



Rheological studies of asphalt modified with elastomeric polymer



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ABSTRACT

Reactive polymers, consisting of glycidyl methacrylate, produce a chemical reaction between the polymer and the asphalt binder that can be beneficial for asphalt application in hot climates. Elastomeric-modified-bitumen mixes were developed using elastomeric polymer (EMA-GMA), high density polyethylene (HDPE) and polyphosphoric acid (PPA 116%). Physical and rheological properties of modified bitumen, complex modulus ($|G^*|$), phase angle (δ), and MSCR test were analyzed. Test results of penetration, softening point and elastic recovery showed an increase of elastic behavior in modified asphalts and produced material properties suitable for application in highway construction. Based on rheological test results, it was observed that the addition of polymer can increase the range of temperature, in asphalt, to resist permanent deformation. MSCR test results characterize the modified asphalt as an elastomeric with good performance at intermediate temperatures.

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1. Introduction

An asphalt-layer's rheological properties can be altered when subjected to ambient-temperature changes, resulting in a reduction of viscosity, making the asphalt more susceptible to permanent deformation. The asphalt can also be affected by other factors such as vehicle type and high-traffic volume—one of the main factors that determines the life of the pavement—which ultimately limit durability. However, it is possible to reduce permanent deformation in asphalt by increasing the stiffness of the binder through modification of its properties with the use of polymeric materials [1].

Polymers used for asphalt modification can be grouped into three main categories: thermoplastic elastomers, plastomers, and reactive polymers. Every polymer used in modification creates a specific effect and alters properties within an asphalt mixture. Thermoplastic elastomers used to achieve good elastic properties in a modified binder, while plastomers and reactive polymers are

added to improve rigidity and reduce deformation under load [2]. Careful measures must be taken when using polymers in asphalt mixtures. It is important to consider the possibility of phase separation due to incompatibility of polymers used, separation can occur when materials are stored at high temperatures.

The functionalization of polymers has shown a promising alternative to reduce disadvantages presented by some types of polymers in modifying asphalt binders. In bitumen polymer modification, functionalization relates to the chemical addition of specific polymers to obtain specific characteristics within modified asphalt. Modified-characteristics such as: good storage stability, excellent ageing resistance, strong adhesion with aggregates, high stiffness at high temperatures and good cracking resistance at low temperatures are desired in asphalt mixes used in hot climates. Functionalization is a tool that can be used to increase the quality level of polymer-modified bitumens which will ultimately affect durability and serviceability in the future [3].

Various mixes of asphalt modified with polymer (PMB) may be obtained through functionalization; however, current investigation is mainly focused on improving compatibility of polymer modifiers with bitumen. Based on test results, reactive polymers are new polymer modifiers that, through functionalization, can be used for the development of new asphalt-modified mixes. Reactive polymers used in bitumen modification are polymers

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believed to chemically react (rather than physically mix or interact) with some components of bitumen.

Reactive polymers are not commonly used as modifiers in asphalt; however previous work has shown that glycidyl-methacrylate-based polymers have shown to chemically react with asphalt binder [4]. This reaction results in the formation of an asphalt copolymer, which causes changes in the properties of the asphalt binder—specifically those regarding temperature sensitivity. In a modified asphalt mixture, better resistance to variation in temperature can result in a mixture which is more resistant to permanent deformation. Additionally, the use of reactive polymers has not shown phase separation problems observed with in mixes using other polymers [3].

Glycidyl-methacrylate polymers (GMA) have shown to improve the storage stability and other binder properties when used as reactive polymers in asphalt binders [4,5–8].

In addition to the previously mentioned polymers, polyphosphoric acid (PPA), has already been used as a binder modifier. The polyphosphoric acid can be used together with other modifiers, like polymers, resulting in a chemical change of the binder which can result in improvement of modified asphalt. [9]. PPA has the following effects on an asphalt when used in modification: As a catalytic, it improves the softening point without changing stiffness; as a direct additive, it increases high-temperature resistivity—due to the reaction of asphaltenes and the acid—and as an accelerator, it can be used to lower amount of polymer needed in a modified mixture [10,11].

An effective way to understand the internal structure of a polymer-modified asphalt binder is through rheological study. Rheological tests measure a wide range of material properties that can be analyzed to determine a binder's fundamental characteristics. The development of property-specific polymer blends is difficult since modification causes a change in both rheological and mechanical properties of a binder [12].

Rheological properties, gathered from rheological tests, are performed under linear viscoelastic conditions (LVE). At linear viscoelastic condition, properties are measured where the relationship between stresses and strains are influenced only by temperature and loading time and not by magnitude. The LVE rheological properties of bitumen are normally presented in the form of both the complex modulus ($|G^*|$) and phase angle (δ) master curves. The $|G^*|$ is defined as the ratio of maximum (shear) stress to maximum strain when subjected to shear loading and δ is the phase difference between stress and strain in harmonic oscillation. The laboratory equipment to determine these rheological properties is the dynamic shear rheometer (DSR). The frequency sweep configuration is normally adopted to establish the response of bitumen to different loading frequencies, in terms of $|G^*|$ and δ . The mechanical response of asphalt composites is frequently modeled by computational methods [13].

The parameter G^* can be related to resistance to permanent deformation when an asphalt road is subjected to shear stress. The phase angle (δ) is a function of a viscoelastic response of the material. When a material is a pure elastic, the δ is zero degrees, and the viscoelastic response to deformation is immediate—however, when δ 90° the material behaves like a purely viscous material. The $\tan \delta$ provides an indication of balance of viscoelastic behavior. High values of G^* represent an increase in stiffness of material, while low values of δ represent improvement in elastic response [14,15]. Classification made through Superior Performance Pavement (SUPERPAVE,SHRP) emphasize the parameter $G^*/\sin \delta$, as a better criterion to determine the maximum use temperature for the binder to ensure good performance.

This paper presents an analysis of rheological properties of binder modified with polymers. Binders were modified using reactive polymer (RET), polyphosphoric acid (PPA 116%) and high density

polyethylene (HDPE). The properties analyzed through laboratory tests are: complex modulus (G^*), temperature sweep, performance grade (PG) and multiple stress creep and recovery (MSCR). Observations made on softening point, elastic recovery, penetration and rheological measurements are also included.

2. Experiment and methods

2.1. Materials

Asphalt cement, with classification PG 64-XX, from Replan refinery was used to produce laboratory modified asphalt samples. The following polymers were used for modification: Ethylene-Methyl-Acrylate-Glycidyl-Methacrylate commercially named by Polimul S74®, High-Density Polyethylene, Polimul SX500®, and Polyphosphoric Acid PPA 116% (manufactured by PRANA Petrochemical Company S.A.).

2.2. Methods

Five different asphalt samples were tested. The samples were comprised of one pure asphalt (PG 67-XX, unmodified), and four binder samples modified with 1.8%wt of S74 plus SX500 (amounts of 0.0, 0.1, 0.3 and 0.5 wt%)—each containing 0.15%wt of PPA as catalyst. The modified binders were prepared in a mechanical mixer model Fisatom 72 mixed at 500 rpm at a temperature of 170 °C.

Modified samples were prepared using 1.8 wt% of Polimul S74 mixed for a period of 1 h, Polimul SX500 was then added (0.0, 0.1, 0.3 or 0.5%wt) and mixed for 30 min and finally, PPA 116% was added and mixed for 30 min. After completion on mixing, samples were oven-cured for a period of 12 h.

Samples were labeled PA (Pure Asphalt), S74 (Polimul S74 added) and S74 SX (Polimul SX500 added follow by amount %wt).

2.3. Test methods

2.3.1. Softening point

Softening Point was performed according to ASTM D36. A steel ball on a ring filled with bitumen sample is cooled in a water bath oven with 5 °C ice water. After 15 min in water bath, the sample is heated with a heat-up rate of 5 °C/min. The temperature is recorded once the steel ball falls 25.4 mm. This temperature is recorded as the softening point of the sample.

2.3.2. Elastic recover

Elastic Recover, by ductilometer, was performed according to ASTM D6084. Specimens are pulled a 20 cm distance at a 5 cm/min rate and at a constant 25 °C temperature. Elastic recovery is the percentage of return of sample to original condition after elongation.

2.3.3. Penetration

Penetration is a depth measurement. The test is performed by vertically penetrating a needle using a 100 g weight, during a 5 s interval at a constant 25 °C temperature. Penetration is related to stiffness of the binder at ambient temperature and serves as a classification parameter for binders.

2.3.4. Rheological measurements

These oscillatory tests are performed using dynamic shear rheometers (DSR), which apply oscillating shear stresses and strains to samples of bitumen inserted between parallel plates at different loading frequencies and temperatures. Measurements of the complex shear modulus (G^*), storage modulus (G') and shear

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