so as to determine the resistance of bituminous binders to thermal cracking at low temperatures. The performance properties of all binders at low temperatures were evaluated using the creep stiffness (S) and creep rate (m-value) values obtained as a result of the test. The relationship between the S value and m-value of the binders and the temperature is shown in Figure 8.

As can be seen in Figure 8, an increase in the PET additive content results in an increase in the hardness of modified bitumens (especially at the rate of 6 % of PET) compared to pure bitumen. However, despite this increase, the creep stiffness of all binders is well below the limit (max.300MPa) stipulated in the specification (ASTM D 6648). This shows that PET-added binders behave like a more elastic solid and are not greatly affected by low temperatures. When the m-value results shown in the figure are examined, it can be seen that all binders meet the specification limit of 0.300 at temperatures of -16°C and -22°C. However, except binders with 6 % and 8 % of PET, other binders remained below this limit at -28°C. This result shows that 6 %PET ratio is a critical value and the change in binder hardness is low at this ratio.

When the S and m-value results were evaluated together, it was determined that the binders were resistant to thermal cracks up to temperatures of -25.7, -27.3, -27.8, -32.0, -28.6, and -26.3°C, respectively. Accordingly, it was determined that the low temperature performance levels of the binders according to the specification limit values were -22, -22, -22, -28, -28, and -22°C, respectively. These results show that 6 %PET ratio has a significant effect on the low performance temperature of the binders. When the high and low temperature performance properties of all binders are evaluated together (Table 6), it can be seen that the performance grades are PG 64-22, PG 64-22, PG 64-22, PG 70-28, PG 64-28, and PG 64-22, respectively.

As a result, it can be stated that the use of 6 % recycled PET

additive in bitumen modification has a very positive effect on both permanent deformation resistance at high temperatures and thermal cracking resistance at low temperatures.



Figure 8. Effects of PET on creep stiffness and m-value of B 70/100

4. Conclusions

The results obtained through the analysis and tests performed in this study are given below.

- Chemical characterization results showed that the TEOA chemical and PET formed a good chemical bond with bitumen and, especially, that the obtained 6 % PET modified blend had a homogeneous single-phase structure. Because of this structure, which is the most obvious result of the study, the problem of phase separation in polymer modified bitumen will be eliminated.

- According to physical test results, and especially those relating to the addition of 6 % PET, the bitumen hardened and turned into B 50/70 bitumen of harder consistency. This change in consistency of modified bitumen means that it can be used against permanent deformations in warmer areas.
- The RV test results show that there was no significant change in the mixing and compaction temperatures, although the consistency and thermal properties of modified bitumen changed at the critical value of 6 % PET. This result shows that bitumen modified with 6 % PET additive (B 50/70) can curb energy consumption when used in road pavements.
- The DSR test results show that the permanent deformation resistance of the binders at high temperatures increased with the addition of PET. The resistance of the pure binder at 65.2°C increased up to 70.0°C with 6 %PET additive. This indicates that the PET-added binders can be used in regions with warmer climates. In addition, although the hardness of the binders increases with PET additive, they have a very positive fatigue resistance at intermediate temperatures because they behave like a more elastic solid.
- BBR test results show that the resistance of the binders to thermal stresses at low temperatures increased with the

REFERENCES

- [1] Xu, D., Yang, S., Su, Y., Xiong, Y., Zhang, S.: Catalytic conversion of plastic wastes using cost-effective bauxite residue as catalyst into H2-rich syngas and magnetic nanocomposites for chrome (VI) detoxification, Journal of Hazardous Materials, 413 (2021), pp. 125289. doi: 10.1016/j.jhazmat.2021.125289
- [2] Jang, Y., Lee, G., Kwon, Y., Lim, J., Jeong, J.: Recycling and management practices of plastic packaging waste towards a circular economy in South Korea, Resources, Conseration and Recycling, 158 (2020), pp.104798, https://doi.org/ 10.1016/j. resconrec.2020.104798
- [3] Bahij, S., Omary, S., Feugeas, F., Faqiri, A.: A Fresh and hardened properties of concrete containing different forms of plastic waste – A review, Waste Management, 113 (2020), pp. 157–175, https://doi.org/ 10.1016/j.wasman.2020.05.048
- [4] Ameli, A., Maher, J., Mosavi, A., Nabipour, N., Babagoli, R., Norouzi, N.: Performance evaluation of binders and Stone Matrix Asphalt (SMA) mixtures modified by Ground Tire Rubber (GTR), waste Polyethylene Terephthalate (PET) and Anti Stripping Agents (ASAs), Construction and Building Materials, 251 (2020), pp. 118932, https://doi.org/ 10.1016/j.conbuildmat.2020.118932
- [5] Almeshal, I., Tayeh, B.A., Alyousef, I., Alabduljabbar, H., Mohamed, A.M., Alaskar, A.: Use of recycled plastic as fine aggregate in cementitious composites: A review, Construction and Building Materials, 253 (2020), pp. 119146, https://doi.org/ 10.1016/j. conbuildmat.2020.119146
- [6] Siddiqui, J., Pandey, G.: A review of plastic waste management strategies, International Research Journal of Environment Science, 2 (2013) 12, pp. 84-88.

addition of PET. The resistance of pure binder at -25.7 °C was obtained at -32.0 °C with the addition of 6 %PET. This decrease shows that the binders can be used in much colder regions by adding PET. It is considered that this result is due to the fact that PET added binders behave like a more elastic solid.

As a result, the combined use of PET and TEOA in bitumen modification enabled the modified bitumen to behave like a homogeneous single-phase structure. It was also observed that 6 % PET is a critical value and that this ratio of PET additive has an important effect on increasing the resistance of bitumen against permanent deformation at high temperatures and thermal cracking at low temperatures. For this reason, it is thought that the PET additive, which is used as a modifier in road engineering, will be beneficial both in terms of the performance of road pavements and in terms of eliminating the damage that PET causes to the environment.

Acknowledgements

This study was supported by the Inonu University Scientific Research Projects (BAP) Coordination Unit in the scope of the project No. IU-BAP FYL 2016/118.

- [7] Plastics the Facts 2017, www.plasticseurope.org/application/ files/5715/1717/4180/Plastics_the_facts_2017_FINAL_for_ website_one_page.pdf. 21.09.2021.
- [8] Moghaddam, T.B., Soltani, M., Karim, M.R., Baaj, H.: Optimization of asphalt and modifier contents for polyethylene terephthalate modified asphalt mixtures using response surface methodology, Measurement, 74 (2015), pp. 159–169, https://doi.org/10.1016/j. measurement.2015.07.012
- [9] Wu, S., Montalvo, L.: Repurposing waste plastics into cleaner asphalt pavement materials: A critical literature review, Journal of Cleaner Production, 280 (2021), pp. 124355, https://doi.org/ 10.1016/j.jclepro.2020.124355
- [10] Behl, A., Sharma, G., Kumar, G.: A sustainable approach: utilization of waste PVC in asphalting of roads, Construction and Building Materials, 54 (2014), pp. 113-117, https://doi.org/ 10.1016/j. conbuildmat.2013.12.050
- [11] Ahmedzade, P., Fainleib, A., Günay, T., Grygoryeva, O.: Modification of bitumen by electron beam irradiated recycled low density polyethylene, Construction and Building Materials, 69 (2014), pp. 1–9, https://doi.org/ 10.1016/j.conbuildmat.2014.07.027
- [12] Murugan, L.: Use of e-plastic waste in bituminous pavements, GRAĐEVINAR, 70 (2018) 7, pp. 607-615, https://doi.org/ https:// doi.org/10.14256/JCE.1375.2015
- [13] Geçkil, T., Önal, Y., İnce, C.B.: Moisture resistance of bituminous hot mixtures modified with waste PET, Journal of Polytechnic, 24 (2021)2, pp. 461-471, https://doi.org/10.2339/politeknik.699662

- [14] Moghaddam, T.B., Soltani, M., Karim, M.R.: Evaluation of permanent deformation characteristics of unmodified and Polyethylene Terephthalate modified asphalt mixtures using dynamic creep test, Materials and Design, 53 (2014), pp. 317– 324, https://doi.org/ 10.1016/j.matdes.2013.07.015
- [15] Shukla, S.R., Harad, A.M.: Aminolysis of polyethylene terephthalate waste, Polymer Degradation and Stability, 91 (2006), pp. 1850-1854, https://doi.org/ 10.1016/j.polymdegradstab.2005.11.005
- [16] Navarro, R., Ferrandiz, S., Lopez, J., Segui, V.J.: The influence of polyethylene in the mechanical recycling of Polyethylene Terephtalate, Journal of Materials Processing Technology, 195 (1) (2008), pp. 110-116, https://doi.org/ 10.1016/j. jmatprotec.2007.04.126
- [17] Almeida e Silva, J.A., Lucena, L.C.F.L., Rodrigues, J.K.G., Carvalho, M.W., Costa, D.B.: Use of Micronized Polyethylene Terephthalate (Pet) Waste in Asphalt Binder, Petroleum Science and Technology, 33 (2015) 15-16, pp. 1508-1515, https://doi.org/ 10.1080/10916466.2015.1079538
- [18] Ameri, M., Nasr, D.: Properties of asphalt modified with devulcanized polyethylene terephthalate, Petroleum Science and Technology, 34 (2016) 16, pp. 1424-1430, https://doi.org/ 10.1080/10916466.2016.1202968
- [19] Leng, Z., Sreeram, A., Padhan, R.K., Tan, Z.: Value-added application of waste PET based additives in bituminous mixtures containing high percentage of reclaimed asphalt pavement (RAP), Journal of Cleaner Production, 196 (2018), pp. 615-625, https://doi.org/ 10.1016/j.jclepro.2018.06.119
- [20] El-Naga, I.A., Ragab, M.: Benefits of utilization the recycle polyethylene terephthalate waste plastic materials as a modifier to asphalt mixtures, Construction and Building Materials, 219 (2019), pp. 81-90, https://doi.org/ 10.1016/j.conbuildmat.2019.05.172
- [21] Ponnada, S., Krishina, V.: Experimental investigation on modification of rheological parameters of bitumen by using waste plastic bottles, Materials Today: Proceedings, 32 (2020) 4, pp. 692-697, https://doi.org/ 10.1016/j.matpr.2020.03.243
- [22] Modarres, A., Hamedi, H.: Effect of waste plastic bottles on the stiffness and fatigue properties of modified asphalt mixes, Materials and Design, 61 (2014), pp. 8–15, https://doi.org/ 10.1016/j.matdes.2014.04.046
- [23] Denghan, Z., Modarres, A.: Evaluating the fatigue properties of hot mix asphalt reinforced by recycled PET fibers using 4-point bending test, Construction and Building Materials, 139 (2017), pp. 384–393, https://doi.org/ 10.1016/j.conbuildmat.2017.02.082

- [24] Ahmadinia, E., Zargar, M., Karim, M.R., Abdelaziz, M., Shafigh, P.: Using waste plastic bottles as additive for stone mastic asphalt, Materials and Design, 32 (2011), pp. 4844-4849, https://doi.org/ 10.1016/j.matdes.2011.06.016
- [25] Jasso, M., Hampl, R., Vacin, O., Bakos, D., Stastn, J., Zanzotto, L.: Rheology of Conventional Asphalt Modified with SBS, Elvaloy and Polyphosphoric acid, Fuel Proccessing Technology, 140 (2015), pp. 172-179, https://doi.org/ 10.1016/j.fuproc.2015.09.002
- [26] Polacco, G., Filippi, S., Merusi, F., Stastna, G.: A Review of the Fundmentals of Polymer-Modified Asphalts: Asphalt/Polymer Interactions and Principles of Compatibility, Advances in Colloid and Interface Science, 224 (2015), pp. 72-112, https://doi.org/ 10.1016/j.cis.2015.07.010
- [27] Xu, X., Leng, Z., Jan, J., Wang, W., Yu, J., Bai, Y., Sreeram, A., Hu, J.: Sustainable Practice in Pavement Engineering through Value-Added Collective Recycling of Waste Plastic and Waste Tyre Rubber, Engineering, (2020) (Pre-proof). https://doi.org/ 10.1016/j.eng.2020.08.020
- [28] Hansen, C.M.: Hansen Solubility Parameters Auser's Handbook, NewYork Washington D.C., 2000.
- [29] Paseta, L., Potier, G., Abbott, S., Coronas, J.: Using Hansen solubility parameters to study the encapsulation of caffeine in MOFs, Organic & Biomolecular Chemistry, 6 (2015), pp. 1724-1731, https://doi.org/10.1039/c5ob90016f
- [30] Redelius, P.: Bitumen Solubility Model Using Hansen Solubility Parameter, Energy & Fuels, 18 (2004), pp. 1087-1092.
- [31] Gupta, S., Patıdar, D., Baboo, M., Sharma, K., Saxena, N.S.: Investigation of Al Schottky junction on n-type CdS film deposited on polymer substrate, Frontiers of Optoelectronics in China, 3 (2010) 3, pp. 321–327, https://doi.org/ 10.1007/s12200-010-0102-0
- [32] Gupta, S., Sharma, K., Saxena, N.S.: Temperature Dependent Mechanical Analysis of Chalcogenide (CdS, ZnS) Coated PET Films, Hindawi Publishing Corporation ISRN Polymer Science, (2013), pp. 952612, https://doi.org/10.1155/2013/952612
- [33] Geçkil, T., Seloğlu, M.: Performance properties of asphalt modified with reactive terpolymer, Construction and Building Materials, 173 (2018), pp. 262–271, https://doi.org/ 10.1016/j. conbuildmat.2018.04.036
- [34] McGennis, R.B., Shuler, S., Bahia, H.U.: Background of Superpave Asphalt Binder Test Methods, Publication FHWA-SA-94-069, Federal Highway Administration, 1994.
- [35] Zaniewski, J.P., Pumphrey, M.E.: Evaluation of Performance Graded Asphalt Binder Equipment and Testing Protocol, Asphalt Technology Program, West Virginia, 2004.