

Modification of bitumen by adding reactive terpolymer, polyolefin elastomer and thermoplastic

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Accepted July 28, 2026

In this study, 50/70 penetration grade TÜPRAŞ bitumen was modified. The reactive elastomeric terpolymer of DuPont (Elvaloy RET), Dow Engage 8411 polyolefin elastomer and Atactic Polypropylene (PP) polymers were used for bitumen modification. Each of the polymers elastomeric terpolymer (Elvaloy RET), Engage 8411 polyolefin elastomer, and atactic polypropylene (PP) was added to the 50/70 penetration grade bitumen at proportions of 0.5%, 1%, 1.5%, 2%, and 2.5% by weight. Additionally, 1% by weight of the other two polymers was added to obtain modified bitumen samples. The samples were subjected to penetration (TS 118 EN 1426) and softening point (TS 120 EN 1427) tests in accordance with the Turkish General Directorate of Highways Modified Bitumen Specification. With the decrease in penetration values and the increase in softening point values, modified bitumen that is more resistant to stress, shock waves, and impacts was obtained. Moreover, the modified bitumen exhibited greater resistance in regions with high air temperatures.

Keywords: Bitumen modification, penetration value, softening point, reactive, elastomeric terpolymer, polyolefin elastomer

INTRODUCTION

The use of pure bitumen as a pavement surface material has been widespread since ancient times [1]. Bitumens generally have complex compositions. Pure bitumen contains high levels of hydrocarbons in varying proportions, primarily asphaltenes and maltenes, and these hydrocarbon compounds form a colloidal dispersion medium [2]. The complex composition of pure bitumen used in asphalt, mainly consisting of asphaltenes and maltenes, provides adequate performance against temperature and load in highway pavements and airport runway application [3]. However, over time, increases in vehicle loads and tire pressures due to the growing mass of road traffic, insufficient maintenance services, rapidly changing climatic conditions, and construction and design errors cause premature deterioration of asphalt pavements, thereby reducing their service life [4–7].

With the increasing demand for higher performance from pure bitumen used in asphalt, polymers with different properties are added to pure bitumen to produce polymer-modified bitumen. The increased resistance of polymer-modified bitumen under load is expected to extend its service life. Furthermore, as a result of modification, the aim is to improve the asphalt's resistance to cracking and fatigue at low temperatures and to increase its stability duration with minimal creep at high tempe-

ratures [8–10]. Polymers used in bitumen modification are generally classified into two groups, namely elastomers and plastomers, and their common disadvantage is phase separation at high temperatures. Among the polymers used to modify bitumen are styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), rubber, ethylene-vinyl acetate (EVA), polyethylene, and others [1, 11–14].

The feasibility of using polyolefin elastomers with a two-phase molecular structure to improve the performance of bitumen at different environmental temperatures has been investigated. The use of polyolefin elastomers (POEs) as different elastomers has demonstrated flexibility, processability, impact resistance, and low-temperature performance.

In the study conducted by Ye and Zhao, polyolefin elastomers with two different molecular structures were used to simultaneously improve both the high- and low-temperature performance of asphalt. Following the evaluation, the storage stability, workability, and rheological properties of asphalt modified with modified polyolefin were measured through the softening point difference test [15]. POE and SBS modified pure bitumen have been used to increase resistance to aging, environmental temperature, and UV radiation, as well as to slow down the degradation of styrene-butadiene-styrene caused by oxygen in the air [16].

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Among commercially developed polymer-modified bitumens, reactive ethylene terpolymers containing ethylene, glycidyl methacrylate (GMA), and an ester group (generally methyl or butyl acrylate) have gained increasing importance over the last 25 years. The Elvaloy series produced by Dow Chemicals are widely used reactive terpolymers in the literature [17].

Bulatovic *et al.* produced polymer-modified bitumen by adding Elvaloy AM and Elvaloy 4170 reactive ethylene terpolymers, which contain different percentages of the reactive functional group glycidyl methacrylate (GMA), to two types of pure bitumen with different asphaltene and maltene contents. It was observed that polymer modification improved the penetration, softening point, and temperature susceptibility performance of the base bitumen [18].

Recent studies have emphasized the effect and importance of reactive terpolymers in polymer-bitumen modification. Geckil and Seloglu [19] highlighted the importance of reactive terpolymers in their study. They determined that the penetration value of polymer-modified bitumen produced by adding Elvaloy RET 4170 at concentrations of 0.5%, 0.75%, and 1% to pure bitumen with a penetration value of 146 decreased by 23% for the 0.5% composition and by 31% for the 1% composition [19].

In the study conducted by Morova and Özel [20], polymer-modified bitumen was produced by adding 1.6%, 1.7%, and 1.8% Elvaloy RET 5160 reactive terpolymer and 0.2% polyphosphoric acid (PPA) as a catalyst to pure bitumen under appropriate temperature, mixing speed, and mixing duration conditions. With the addition of Elvaloy RET 5160 and PPA, the penetration value decreased from 58 (for pure bitumen) to approximately 45–48 (a reduction of about 17–22%). Therefore, a significant increase in hardness and load resistance was achieved. The softening point increased markedly from 51 °C to 60–62.4 °C (an increase of approximately 18–22%), confirming that Elvaloy RET 5160 and PPA significantly improve the high-temperature stability of bitumen [20].

In the study by Taciroğlu [21], the penetration value of 50/70 penetration grade pure bitumen was determined as 53, and its softening point was measured as 52 °C. When 1.6% Elvaloy RET was added to the pure bitumen, the penetration value decreased to 45.5, while the addition of 1.8% Elvaloy RET reduced the penetration value further to 31.7. In terms of softening point values, according

to the “Polymer Modified Bitumen (PMB) Technical Specification” table included in the 2013 Highway Technical Specifications of the General Directorate of Highways of Türkiye, the PMB produced with 1.6% Elvaloy RET falls within the usable range for PMB 58-28, PMB 64-28, PMB 70-16, PMB 70-20, and PMB 70-22 classes among the ten different polymer-modified bitumen classes. The sample containing 1.8% Elvaloy RET could not be used for PMB 82-16 and PMB 82-22 classes, but it was suitable for the other eight PMB classes.

Regarding penetration values, all samples containing 1.6% Elvaloy RET were suitable for nine PMB classes except PMB 58-28. The sample containing 1.8% Elvaloy RET satisfied the requirements for PMB 76-16, PMB 76-22, PMB 76-28, PMB 82-16, and PMB 82-22 classes. The sample containing 1.6% Elvaloy RET can be used for the PMB 58-28 class, as it satisfies both the softening point and penetration value requirements, while the sample containing 1.8% Elvaloy RET is suitable for the PMB 82-16 and PMB 82-22 classes [21]. In this study, polymer-modified bitumen was produced using 50/70 penetration grade raw bitumen (RAWB) produced at the Tüpraş Refinery, Dow Engage 8411 polyolefin elastomer, reactive terpolymer (Elvaloy RET 4170), and atactic polypropylene (PP) [22].

Fifteen polymer-modified bitumen (WPMB) samples were produced by separately incorporating three different polymers with distinct properties: reactive elastomeric terpolymer (Elvaloy RET), Engage 8411 polyolefin elastomer, and atactic polypropylene (PP). Penetration and softening point tests specified in the 2013 Highway Technical Specifications of the General Directorate of Highways of Türkiye for polymer-modified bitumen were conducted. The changes in the softening point and penetration values of the fifteen polymer-modified samples were evaluated and compared with the requirements of the ten different PMB classes specified in the bitumen standards.

EXPERIMENTAL

The General Directorate of Highways (KGM) has prepared the “Technical Specification for Modified Bitumen” to delay common pavement distresses such as rutting and cracking observed in hot mix asphalt layers and to enhance traffic safety by increasing skid resistance. Therefore, the bitumen grades used on Turkish highways, as specified by KGM, as well as the test criteria for polymer-modified bitumen applied in Turkey, are given in Tables 1 and 2, respectively [23].

Table 1. Bitumen grades used on Turkish highways

Experiment name (E.N.)	Standard (S.T)	Types of bitumen				
		B 40/60	RAW B 50/70	B 70/100	B 100/150	B 160/220
Penetration (P.N.T), (25°C), 0,1 mm	TS 118 EN 1426 ASTM D5	40-60	50-70	70-100	100-150	160-220
Softening point (S.P.), °C	TS 120 EN 1427 ASTM D36	48-56	46-54	43-51	39-47	35-43

Table 2. Physical properties of polymer-modified bitumen used on Turkish highways (TS EN 14023)

E.N	WPMB	PMB 58-28	PMB 64-28	PMB 70-16	PMB 70-22	PMB 70-28	PMB 76-16	PMB 76-22	PMB 76-28	PMB 82-16	PMB 82-22
P.N.T (25°C, 100g, 5sn.), 0.1mm	26-39	90-150	40-100	45-80	45-80	45-80	25-55	25-55	25-55	25-55	25-55
S.P., °C	58-74.6	45	50	60	60	55	65	65	60	70	70

Penetration (TS 118 EN 1426)

Penetration is a measure of the hardness and consistency of bitumen. The penetration test consists of measuring the depth to which a standard needle penetrates vertically into a bitumen sample under specified temperature, load, and time conditions. The bituminous material is tested at 25 °C under a load of 100 g for a duration of 5 sec.

Softening point (TS 120 EN 1427)

The softening point is generally defined as the temperature at which a bituminous material, placed in a standard mold with a steel ball on top and immersed in a water bath, softens upon heating at a controlled rate and reaches the bottom. This temperature is recorded from a thermometer at the moment the material touches the base.

Preparation of PMB samples

Experimental procedure

A total of 4–5 kg of 50/70 penetration grade bitumen produced by TÜPRAŞ is weighed, and polymers with predetermined percentages are added sequentially. The mixture is heated up to 200 °C and stirred at a speed of 120 rpm.

- Start: At 200 °C, ENGAGE 8411, at a specified percentage, is added to the base bitumen.

- 2nd hour: The base bitumen and ENGAGE are mixed for 2 hours. A 200 g sample is taken (1). The temperature is then reduced to 195 °C and maintained at this level until the end of the experiment. Polypropylene (PP), at a specified percentage, is added to the mixture.

- 3rd hour: ENGAGE 8411 and PP are mixed. A 200 g sample is taken (2), and Elvaloy RET along with super polyphosphoric acid (SPFA) are added and mixed.

- 4th hour: A 200 g sample (3) is taken from the mixture containing ENGAGE, PP, and Elvaloy RET. SPFA is then added at the same temperature and mixing continues.

- 5th hour: A 200 g sample (4) is taken from the mixture containing ENGAGE, PP, and Elvaloy RET. Then, 0.2% super polyphosphoric acid (SPFA) is added, and mixing is continued at the same temperature. SPFA accelerates the reaction of Elvaloy RET 4170 with asphaltenic acids.

- 6th hour: A 200 g sample (5) is taken from the mixture containing ENGAGE, PP, and Elvaloy RET reacted with asphaltenic acids.

- 7th hour: A 200 g sample (6) is taken from the same mixture. The process is continued until no further change is observed in the softening point based on physical testing.

RESULTS AND DISCUSSION

The penetration and softening point test results of bitumen containing 0.5%, 1%, 1.5%, 2%, and 2.5% ENGAGE 8411, polypropylene (PP), and Elvaloy RET 4170 are presented below. The penetration and softening point tests applied to the modified bituminous binders yielded the following results (Figs. 1-6).

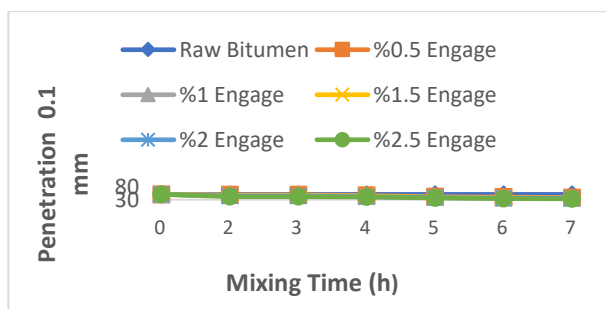


Figure 1. Penetration change for Engage 8411 Series and 1% PP 1% RET

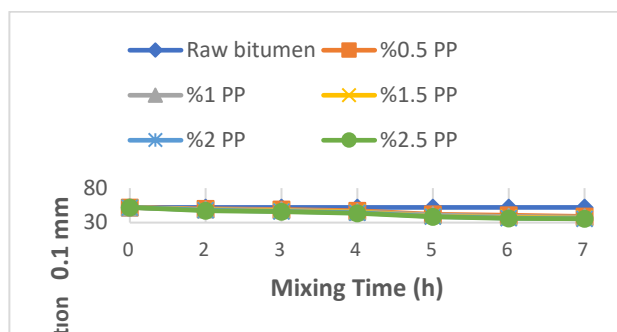


Figure 2. Penetration change for PP Series and 1% Engage 1% RET.

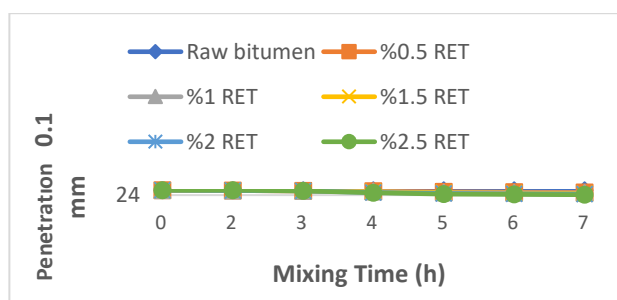


Figure 3. Penetration change for RET Series and 1% Engage 1% PP.

Softening point (TS EN 1427, ASTM D36)

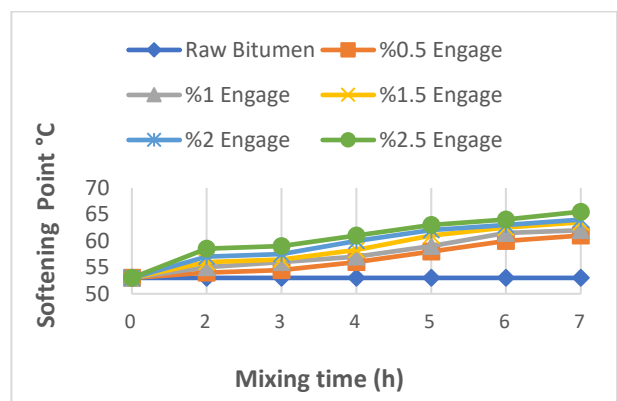


Figure 4. Softening point for Engage 8411 Series and 1% PP 1% RET.

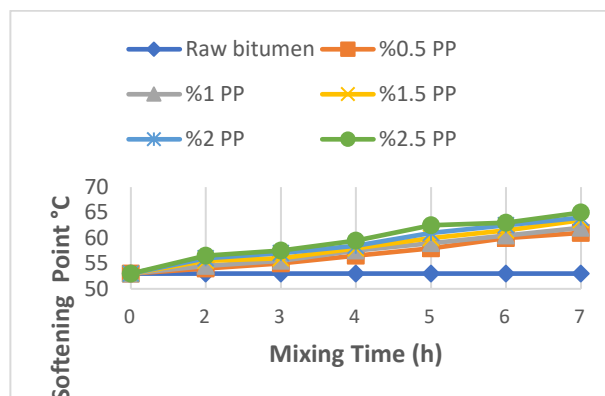


Figure 5. Softening point for PP Series and 1% Engage 8411 1% RET.

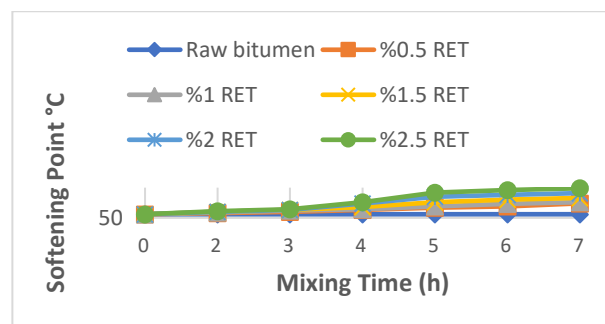


Figure 6. Softening point for RET Series and 1% Engage 1% PP.

Table 3 summarizes the maximum and minimum ranges of the penetration and softening point values.

Table 3. Minimum and maximum values of softening point and penetration according to the percentage composition of polymers by weight.

Composition of polymers by weight	Penetration, 25°C, 100 g, 5 sn, 0.1 mm	Softening point, °C
0.5 % Engage 8411, 1% PP, 1% RET.	39	61
2.5 % Engage 8411, 1% PP, 1% RET.	33	64.5
0.5 % PP, 1% Engage 8411 1% RET.	39	61
2.5 % PP, 1% Engage 8411, 1% RET.	36.2	64
0.5 % RET, 1% Engage 8411, 1% PP.	39	58
2.5 % RET, 1% Engage 8411, 1% PP.	26	74.5

CONCLUSION

The physical properties of the base bitumen were enhanced through the incorporation of a reactive elastomeric terpolymer (Elvaloy RET), Dow Engage 8411 polyolefin elastomer, and atactic polypropylene (PP). The evaluation of polymer-modified bitumen performance relies significantly on penetration and softening point tests. For the RAWB 50/70 base bitumen used in Turkish highways, the penetration value was determined to be 52 (0.1 mm), while the softening point was measured at 53°C. The incorporation of varying proportions of Engage 8411, PP, and RET into the neat bitumen resulted in an increase in softening point values ranging from 15% to 40.7%. Conversely, the addition of these polymers in different compositions led to a reduction in penetration values, with decreases observed in the range of 25% to 50%. When the PMB classes in Table 2 were evaluated together with the softening point values obtained in this study, the penetration and softening point values of fifteen different polymer-modified bitumen (WPMB) compositions were determined. The polymer-modified bitumen containing 1.5% RET, 1% Engage 8411, and 1% PP exhibited a softening point of 66.5 °C; the sample containing 2% RET, 1% Engage 8411, and 1% PP showed a softening point of 70.5 °C; and the sample containing 2.5% RET, 1% Engage 8411, and 1% PP had a softening point of 74.5 °C. These values were found to be suitable for all PMB class requirements. The other twelve polymer-modified bitumen samples produced in this study were suitable for all PMB classes except PMB 82-16, PMB 82-22, PMB 76-16, and PMB 76-22. When the PMB classes in Table 2 were compared with the penetration values obtained in this study, it was observed that all fifteen polymer-modified bitumen (WPMB) samples satisfied the penetration requirements for all ten PMB classes.

In the studies on polymer-modified bitumen (WPMB) produced using a blend of ENGAGE 8411, polypropylene (PP), and Elvaloy RET 4170, the softening point increased additionally due to the synergistic effect caused by the intertwining of the chemical bond chain of Elvaloy RET with the two polymer chains.

In contrast, the penetration value decreased further. Compared with the Elvaloy RET studies and polymer-modified bitumen studies obtained from different polymer blend systems reported in the literature, improvements in both penetration and softening point values were observed.

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