

Effect of polyester resin additive on the properties of asphalt binders and mixtures

Perviz Ahmedzade ^{*}, Mehmet Yilmaz

Department of Civil Engineering, Firat University, Elazig, Turkey

Received 28 March 2006; received in revised form 2 November 2006; accepted 20 November 2006

Available online 4 January 2007

Abstract

The properties of AC-5 control asphalt binder, mixture containing the same asphalt were compared with the properties of AC-10 asphalt binder modified by 0.75%, 1%, 2%, and 3% of polyester resin (PR), mixture containing pure AC-10 and AC-10 modified by 0.75% of PR, respectively.

Initial research was done to determine the physical properties of unmodified and PR modified asphalt binders. The AC-10 asphalt binder modified by 0.75% of PR had good results compared to AC-5 control asphalt binder and all other modified binders, and hence this modified binder as well as unmodified binders were used to prepare Marshall samples for Marshall stability and flow, indirect tensile stiffness modulus (ITSM), indirect tensile strength (ITS) and creep stiffness tests.

The results of investigation indicate that AC-10 + 0.75% PR binder has better physical properties than AC-5 control asphalt binder and, at the same time, PR improves mechanical properties of asphalt mixture.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Bitumen; Polyester resin; Modified mixtures; Creep stiffness

1. Introduction

The increasing demands of traffic on road building materials in recent years has resulted in a search for binders with improved performance relative to normal penetration grade bitumens. This effort to obtain improved binder characteristics has led to the evaluation, development and use of a wide range of bitumen modifiers which enhance the performance of the basic bitumen and hence the asphalt on the road [1].

Polymers are playing an increasingly important role in the asphalt industry and are the most technically advanced bitumen modifiers currently available. To achieve the goal of improving bitumen properties, a selected polymer should create a secondary network or new balance system

within bitumens by molecular interactions or by reacting chemically with the binder. The formation of a functional modified bitumen system is based on the fine dispersion of polymer in bitumen for which the chemical composition of bitumens is important. The degree of modification depends on the polymer property, polymer content and nature of the bitumen [2].

Polymers can be classified into four broad categories, namely plastics, elastomers, fibres and additives/coatings. Plastics can in turn be subdivided into thermoplastics and thermosets (or thermosetting resins) and elastomers into natural and synthetic rubber. Some of the principal thermoplastics, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and ethylene vinyl acetate (EVA), have been examined in bitumen modification. These materials, when mixed with bitumen, associate at ambient temperatures and increase the viscosity and stiffness of bitumen at normal service temperatures.

^{*} Corresponding author. Tel.: +90 424 2479117; fax: +90 424 2415526.
E-mail address: pahmedzade@firat.edu.tr (P. Ahmedzade).

Unfortunately, most of them do not significantly increase the elasticity of bitumen and, on heating, they tend to separate, giving rise to coarse dispersions on cooling [3–7].

Thermoset materials (thermosetting resins) are produced by the direct formation of network polymers from monomers, or by crosslinking linear prepolymers. Important thermosets include alkyds, amino and phenolic resins, epoxies, unsaturated polyesters and polyurethanes. Thermosetting polymers consist of two liquid components, one containing a resin and the other the hardener [8].

The main objective of this research is to study the influences of PR modifier on the physical and mechanical properties of asphalt binders and mixtures.

2. Experimental procedure

2.1. Materials

Crushed limestone aggregate was used in this study. The combined gradation of aggregate is given in Fig. 1. Table 1 gives a summary of the properties of the aggregate. AC-10 and AC-5 asphalt cements were used in this study. Both asphalts were obtained from Turkey Petroleum Refinery. Table 2 gives a summary of the results of some tests performed on the asphalt cements. As the modifier was chosen unsaturated polyester resin (PR), which belongs to the general group of thermosets, but in the current study, it was used without component containing the hardener. The unsaturated PR used in this study was Aropol Q6585, which was provided by Ashland Chemical. Q6585 is a 1:1 maleic anhydride and propylene glycol mixture with an average of 10.13 vinylene groups per molecule and an aver-

age molecular weight of 1560 g mol^{-1} , and contains 35% styrene.

2.2. Preparation of samples

AC-10 and AC-5 asphalt cements were heated in an oven at a temperature of at least 160°C . For modification, to the required amount of AC-10 was added 0.75%, 1%, 2% and 3% PR by total weight of binder and stirred into the asphalt. The mixing was continued for a further 20 min at 500 rpm to achieve a homogeneous binder mix. Two types of unmodified binders and PR modified binders were used to prepare specimens for the specific gravity, ductility, penetration, softening point and Fraass breaking point tests. At the end, AC-10, AC-5 and AC-10 + 0.75% PR binders were mixed with the heated aggregate to prepare unmodified and modified Marshall asphalt concrete specimens. Asphaltic concrete mixture samples were prepared in triplicate for each asphalt binder formulation.

3. Testing program

3.1. Thermogravimetric analysis (TGA)

Thermal analysis was performed in nitrogen atmosphere by using a TGA-50 thermobalance at a heating rate of $10^\circ\text{C min}^{-1}$.

3.2. Marshall stability, flow and Marshall quotient tests

Marshall stability and flow tests were carried out on compacted specimens at various binder contents according to ASTM D1559. The Marshall test is an empirical test in which cylindrical compacted specimens, 100 mm diameter by approximately 63.5 mm high are immersed in water at 60°C for 30–40 min and then loaded to failure using curved steel loading plates along a diameter at a constant rate of compression of 51 mm/min. The Marshall stability value (in kN) is the maximum force recorded during compression whilst the flow (in mm) is the deformation recorded at maximum force.

The binder contents at maximum bulk specific gravity, maximum stability, 4% air voids in the total mixture, and 80% voids in the aggregate mass filled with binder are used in order to determine the optimum binder content [9].

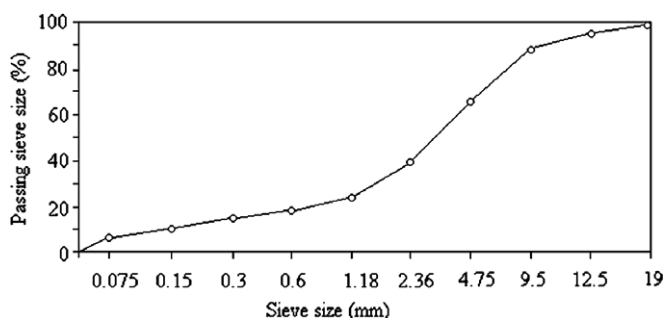


Fig. 1. Combined aggregate gradation.

Table 1
Properties of aggregate

Properties	Standard	Aggregate		
		Coarse	Fine	Filler
Abrasion loss (%) (Los Angeles)	ASTM DC-131	29		
Frost action (%) (with Na_2SO_4)	ASTM C-88	3.74		
Specific gravity (g/cm^3)	ASTM C-127	2.627		
Specific gravity (g/cm^3)	ASTM C-128		2.639	
Specific gravity (g/cm^3)	ASTM D-854			2.632

Table 2
Changes in conventional binder properties following PR modification

Properties	Standard	Binder types		
		AC-10	AC-5	AC-10 + 0.75% PR
Specific gravity at 25 °C	ASTM D70	1.036	1.035	1.033
Ductility (cm) at 25 °C	ASTM D113	100	100	100
Penetration, (0.1 mm), 100 g, 5 s	ASTM D5	90	138	142
Softening point (°C)	ASTM D36	48.2	46.7	47.1
Fraass breaking point (°C)	IP 80	−27.1	−21.4	−24.3
		AC-10 + 1% PR	AC-10 + 2% PR	AC-10 + 3% PR
Specific gravity at 25 °C	ASTM D70	1.032	1.030	1.027
Ductility (cm) at 25 °C	ASTM D113	85	76	68
Penetration, (0.1 mm), 100 g, 5 s	ASTM D5	167	184	237
Softening point (°C)	ASTM D36	46.6	46.3	44.7
Fraass breaking point (°C)	IP 80	−21.1	−20.8	−19.7

The Marshall quotient (MQ) (kN/mm), calculated as the ratio of stability (kN) to flow (mm) and thereby representing an approximation of the ratio of load to deformation under the particular conditions of the test, can be used as a measure of the material's resistance to permanent deformation in service [10].

3.3. Indirect tensile stiffness modulus test (ITSM)

Stiffness modulus is considered to be a very important performance characteristic of the roadbase and base-course layers. The ITSM test defined by BS DD 213 is a nondestructive test and has been identified as a potential means of measuring this property. The test was performed by Universal Testing Machine (UTM-5P) [11]. The ITSM S_m in MPa is defined as:

$$S_m = \frac{L(v + 0.27)}{Dt} \quad (1)$$

where L is the peak value of the applied vertical load (N), D is the mean amplitude of the horizontal deformation obtained from two or more applications of the load pulse (mm), t is the mean thickness of the test specimen (mm), and v is the Poisson's ratio (a value of 0.35 is normally used).

During testing, the rise time, which is measured from when the load pulse commences and is the time taken for the applied load to increase from zero to a maximum value is set at 124 ± 4 ms. The load pulse, defined as the period from the start of the load application until the start of the next load application is equated to 3.0 ± 0.05 s. The peak load value is adjusted to achieve a peak transient horizontal deformation of 0.005% of the specimen diameter. The test is normally performed at 20 °C but for this investigation, additional tests were performed at 0 °C and 40 °C.

3.4. Creep stiffness

One method for the assessment of resistance to permanent deformation is the creep test. Typical conditions

under which the unconfined static uniaxial creep test is carried out are: (a) standard test temperature 40 °C, for very hot climates 60 °C; (b) preloading for 2 min at 0.01 MPa, as a conditioning stress; (c) constant loading stress during the test equal to 0.1 MPa; (d) duration of test: 1 h loading and 1 h unloading [12]. During the test, axial deformation is measured as a function of time. Thus knowing the initial height of the specimen, the axial strain, ϵ , and therefore the stiffness modulus S_{mix} , at any loading time can be determined:

$$S_{mix} = \frac{\text{applied stress } (\sigma)}{\text{cumulative irrecoverable axial strain } (\epsilon)} \quad (2)$$

3.5. Indirect tensile strength test (ITS)

The indirect tensile strength test (ITS) is performed at loading rate of 51 mm/min by using the Marshall apparatus. The ITS test involves loading a cylindrical specimen with compressive loads that act parallel and loading the vertical diametrical plane. The ITS test is carried out to define the tensile characteristics of the asphalt concrete which can be further related to the cracking properties of the pavement. To compute the ITS, according to the maximum load carried by a specimen at failure, is used the following equation:

$$ITS = \frac{2P_{max}}{\pi t d} \quad (3)$$

where P_{max} is the maximum applied load (kN), t is thickness of specimen (mm), d is diameter of specimen (mm).

3.6. Resistance to moisture damage

Moisture susceptibility of asphalt mixtures is defined as the vulnerability of the mixture to be damaged by water. As moisture is collected within the asphalt mixture, it can damage the bond between the asphalt binder and the aggregates resulting in stripping. The moisture susceptibility of asphalt mixtures was evaluated using the AASHTO

T283 test. The specimens were sorted into two subsets were approximately equal. One subset was conditioned by vacuum saturating with distilled water to 55–80% of the air void volume. These specimens were then placed in a freezer at $-18\text{ }^{\circ}\text{C}$ for a minimum of 16 h. After removal from the freezer, they were placed in a $60\text{ }^{\circ}\text{C}$ water bath for 24 h. The specimens are then placed in a $25\text{ }^{\circ}\text{C}$ bath for 2 h. Also at this time the unconditioned specimens were placed in the $25\text{ }^{\circ}\text{C}$ bath. After these 2 h of temperature stabilization, the indirect tensile strength was determined on all the specimens.

The ratio of conditioned indirect tensile strength to dry indirect tensile strength is calculated from following equation:

$$\text{ITSR} = \frac{\text{ITS}_{\text{cond}}}{\text{ITS}_{\text{dry}}} \quad (4)$$

where ITSR is indirect tensile strength ratio, ITS_{cond} is average indirect tensile strength of conditioned subset (kPa), ITS_{dry} is average indirect tensile strength of dry subset (kPa).

Mixture with tensile strength ratios less than 0.7 are moisture susceptible and mixtures with ratios greater than 0.7 are relatively resistant to moisture damage.

4. Results and discussion

4.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to characterize the thermal behavior of the AC-10, AC-5 and PR (Fig. 2a–c) The initial decomposition temperatures of these materials, which were determined by TGA, were as following: $227\text{ }^{\circ}\text{C}$ (AC-10), $225\text{ }^{\circ}\text{C}$ (AC-5) and $176\text{ }^{\circ}\text{C}$ (PR).

Fig. 2 shows that the initial decomposition temperatures of the asphalt cements and modifier are higher than the temperature of mixing and preparing of the asphalt concrete samples. It follows that this modifier can be used in asphalt cement modification.

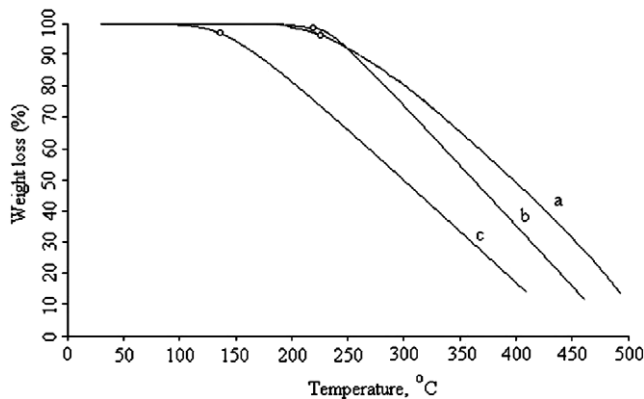


Fig. 2. Thermogravimetric analysis curves of AC-10 (a), AC-5 (b) and PR (c).

4.2. Conventional binder properties

The results obtained using conventional test methods are summarized in Table 2. As can be seen, there is a substantial reduction in ductility associated with higher PR levels. Typical pavement asphalt required a ductility of 100 cm or more; therefore, addition above 0.75% of PR would violate the ductility specifications. Table 2 shows that penetration values decrease, but softening point and Fraass breaking point values increase with increasing PR content in AC-10. Binder modified by 0.75% PR gives the higher softening point and the lower Fraas breaking point values than AC-5 control binder, despite the fact that the both binders have identical penetration limits (100–150). According to results shown in Table 2, it can be seen, that AC-10 + 0.75% PR binder has good results compared to AC-5 control asphalt binder and all other modified binders, therefore this modified binder was used to prepare asphalt concrete mixtures, as well as unmodified binders.

4.3. Marshall stability and flow tests

AC-10, AC-5 and AC-10 + 0.75% PR asphalt concrete mixtures with 4, 4.5, 5, 5.5 and 6% binder content by mass of aggregate were prepared in order to determine optimal binder content (o.b.c.). The o.b.c. for the AC-10, AC-5 and AC-10 + 0.75% PR mixtures were as following: 5%, 4.85% and 4.74%, respectively. Marshall design results are obtained from compacted specimens at the o.b.c. of each binder type and each result is from an average of three test specimens are given in Table 3. The important criteria for Marshall stability and flow tests is the combination of high stability and low flow values. As it seen from Table 3 the best results of Marshall stability and flow values were obtained with mixture modified by PR. The increasing of stability indicates that the PR mixture is stronger than the unmodified mixtures.

Since MQ is an indicator of the resistance against the deformation of the asphalt concrete, MQ values are calculated to evaluate the resistance of the deformation of the all mixtures. The PR mixture has higher MQ value than both AC-5 control mixture and AC-10 pure mixture. A higher

Table 3
Marshall design results

Property	Binder types		
	AC-10	AC-5	AC-10 + 0.75 PR
Optimum binder content (%)	5.0	4.85	4.74
Aggregate bulk specific gravity (g/cm^3)	2.634	2.634	2.634
Mix bulk specific gravity (g/cm^3)	2.392	2.385	2.396
Air void (%)	2.53	2.97	2.68
Voids in mineral aggregate (%)	13.51	13.65	13.15
Marshall stability (kN)	17.46	16.50	17.72
Flow (mm)	2.97	2.86	2.80
MQ (kN/mm)	5.88	5.77	6.33

value of MQ indicates a stiffer mixture and, hence, indicates that the mixture is likely more resistant to permanent deformation.

4.4. Indirect tensile stiffness modulus (ITSM) and creep stiffness tests

Table 4, Fig. 3 show the ITSM results for all mixtures at 0 °C, 20 °C and 40 °C. The results obtained at 0 °C indicate, that the ITSM values of the PR modified mixture increased in 3.2 and 1.6 times in comparison with AC-5

Table 4
Indirect tensile stiffness modulus and creep stiffness test results

Property	Mixture type		
	AC-10	AC-5	AC-10 + 0.75% PR
Indirect tensile stiffness modulus at (MPa)			
(a) 0 °C	10,770.5	5474.0	17,372.5
(b) 20 °C	1962.5	1465.0	1986.5
(c) 40 °C	340.5	247.8	462.8
Creep stiffness at 1 h loading at (MPa)			
(a) 40 °C	34.28	24.67	55.15
(b) 60 °C	20.75	18.42	34.62

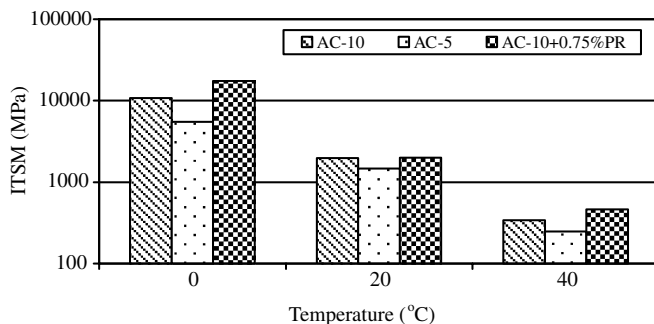


Fig. 3. ITSM values of the unmodified and PR modified asphalt mixtures.

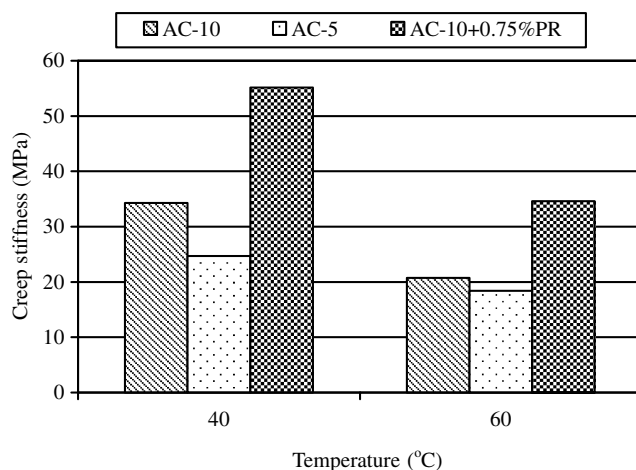


Fig. 4. Creep stiffness values of the unmodified and PR modified asphalt mixtures.

Table 5
Indirect tensile strength test results

Property	Mixture type		
	AC-10	AC-5	AC-10 + 0.75% PR
Indirect tensile strength of dry subset, ITS _{dry} (kPa)	758	489.41	806.84
Indirect tensile strength of cond. subset, ITS _{cond} (kPa)	721.07	452.87	770.53
Indirect tensile strength ratio, ITS _{cond} /ITS _{dry}	0.951	0.925	0.955

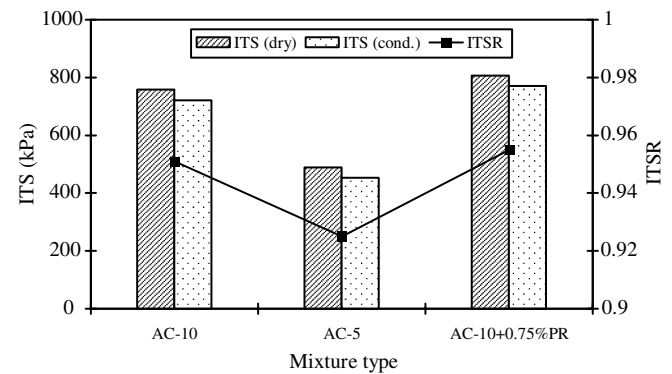


Fig. 5. ITS and ITSR values of the unmodified and PR modified asphalt mixtures.

control mixture and AC-10, respectively, but at higher temperatures the values tend to converge. Based on results shown in Table 4, Fig. 4 the creep stiffness values of the PR modified mixture were found to be higher than that of the unmodified mixtures.

4.5. Indirect tensile strength test

Table 5, Fig. 5 present the indirect tensile test results. The best results of ITS values were obtained with mixture modified by PR. The addition of PR to AC-10 mixture increased the both ITS_{dry} (in 1.6 times) and ITS_{cond} (in 1.7 times) values compared to AC-5 control mixture. The relationship between ITSR and mixtures with different binder types can be seen in Fig. 5. Mixture with PR has the maximum ITSR value (0.955).

5. Conclusions

The study evaluated the effect of PR on asphalt binders and mixtures. On the basis of the results, the following conclusions are drawn:

- The penetration, softening point and Fraass breaking point data of the AC-10 + 0.75%PR binder demonstrated the increased stiffness (hardness) and improved temperature susceptibility compared to AC-5 control asphalt binder.

- PR mixture has the highest stability and the lowest flow. A stability increase indicates that the modified mixtures are stronger than the other mixtures. The combination of high stability with low flow values and hence high MQ value indicates a high stiffness mix with a greater ability to spread the applied load and resist creep deformation.
- The results obtained at both low and high temperatures indicate, that the ITSM values of PR modified mixture higher than of AC-5 control mixture. To determine the effect of the modification on the susceptibility to rutting, the creep stiffness test was performed. As was found out from this test results, the PR modifier decreased the permanent strain of asphalt concrete mixture.
- The ITS test results denote that PR has the effect in improving a mixture's resistance to moisture damage and strength properties.

The results of this study indicate that mixture modified by 0.75% PR gives the best overall performance in the tests carried out, so that, addition of PR increases physical and mechanical properties of asphalt binders and mixtures.

References

- [1] Nicholls C. Asphalt surfacings. London: E and FN Spon; 1998. p. 68–79.
- [2] Isacson U, Lu X. Testing and appraisal of polymer modified road bitumens. In: Francken L, editor. Bituminous binders and mixes, Rilem Report 17. London: E and FN Spon; 1998. p. 13–38.
- [3] Whiteoak D. The Shell Bitumen handbook. UK: Shell Bitumen; 1991 [Chapter 10].
- [4] Airey GD. Rheological evaluation of ethylene vinyl acetate polymer modified bitumens. *Constr Build Mater* 2002;473–87.
- [5] Downes JW. Modified binders to the year 2000. In: 6th International asphalt conference, Sydney, Australia; 1986. p. 35–9.
- [6] Aglan H, Othman A, Figueroa L, Rollings R. Effect of styrene–butadiene–styrene block copolymer on fatigue crack propagation behavior of asphalt concrete mixtures. *Transportation Research Record* 1417 [Washington, DC]. TRB, National Research Council; 1993. p. 178–86.
- [7] Nolan KL, Hesp Simon AM. Low- temperature fracture toughness of polyethylene-modified asphalt binders. *Transportation Research Record* 1417. Washington, DC: TRB, National Research Council; 1994. p. 54–9.
- [8] Hall C. Polymer materials. Higher and Further Education Division, Macmillan Publishers Ltd; 1985.
- [9] Resistance to plastic flow of bituminous mixtures using the Marshall apparatus, ASTM D 1559.
- [10] Zoorob SE, Suparma LB. Laboratory design and investigation of the properties of continuously graded Asphaltic concrete containing recycled plastics aggregate replacement (Plastiphalt). *Cement Concr Compos* 2000;22:233–42.
- [11] British Standards Institution. Method for the determination of the indirect tensile stiffness modulus of bituminous mixtures. Draft for development DD-213; 1993.
- [12] British Standards Institution. Method for the determination of creep stiffness of bituminous aggregate mixtures subject to unconfined uniaxial loading, Draft for development DD-185; 1990.