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Polymer-Modified Bitumen Using Ethylene Terpolymers

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Abstract: Polymer modified bitumen (PMB) is used in various construction applications, especially in motorways. The aim of this study is to improve features of 60/70 penetration grade, modified bitumen used on highways. Increasing the sensitivity to temperature and oxidation resistance are very important points for the modified bitumen. This condition was provided by reacting the carboxylic acid groups in asphaltene with the reactive ethylene terpolymer to form ester. Reactive ethylene terpolymer (RETP) and ethylene terpolymer (ETP) manufactured by DuPont USA were used as additives in this study. Infrared Spectrophotometer (IR) graphics and optical pictures of the modified bitumen have been examined. It has been observed that the softening point has increased on the other hand, the penetration and ductility values have decreased according to the test results.

Keywords: ductility, penetration, polymer modified bitumens, reactive terpolymer, softening point

INTRODUCTION

At present, polymer modified bitumen (PMB) is widely used in many construction applications and roadways (Yousefi, 2004). However in recent years, increased traffic loads, heavier trucks, and increased tire pressures have added a severe strain on the highway system (Airey, 2002). As a viscoelastic material, bitumen has a prominent role in determining many aspects of road performance (Gonzalez et al., 2004). Polymer modification of bitumens is not a new process, but interest in this technique has increased considerably during the past decade due to the increased performance-related requirements

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on roads. There are relatively few types (i.e., SBS, PP, PVC, rubber) that are suitable for bitumen modification, despite the large number of polymeric product. The degree of modification depends on the characteristics of bitumens, polymer type, and content, as well as the blending process (Isacsson and Lu, 1995; Lu and Isacsson, 1998, 1997). Mixing the bitumen and modifier at a certain temperature and for a prescribed amount of time has a great influence on the asphalt characteristics (Hınıslıoğlu and Agar, 2004). In PMB, the polymer is an elastomer or a thermoplastic which allows for a greater performance than possible with bitumen alone (Masson et al., 2001). Generally, polyethylene, ethylene-vinyl acetate (EVA) and polypropylene are some plastomers. On the other hand, styrene-butadiene-styrene block copolymer (SBS), styrene-butadiene rubber (SBR), polyisoprene, and isobutane are also elastomers used for bitumen modification (Hesp and Woodhams, 1991; Ait-Kadi et al., 1996; Newman and Kent, 1998; Pe'rez-Lepe et al., 2003; Ho et al., 1997). Moreover, the other elastomeric materials are ethylene terpolymer and reactive ethylene terpolymers (RETP) used in bitumen modification. According to studies by Selvavathi et. al. (2002), the addition of reactive ethylene terpolymer and crumb rubber added separately into the 60/70 penetration grade bitumen have been compared. Furthermore, an acid-reacted, polymer-modified asphalt composition (including 80-weight percent asphalt, 0.2 to 15-weight percent polymer containing available epoxy groups, and an acid as catalyst for promoting chemical bonding between the asphalt and epoxy groups) is the underdeveloping method of forming bitumen modification (Engber and Reinke, 2000). The aim of this study is to research improving properties of 60/70 penetration grade modified bitumen used in highways in Turkey. Reactive ethylene terpolymer and elastomeric ethylene terpolymer, which were recommended by DuPont, were used as additives and in some trials.

EXPERIMENTAL WORK

Middle East-oriented 60/70 penetration grade bitumen provided by Tupras (Turkey), was used in this study. Reactive ethylene terpolymer and ethylene terpolymer were used as modifying agents. 105% super phosphoric acid (SPA) was used as a catalyst.

The blending was carried out at 190°C in a stainless steel reactor. 2600 grams of modified bitumen were prepared with 10.44 grams of reactive ethylene terpolymer and 62.4 grams of ethylene terpolymer in a hot bitumen binder. Modifiers were added by 5 gr/sec speed and mixed with a Marshall (Germany) mixer at 90 rpm for 6 hr. After 2 hr, 5.7 grams of phosphoric acid, which was equal to 0.2% of the mixing weight, was added. The trials were completed by keeping a constant quantity of ethylene terpolymer but increasing the reactive ethylene terpolymer quantity by 0.2% which was equal to the total mixing weight at each trial.

TESTING METHODS

The modified bitumen was determined for the following tests.

Morphological Analysis

A sample of 10–15 mg of modified bitumen was heated and slowly pressed between glass slides; then micrographs (using a Leica Polarization Microscope, Germany) were taken.

Softening Point Temperature

The softening point of 60/70 grade bitumen and modified bitumens were measured according to ASTM D 36.

Penetration Test

The penetration tests were carried out at 25°C according to ASTM D 5. The bitumen was heated in a water bath and penetration of a standart needle under a total standart load (100 gr) was measured and reported in tenths of mm.

Ductility Test

In the ductility test, the sample is elongated at 5 cm/min until it breaks. A straight-sided mold is used for elastic recovery and a v-shaped mold is used for ductility. The ductility tests were carried out at 25°C according ASTM D 113.

RESULT AND DISCUSSION

Characterization of Bitumen

The functional groups of the bitumens were investigated using Mattson 1000 Fourier-Transform IR Spectrophometer (Unicom, England). The IR spectrum of the asphaltenes is recognizable by a strong absorption in the wavelength regions of 3500–3150 cm^{-1} (OH bond in dimeric and polymeric form), 1780–1630 cm^{-1} (carboxyl group C = O) (Figure 1). On the modified bitumen graph in 1780–1630 cm^{-1}, it has been determined that the carboxylic group peak was more evident according to pure bitumen at 1735 cm^{-1}. This peak indicates that reactive ethylene terpolymer reacts with carboxylic acid groups in asphaltene to form ester. This reaction is given in Figure 2.

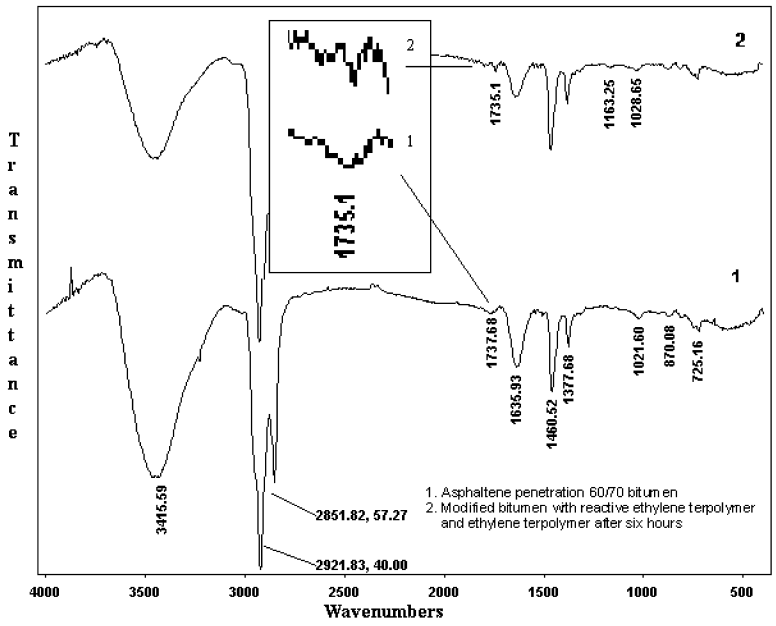


Figure 1. The comparison of FTIR spectroscopy of bitumen and modified bitumen.

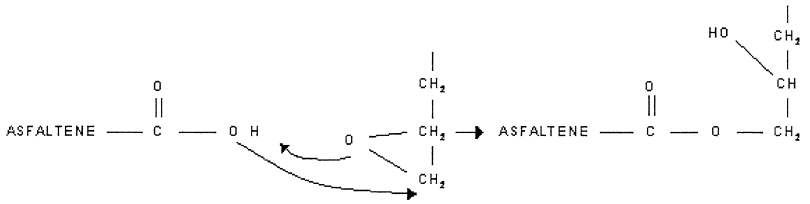


Figure 2. Synthetic ethylene terpolymer reaction with carboxylic acid groups in asphaltene.

Characterization of Optical Photographs

Optical photographs of pure bitumen and modified bitumen were taken at certain time intervals by a Leica Polarization Microscope. Figure 3 shows homogenous distribution of pure bitumen; Figure 4 shows big and little reactive ethylene terpolymer and ethylene terpolymer in the shape of a water drop at the end of first hour; Figure 5 shows the effect of an increasing reaction rate to the structure of drops by adding phospohoric acid at the end of the second hour; Figure 6 shows ethylene terpolymer which causes physical mixing due to viscous form distributed as thread.

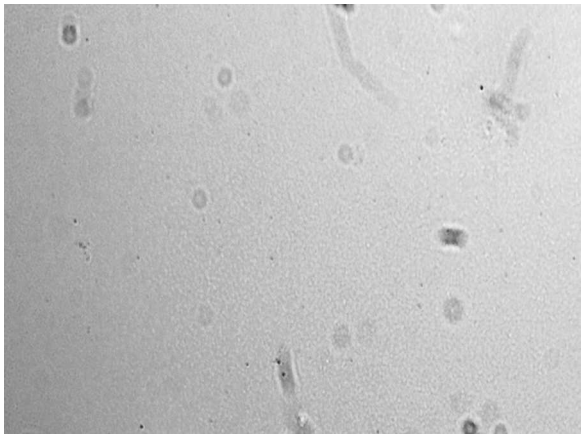


Figure 3. The optical photograph of 60/70 AC bitumen magnified ×200.

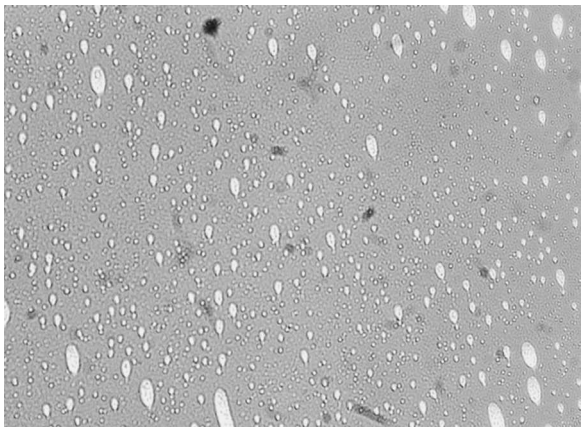


Figure 4. The optical photograph of modified bitumen after 1 hr.

Graphics

In Figure 7 it is seen that the relatively slow reaction rate suddenly increases by the addition of phosphoric acid at the end of 2 hr and reaches to the maximum point at the third hour. By the addition of reactive ethylene terpolymer, the softening point increases relatively. After the third hour, the reaction rate becomes slower and then remains constant.

In Figure 8 penetration value of pure bitumen remains constant till the second hour. Then the increase of viscosity by oxidation decreases the penetration value of pure bitumen. In modified bitumen, phosphoric acid and reactive ethylene terpolymer cause increasing viscosity and decreasing penetration

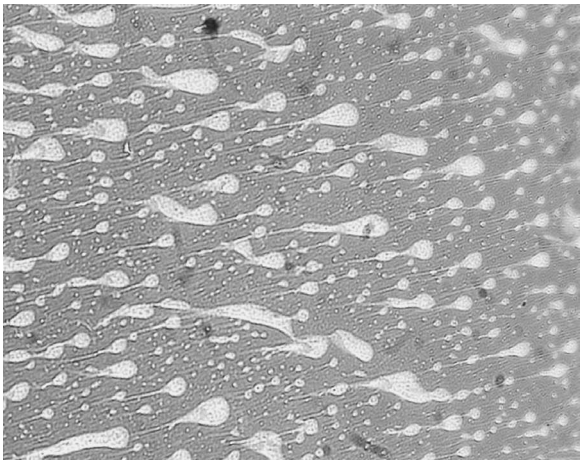


Figure 5. The optical photograph of modified bitumen with the addition of super phosphoric acid at third hour.

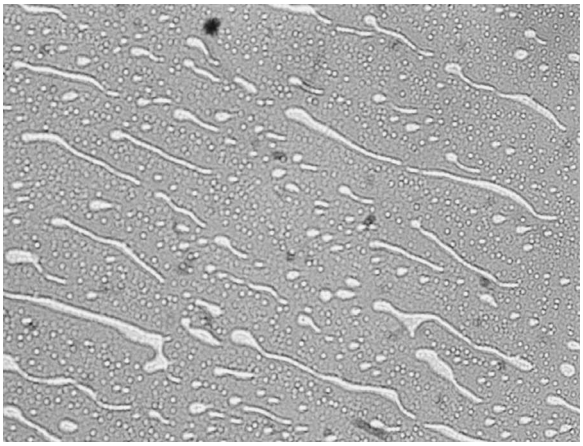


Figure 6. The optical photograph of modified bitumen with the addition of super phosphoric acid after 6 h.

value. Moreover, it is seen that additives decrease the effect of the oxidation. After the second and third hours, the penetration value decreases.

In Figure 9 it is seen that the addition of ethylene terpolymer at a constant value and reactive ethylene terpolymer with a 0.2% increment in weight at each trial caused a significant decrease in the ductility value of modified bitumen. It is seen that the ductility decreases sharply when the reactive ethylene terpolymer concentration (PMB concentration) is at 0.4%.

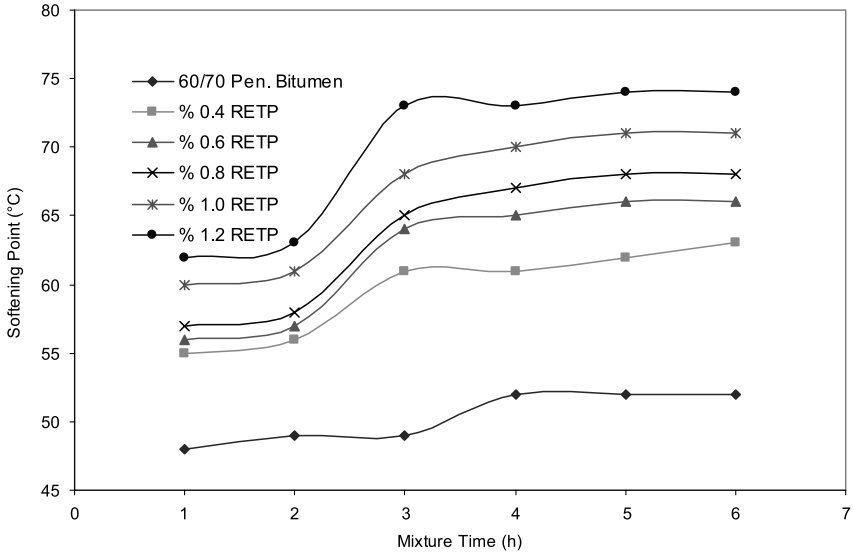


Figure 7. The softening point changes versus time according to ASTM D 36 (2.4% ethylene terpolymer is constant).

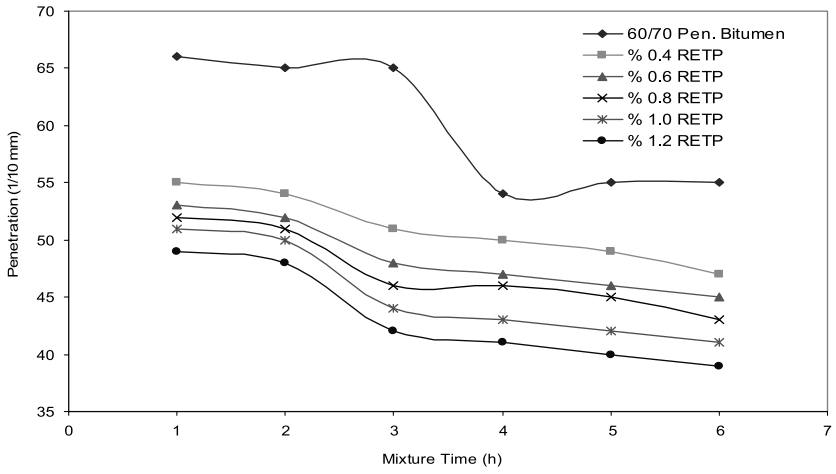


Figure 8. The penetration changes versus time according to ASTM D 5 (2.4% ethylene terpolymer is constant).

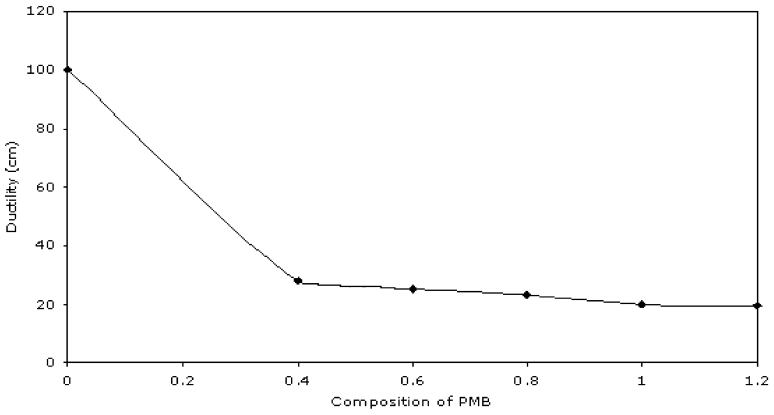


Figure 9. The ductility changes versus composition of polymer modified bitumen (PMB) according to ASTM D 113 (2.4% ethylene terpolymer is constant).

CONCLUSION

With the increase of RETP, the softening point reaches a maximum value at the beginning of the third hour. With the increase of RETP, the penetration value change decreases after the second hour. An increase of the softening point and a decrease in penetration and ductility has been observed by adding reactive ethylene terpolymer and ethylene terpolymer to bitumen. It has been observed that phosphoric acid has increased the reaction rate between reactive ethylene terpolymer and asphaltene acid groups. It has been observed that ethylene terpolymer has mixed physically with bitumen. Oxidation has decreased by adding reactive ethylene terpolymer and ethylene terpolymer in bitumen.

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