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Measure of asphalt emulsions stability by oscillatory rheology

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HIGHLIGHTS

- Asphalt emulsions stability can be followed-up by a rheometry method.
- Traditional techniques are less reliable than optical and rheological ones when measuring asphalt emulsion stability.
- Asphalt emulsions must exhibit viscoelasticity in order to use our proposed method.
- Asphalt become less elastic as long as asphalt droplets coalescence takes place.

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ABSTRACT

A new methodology to monitoring an asphalt emulsion destabilization process is proposed. This method is based on the evolution of some rheological properties along time such as the viscosity, the Cross-rate constant and the elastic and viscous modulus of the emulsion. Two concentrated asphalt emulsions (70% of asphalt) have been formulated to study their stability using cationic emulsifiers. Results suggest that emulsions viscosity and consequently the Cross-rate constant decrease over time. The rheological behavior of emulsions evolves from shear-thinning to Newtonian as coalescence takes place. Coalescence was verified by the measure of the droplets size distribution against time using a laser light scattering equipment. This parameter evolves during time and reaches values of about 400 and 900% of increase in the emulsions studied. The elastic and viscous modulus of the emulsions tend also to decrease as long as coalescence occurs and were followed-up in time. In our systems, a drop of about 90% has been calculated as soon as emulsions become unstable. Results of this methodology were compared to those of traditional methods used in industry. Finally, the applicability of this test is conditioned to viscoelastic asphalt emulsions. The minimal requirements of asphalt content were found for one of the emulsions. However, the viscoelasticity of the testing emulsion must be the first parameter to be checked out, and this factor depends on many formulation parameters.

1. Introduction

The technology of asphalt emulsions is today a very useful tool that is being applied in the majority of applications where the use of asphalt is required. Although this technology needs a good understanding of the involved physical and chemical phenomena for an efficient application, its use is increasing due to the many benefits it offers over traditional techniques. Advantages are in terms of energy saving, reduced environmental impact and durability of the final product [1]. Asphalt emulsions are easy to handle because of its low viscosity compared to the original asphalt. Nowadays they are essential for the construction of roads. Some techniques such as slurry seal and microsurfacing (among many others), have been developed based on these types of emulsions. On the other hand, other techniques have been improved [2], such as primes, surface treatments, soil stabilization, asphalt mixtures in general, etc.

For the characterization of asphalt emulsions, it is essential to evaluate their quality and according to some tests, one can establish if the emulsion can be used for a given application. Among the most important parameters to evaluate are the viscosity, the type of emulsion, the emulsion grade (slow, medium or rapid setting) and its stability.

The stability of an emulsion can be characterized by a constant behavior of its fundamental parameters over time, namely, the dispersity and the uniform distribution of the disperse droplets [3]. These are actually some of the most important characteristics evaluated in asphalt emulsion and can be related to its storage capacity. It is important to distinguish stability and do not confuse it

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with the grade of the emulsion. Last parameter evaluates the ability of the emulsion to break when brought into contact with a solid aggregate. That is, the grade of an asphalt emulsion assesses whether this is suitable for use in an asphalt mixture, a primer irrigation, etc.

Generally, the stability of emulsions is quite difficult to measure, it is often evaluated with respect to some kinetic criterion, such as flocculation, creaming, or partial phase separation [4]. In order to evaluate this parameter, some tests have been developed such as the measurement of phase separation or the evolution of droplets size in time. In the case of asphalt emulsions, stability can be evaluated through traditional standard test methods ASTM D6930 (Settlement and Storage Stability of Emulsified Asphalts) and ASTM D6933, (Oversized Particles in Emulsified Asphalts). In the first standard, the ability of an emulsified asphalt to remain as an uniform dispersion during storage is evaluated [5]. The asphalt content of the emulsion at the bottom and the top of a standard cylinder is compared. Many agencies will accept the 24-h test, while others require a five-day test [2]. This test provides a measure of settlement. Thus, if the emulsion is unstable, an important difference between the asphalt content of the top and bottom is obtained.

In the second ASTM test, the degree to which an emulsified asphalt may contain particles of asphalt or other discreet solids retained on a 850-μm mesh sieve is evaluated [6]. The retention of an excessive amount of asphalt particles on the sieve indicates that problems may occur in the handling and application of the material [2].

Recently, Wang et al. studied the stability of asphalt emulsion by laser diffraction [7]. They measured the particle size variations of asphalt emulsions under stress conditions to evaluate their storage stability. This is a good example of how modern techniques can provide more useful information about the stability of asphalt emulsions than traditional techniques. In fact, other modern techniques have been used to characterize asphalt emulsion, such as atomic force microscopy [8], microelectrophoresis [9] and other imaging techniques summarized in the work of Martinez-Valverde et al. [10]. Otherwise, rheology is a very important tool used currently for the characterization of many industrial products, including emulsions. Rheology can provide important information about the deformation of the emulsion when it is subjected to shear stress. Its response depends on many parameters such as the internal phase content, the droplet size distribution, the viscosity of the phases, etc. [11]. In this sense, very important information, related to the emulsion granulometry can be obtained from its rheological behavior.

Viscosity is a very important parameter in the asphalt industry. This is why rheology is often used to characterize asphalts. Some rheological parameters can be related to the asphalt binder microstructure [12]. Different studies have been performed to evaluate the effect of polymer modification on asphalt using rheology as the main tool to track these changes [13–16]. Moreover, rheology has also been used to characterize residues of asphalt emulsions [17], aged asphalts [18] and emulsions in general.

The rheological behavior of concentrated bitumen in water emulsions has been studied by Nuñez et al. [19]. They studied the effect of the concentration of bitumen and droplet size distribution in the rheological properties of asphalt emulsions. In addition, they also evaluated the impact of changes in these parameters in transport processes. Another very important study was performed by Romero et al. [20]. They studied the influence of bitumen concentration, presence of electrolytes, mean droplet diameter and size distribution, and storage temperature on the dynamic shear rheology of emulsions stabilized using non-ionic surfactants. Their findings showed that emulsions exhibit a viscoelastic behavior when the bitumen concentration increased above 60% (v/v) and also exhibited an increase in the shear modulus when the mean droplet diameter decreased (at a constant volume fraction of bitumen), or when the bitumen volume fraction increased at a constant mean droplet diameter. According to these results, the stability of an asphalt emulsion could be determined by oscillatory rheology as long as the emulsion exhibits viscoelasticity.

The aim of this work is to develop a simple rheological method for estimating the stability of asphalt emulsions. This is intended to do from oscillatory tests (also known as mechanical vibrational spectroscopy), and using a rheometer commonly available in the asphalt industry. Finally, this study aims to provide the necessary conditions to apply this method and get accurate and reliable data.

2. Experimental procedures

2.1. Materials

Asphalt from Barrancabermeja refinery (Colombia) was used as disperse phase for emulsion fabrication, a general characterization is reported in Table 1. Asfier-100 and Emulsamine-540 provided by Quimikao and CECA-Arkema were used as emulsifiers to fabricate emulsions A and emulsion B respectively.

Asfier-100 is a cationic fatty diamine mixture used as emulsifier for the production of rapid and medium setting emulsions used in some applications such as chip seal and cold recycling mixtures; some properties are described in Table 2. On the other hand, Emulsamine 540 is a fatty amine mixture used as emulsifier for the production of rapid setting emulsions for surface dressing and tack coat based on pure and polymer modified bitumen; some properties are presented in Table 2. Hydrochloric acid (37%) from Merck and distilled water (electrical conductivity of 6,92 μS/cm) were used to prepare all aqueous acid emulsifier solutions.

2.2. Emulsification process

A colloid mill, model CVERP-50 and fabricated by Alcasa Molinos Coloidales (Argentine) was used to prepare asphalt emulsions. Some formulation parameters such as emulsifier concentration and weight Water-Oil Ratio (WOR) were set according to some preliminary results. Emulsions formulation was intended to obtain sufficient stable emulsions exhibiting main droplets sizes smaller than 8 μm. Other desired properties for testing emulsions were less than 1% and 0,1% for ASTM D6930 and D6933 test respectively. An initial WOR of 30/70 was established in order to prepare all asphalt emulsions. According to the preliminary results, this ratio let us to obtain small droplets and sufficient stable emulsions for further studies. Lastly, two emulsions were prepared using two different emulsifiers (Asfier-100 and Emulsamine-540). In emulsion A, Asfier-100 concentration in aqueous phase (soap water) was set to 10 g/L. In emulsion B, Emulsamine-540 concentration was set to 65 g/L. In all cases, soap water pH was fixed to 2,0 (before emulsification process). Acid pH values were obtained by addition of hydrochloric acid (1N) during the preparation of the surfactant solutions. pH was measured using a Hanna Instruments pH meter (model HI-221-01). The asphalt and the soap solution were fed to the mill at 140 °C and 40 °C respectively. The mill temperature was set to 90 °C, the input power to 60% and the emulsification process was conducted during 3 min. The emulsification process was followed by several characterizations, see Fig. 1.

2.3. Emulsion storage and sampling

Once emulsions are prepared, they are collected in a 500-ml glass recipient. After emulsions reach atmospheric temperature, they are stored at 20 °C into a fridge. Before sampling (days 10, 20, etc.), 24 h before its rheological and stability characterization, emulsions are softly stirred using a glass rod, e.g. the reported settlement data and rheological characterization for a given emulsion on day 30, means that it was softly stirred 24 h before (day 29). This procedure is necessary in order to homogenize emulsions before tests and to avoid creamed emulsion sampling. It is important to emphasize that emulsions must be stirred very softly,

Table 1
Asphalt properties.

Property	ASTM Test	Value
Penetration	D-5	60,2 ± 0,1 (0,1 mm)
Soft point	D-36	50,0 ± 0,1 °C
Viscosity	D-2171	342 ± 1 cP at 140 °C