Evolution of the rheological behavior of asphalt emulsions

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ABSTRACT

It has been more than a century since asphalt emulsions appeared in the market; nevertheless, in Mexico its use has decreased due to the lack of knowledge, standards and regulation. Nowadays emulsions are classified according to their breaking index; however, a direct relation between the breaking index and the breaking process in field has not been found. On this basis, in this research we present a new approach to study the breaking process and measure the required breaking time of asphalt emulsions. We studied the breaking process of emulsions using rheological measurements. Three different emulsions were studied: ECL60-90P, ECL60-90PL (Emulsion modified by adding SB in latex) and ECL60-90PS (Modified asphalt with SB was emulsified). Silicon-rubber recipients were fabricated in order to contain emulsion samples. These samples were subjected to a controlled curing at three different temperatures (30, 40 and 50°C) during 10 days for each temperature. Each day a frequency sweep test was performed at three different temperatures (30, 40 and 50°C) in order to obtain a Master Curve for each day. We have found that the development of the dynamic modulus for the studied emulsions presents a similar behavior and can be adjusted to a logarithmic equation. These results suggest that it may be possible to measure the breaking time of asphaltic emulsions by means of rheological measurements.

Keywords: Emulsions, Rheology

1. INTRODUCTION

Emulsions are defined as "*An heterogeneous system of two or more liquids consisting in a continuous liquid phase and at least a second phase dispersed as small droplets within the first phase*"[1]. Two immiscible liquids are meant to be apart, so emulsions are thermodynamically unstable and kinetically not labile systems. This is, they are not in equilibrium, but, they do not present significant changes through long periods of time (some of them for decades) [2, 3]. The stability of emulsions is well known to be explained by the DLVO theory, which considers that the electrostatic attraction and repulsion interactions between micelles are in equilibrium [2, 4-6]. When this equilibrium is lost, the breaking process of the emulsion starts. The breaking process involves different phenomena occurring simultaneously or separately such as creaming, sedimentation, flocculation, phase inversion, coalescence and Ostwald ripening [4]. Nowadays, bitumen emulsions are classified as rapid, medium, slow, quick or super stable setting, depending on how fast they break [7]. This breaking process is poorly characterized in quality control laboratories by performing demulsibility and breaking index tests [8-11]. Nevertheless, no direct relationship between results obtained by this tests and the actual on-site behavior has been found yet. This lack of understanding and accuracy in predicting the breaking time of bitumen emulsions causes delays in the construction of cold mix layers. The rheological behavior of emulsions is highly dependent of its concentration and flocculation rate, therefore the rheological behavior of an emulsion is deeply related to its stability [3]. Different methods for studying this rheological behavior have been developed *i.e.* deformation, temperature, stress and frequency sweeps. The objective of these tests is the deconvolution of the complex modulus (G*) into the storage (G') and the loss (G'') modulus in order to analyze both, the viscous and the elastic contributions of viscoelastic materials. Among the mentioned tests, frequency sweep is used to study emulsions stability [12]. If a frequency sweep test is performed to a stable emulsion, a clear relationship will be observed: G' < G''. When this test is performed to an emulsion whose breaking process has started, G' < G'' will be true for low frequencies, nevertheless, as the frequency increases, there will be a point (gel point) where G' = G''. This point is called the crossover or gel point, after this the relationship between G' and G'' will invert and become G' > G'' [3, 13-15]. In recent years, researchers have studied the breaking process of bitumen emulsions using different methods, *i.e.* optic measures of bitumen emulsion droplets [16], dynamic modulus of cold asphalt mixes [17], laser beam diffraction [18], thermogravimetric analysis [19], electrokinetic techniques [20], viscosity tests [21] and weight loss [22], among others. As observed in the literature, there is an increasing need of new methods that are capable of determining accurately the breaking speed of bituminous emulsions.

2. EXPERIMENTAL SECTION

2.1 Materials

Three slow setting bituminous emulsions were analyzed; all of them were fabricated using the same kind of bitumen obtained from Salina Cruz, Oaxaca refinery. Two of these emulsions were modified using styrene-butadiene (SB) copolymer; in one of them the bitumen was modified prior the emulsification process (ECL60-90PS), to the other one SB was added in latex to the emulsified bitumen (ECL60-90PL). The third emulsion was produced with virgin bitumen (ECL60-90P). The three emulsions were formulated and produced by SemMaterials México®.

Silicon rubber molds were manufactured with circular cavities of approximately 25mm diameter and 1.5 mm depth in order to contain the emulsion samples.

A Digitherm DT2-MP incubator was used to cure the bitumen emulsion samples and a TA Instruments AR550 rheometer was used to test them.

2.2 Methods

Thirty samples of approximately 2.3g of each bituminous emulsion were carefully poured to avoid the formation of air voids into the silicon rubber mold cavities, then subjected to a ten days curing process at a controlled temperature of 30°C inside the incubator. During this curing process, three samples were taken each day for testing them in the rheometer. The three samples were subjected to a frequency sweep of 0.01 to 40Hz with a controlled strain of 0.01% using parallel plates of 25mm diameter. The first sample was tested at 30°C, the second one at 40°C and the last one at 50°C. This methodology was repeated for the three emulsions for curing temperatures of 40 and 50°C.

3. RESULTS AND DISCUSSION

With the obtained data, a master curve was constructed for each day for each emulsion for each curing temperature. Figure 1 shows the curves graphed for the curing temperature of 30°C exhibit an abrupt increment in the values of |G*| for the first days of the curing process. As the curing process advances, the values of |G*| tend to remain the same. For the curing temperatures of 40°C and 50°C the |G*| values show no significant change and the master curves appear overlapped, meaning that the increment in |G*| values observed for the 30°C curing time occurs within the first 24 hours of the process.

natural

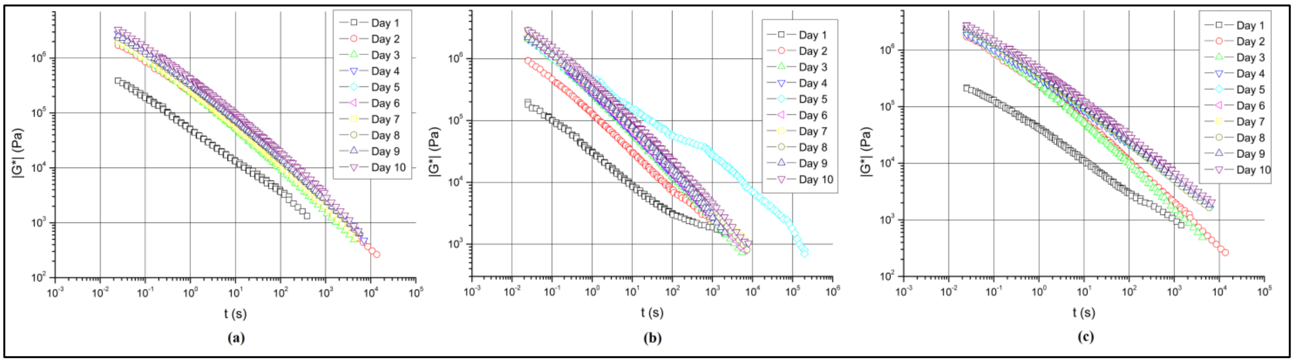
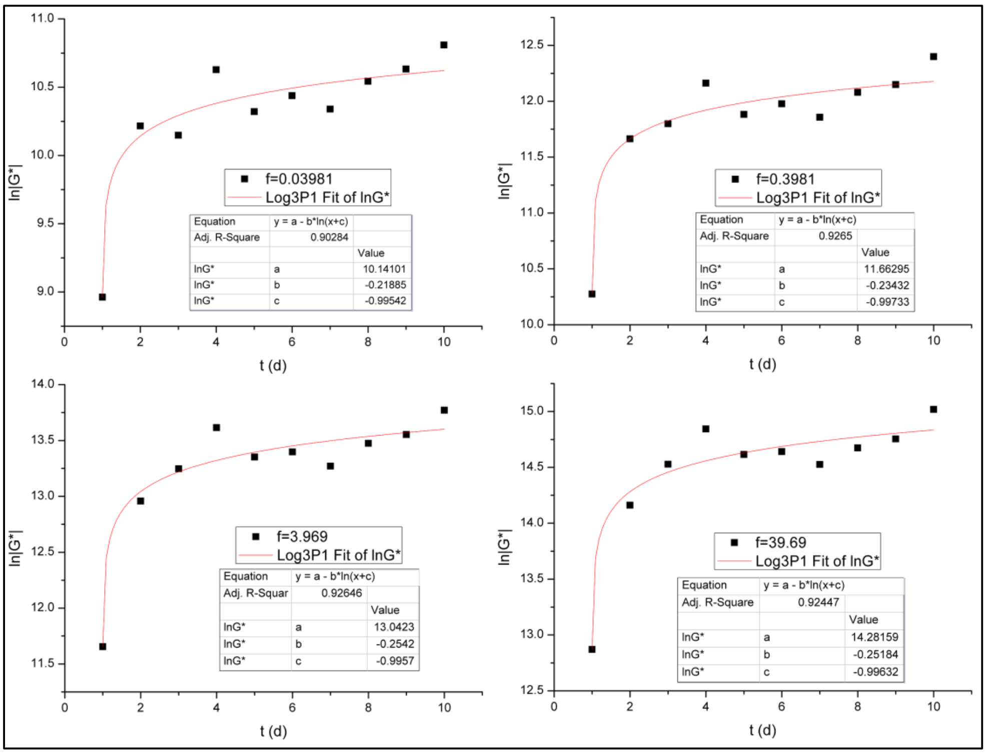


Figure 1: Master curves for bituminous emulsions (a) ECL60-90P (b) ECL60-90PL (c) ECL60-90PS for curing temperature of 30°C

Four frequencies were selected (0.03981, 0.3981, 3.969 and 39.69Hz) and plots of the natural logarithm of $|G^*|$ ($ln|G^*|$) *vs* curing time (t_{curing}) were constructed in order to observe the evolution of |G*| through the breaking process and adjust it to an empirical model. In Figure 2 we can observe results of $ln|G^*|$ *vs* t_{curing} for the bituminous emulsion ECL60-90P subjected to a curing temperature of 30°C. A rapid increment in the values of $ln|G^*|$ for the first four to five days is evident. This behavior is also noticeable in the master curves shown in Figure 1. Also, as observed in the master curves, after the fifth day of the curing process, the values of $ln|G^*|$ exhibit no significant variation. This kind of behavior was also observed in the curves obtained for bituminous emulsions ECL60-90PS (Figure 3) and ECL 60-90PL (Figure 4). This abrupt increase in the values of $|G^*|$ for the first days of the curing process is thought to be caused by the flocculation of bitumen globules, and the fact that the $|lnG^*|$ values remain without changes may be caused by the breaking of bitumen globules, which generates a continuum bitumen phase developing finally in the complete breaking of the emulsion. Plots of *G'* and *G''* *vs* *t* were also constructed in order to observe the appearance of the gel point, this graphs confirmed the behavior observed in the master curves and in the $ln|G^*|$ *vs* t_{curing} graphs, since the appearance of the gel point concurs with the change of the slope of the $ln|G^*|$ and the overlapping of the master curves. For temperatures of 40 and 50°C the values of $ln|G^*|$ remained with no changes, implying that the interval of analysis was not adequate to observe the evolution of the rheological process throughout the breaking process.
The evolution of $ln|G^*|$ for the three emulsions for the curing temperature of 30°C was adjusted with a good correlation ($R^2 \approx 1$) to the empirical model:

$$\ln|G^*| = \ln\left|G^*_{final}\right| - b\ln(t_{curing} + c)$$

Comparing the results of the values obtained for variables *b* and *c* for the three emulsions we can observe that they do not present significant variation when changing the analyzed frequency, so it is possible to infer that these variables are dependent of the type of emulsion and the curing temperature.



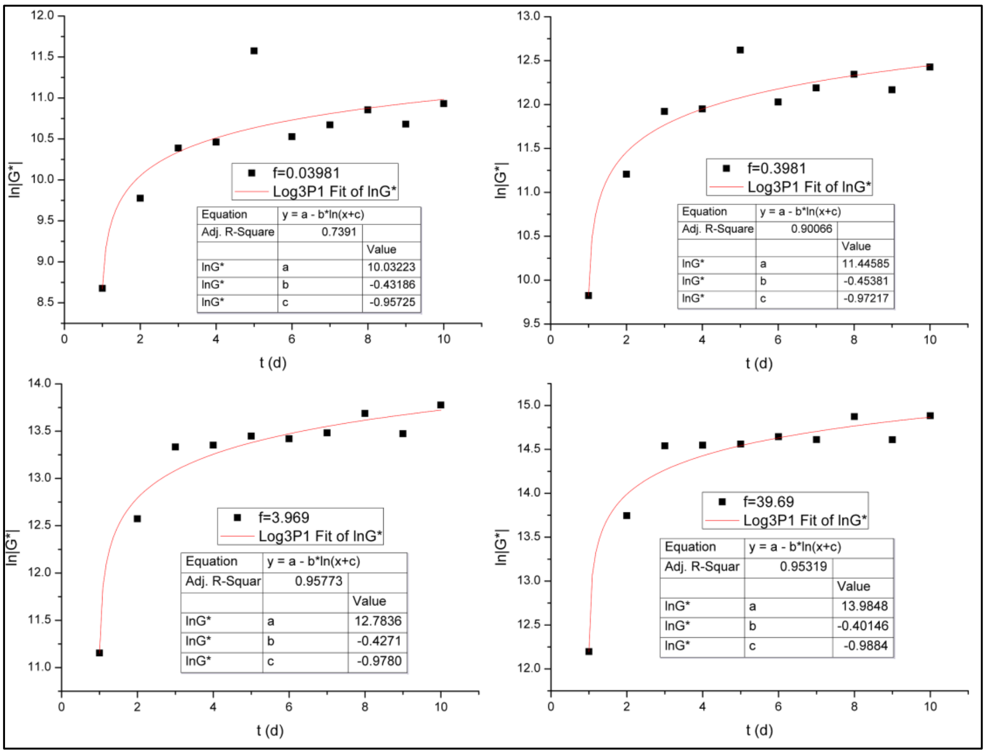
Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.90284	
		Value
lnG*	a	10.14101
lnG*	b	-0.21885
lnG*	c	-0.99542

Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.9265	
		Value
lnG*	a	11.66295
lnG*	b	-0.23432
lnG*	c	-0.99733

Equation	y = a - b*ln(x+c)	
Adj. R-Squar	0.92646	
		Value
lnG*	a	13.0423
lnG*	b	-0.2542
lnG*	c	-0.9957

Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.92447	
		Value
lnG*	a	14.28159
lnG*	b	-0.25184
lnG*	c	-0.99632

Figure 2 $ln|G^*|$ vs t_{curing} for ECL60-90P



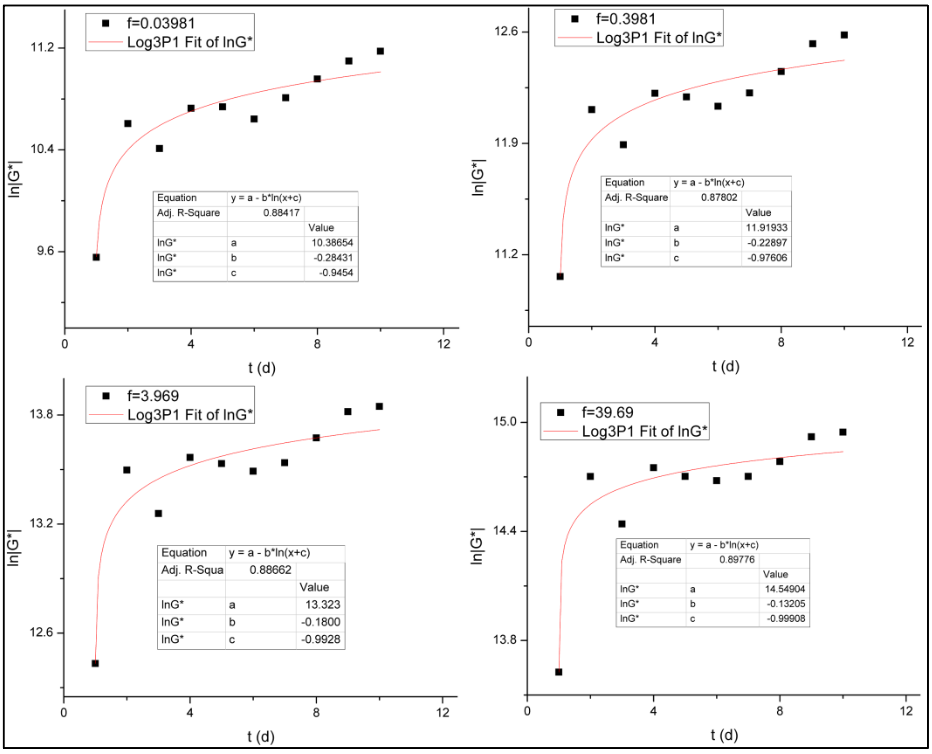
Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.7391	
		Value
lnG*	a	10.03223
lnG*	b	-0.43186
lnG*	c	-0.95725

Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.90066	
		Value
lnG*	a	11.44585
lnG*	b	-0.45381
lnG*	c	-0.97217

Equation	y = a - b*ln(x+c)	
Adj. R-Squar	0.95773	
		Value
lnG*	a	12.7836
lnG*	b	-0.4271
lnG*	c	-0.9780

Equation	y = a - b*ln(x+c)	
Adj. R-Squar	0.95319	
		Value
lnG*	a	13.9848
lnG*	b	-0.40146
lnG*	c	-0.9884

Figure 3 $ln|G^*|$ vs t_{curing} for ECL60-90PL



Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.88417	
		Value
lnG*	a	10.38654
lnG*	b	-0.28431
lnG*	c	-0.9454

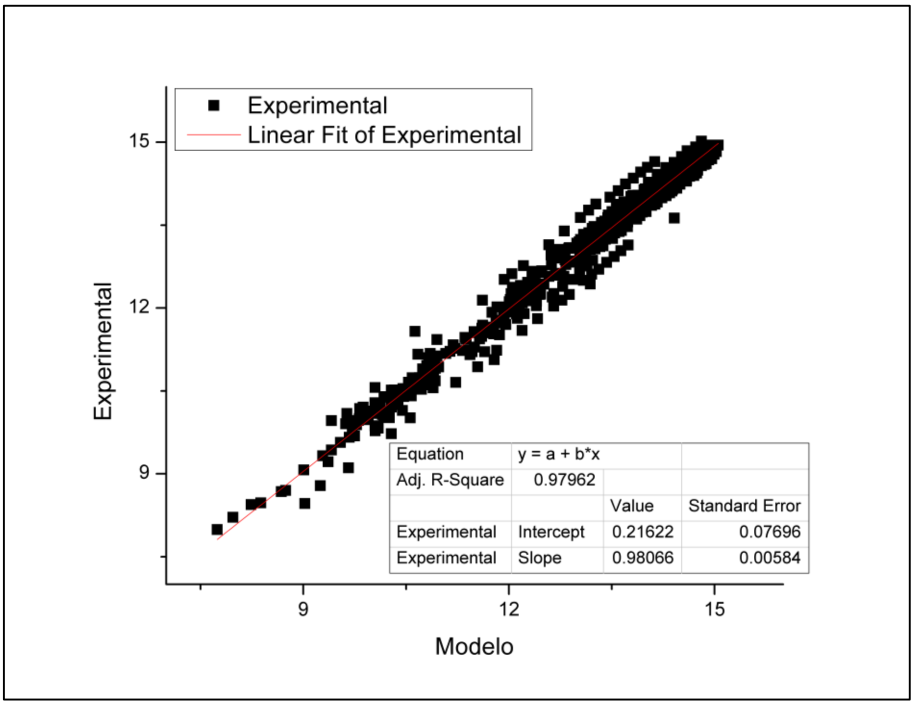
Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.87802	
		Value
lnG*	a	11.91933
lnG*	b	-0.22897
lnG*	c	-0.97606

Equation	y = a - b*ln(x+c)	
Adj. R-Squa	0.88662	
		Value
lnG*	a	13.323
lnG*	b	-0.1800
lnG*	c	-0.9928

Equation	y = a - b*ln(x+c)	
Adj. R-Square	0.89776	
		Value
lnG*	a	14.54904
lnG*	b	-0.13205
lnG*	c	-0.99908

Figure 4 *ln*|*G| *vs* t_{curing} for ECL60-90P**

In order to give the empirical model an initial validation, values of *ln*|*G**| were calculated and compared to those values obtained experimentally (Figure 5). A linear relationship was observed (R^2=0.9796, slope=0.9806, intersection=0.2162).



Equation	y = a + b*x		
Adj. R-Square	0.97962		
		Value	Standard Error
Experimental	Intercept	0.21622	0.07696
Experimental	Slope	0.98066	0.00584

Figure 5 Experimental vs model data

4. CONCLUSIONS

It was possible to construct master curves from the frequency sweeps and there exists an agreement between the three different type of plots observed. Results found in this research suggest that it is possible to use a predictive model to determine the curing time necessary for the use of bituminous emulsions. In order to validate the empirical model presented in this paper, further research is needed in order to study the effect of the addition of additives, other polymers, emulsifiers, among other factors. Also, it will be interesting and of vital importance, to conduct a study with shorter sampling periods, in order to focus in the first stage of the breaking process. Nevertheless the results are encouraging to continue with this research line.

5. ACKNOWLEDGEMENTS

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