Viscosity properties of bimodal bitumen emulsions: new approach

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Propiedades de viscosidad de emulsiones bimodales de betún: nueva aproximación

Propietats de viscositat d'emulsions bimodals de betum: nova aproximació

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SUMMARY

The emulsions used in the manufacture of half warm asphat should contain very little water in their formulation. Conventional monomodal emulsions have a maximum dispersed phase concentration, φ, of 0.69. Recent research in this field is focused on the development of concentrated emulsions, φ = 0.70-0.74, or highly concentrated emulsions, φ >0.74. The concentrated or highly concentrated emulsions have little water in their formulation, <30%, but consequently have very high viscosities. This article summarizes the main conclusions related with the design, formulation and viscosity of bimodal concentrated bitumen emulsions. To formulate a bimodal emulsion is necessary to firstly manufacture two monomodal emulsion with a controlled drop size distribution from 1 and 5 μm respectively. These emulsions should be prepared with a system able to control the final drop size. In this study we have used the HIPR (High Internal Phase Ratio) procedure. The emulsions formulated in this paper are characterized by having viscosities up to ten times lower than their small monomodal size counterparts.

Keywords: Warm mix asphalt; bimodal bitumen emulsions; decrease viscosity; particle size distribution.

RESUMEN

Las emulsiones usadas en la fabricación de mezclas asfálticas templadas deberían contener baja cantidad de agua en su formulación. Las emulsiones monomodales convencionales tienen una concentración de la fase dispersa, ϕ, máxima de 0,69. La investigación reciente en este campo se centra en el desarrollo de emulsiones concentradas, ϕ = 0,70-0,74, o emulsiones altamente concentradas, ϕ >0,74. Las emulsiones concentradas o altamente concentradas tienen poca agua en su formulación, <30%, pero consecuentemente tienen alta viscosidad. Este artículo resume las principales conclusiones relacionadas con el diseño, formulación y viscosidad de emulsiones bimodales concentradas de betún. Para formular una emulsión bimodal es necesario primero fabricar dos emulsiones monomodales con una distribución de tamaño de gota de 1 y 5 μm, respectivamente. Estas emulsiones deberían prepararse con un sistema capaz de controlar el tamaño de gota final. En este estudio, se utiliza el proceso HIPR (del inglés High Internal Phase Ratio, ratio de fase interno alto). Las emulsiones formuladas en este artículo se caracterizan por tener viscosidades hasta diez veces menor que sus homologas monomodales de tamaño de gota pequeño.

Palabras clave: mezclas asfálticas templadas; emulsiones bimodales de betún; reducción de viscosidad; distribución de tamaño de partícula

RESUM

Les emulsions utilitzades en la fabricació de mescles asfàltiques temperades haurien de tenir baixa quantitat d'aigua a la seva formulació. Les emulsions monomodals convencionals tenen una concentració de la fase dispersa, ϕ, màxima de 0,69. La recerca recent en aquest camp es centra en el desenvolupament d'emulsions concentrades, ϕ = 0,70-0,74, o emulsions altament concentrades, ϕ >0,74. Les emulsions concentrades o altament concentrades tenen poca aigua en la seva formulació, <30%, però conseqüentment tenen alta viscositat. Aquest article resumeix les principals

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conclusions relacionades amb la mida, formulació i viscositat d'emulsions bimodals concentrades de betum. Per formular una emulsió bimodal és necessari primer fabricar dues emulsions monomodals amb una distribució de mida de gota d'1 i 5 µm, respectivament. Aquestes emulsions haurien de preparar-se amb un sistema capaç de controlar la mida de gota final. En aquest estudi, s'utilitza el procés HIPR (de l'anglès High Internal Phase Ratio, rati de fase intern alt). Les emulsions formulades en aquest article es caracteritzen per tenir viscositats fins a deu vegades menors que les homologues monomodals de mida de gota petita.

Mots clau: Mezclas asfàltiques temperades; emulsions bimodals de betum; reducció de viscositat; distribució de mida de partícula.

INTRODUCTION

Bitumens are the most versatile, practical and manageable materials used in road construction. They are cohesive, waterproof, flexible and ductile materials which properties change primarily by the action of temperature and rate of the applied loads. These properties make them materials difficult to replace in road construction field. But as shown in Figure 1, their main handicap to use them is its high viscosity. This could be, depending on the bitumen penetration grade, between 1000 mPa·s and 20000 mPa·s at 100 °C[1,2].

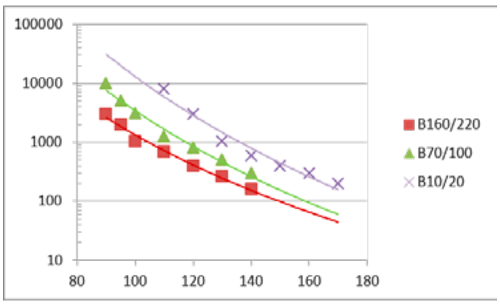

Figure 1. *Viscosity in front of temperature for three different bitumen [1].r*

Bitumen emulsions are undoubtedly the most economical, less polluting and lower energy consumption way that exists to apply bitumen in a road pavement[3]. However, nowadays the consumption of bitumen is well above the consumption of emulsions in road industry (Figure 2). The application of bitumen emulsions is focused on cold techniques, surface dressing and tack coating[4].

Currently, the emulsions are mostly produced colloid mills. The hot bitumen, at about 140 °C, is added for a very short time through a small opening, less than 1 mm, and a high shear, approximately 5000 rpm, with the aqueous phase carrying the emulsifier[5]. With this system bitumen emulsions of high quality are obtained; nevertheless the resulting emulsions have a rather wide particle size distribution curve, from 3 to 6 microns, and also the maximum concentra[illegible][6-8].

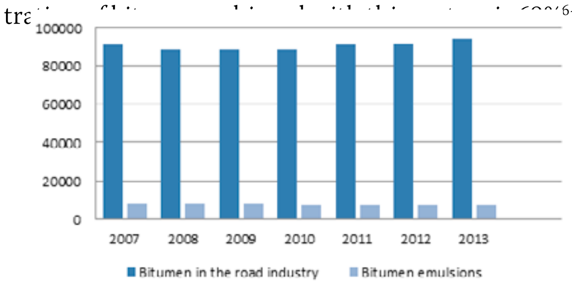

Figure 2. *World consumption of bitumen in the road industry vs. bitumen emulsions consumption[4].*

Therefore, if concentrated emulsions, 70-95%, need to be produced, a different manufacturing system from the typical colloid mill should be used. The method used for preparation of concentrated emulsions is the procedure known as HIPR[8,9]. This method requires the initial dispersion be carried out to internal phase fractions above the critical packing. This facilitates the formation of emulsions with a narrow drop diameter distribution. According to this method, emulsions with controlled final morphology can be produced[10].

To increase the consumption of emulsions in asphalt roads, emulsions with specific viscosity behaviour should be formulated[11]. In other to adapt the use of emulsion in the manufacture of warm mix asphalt the emulsions should contain minimum quantity of water possible, that is, they should have high bitumen concentration, but as the concentration of residual bitumen is increased the viscosity increases exponentially, so we need emulsions with high bitumen content but with low viscosity, that is, emulsions with special rheological behaviour and this is achieved using bimodal emulsions.

Bimodal emulsions are characterized by having two different and controlled droplet size and distribution. The optimal formulation contain a first small size of about 1 µm and a second size of about 5 µm with a proportion of 1/3 respectively. The decrease in viscosity that can be observed in bimodal emulsions when compared to their equivalents monomodal emulsions can be attributed to the packing of the emulsions droplets. In bimodal emulsions droplets try to place themselves in the empty voids of the cubic matrix generated by the distribution of the large droplets (Figure 3)[12,13].

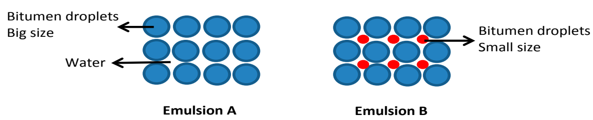

Figure 3. *Schematic representation of a monomodal emulsion (left) and a bimodal emulsion (right).*

MATERIALS AND METHODS

Materials

The bitumen used was a 50/70 bitumen Pen, with a penetration of 62 x 0.1 mm, a softening point of

51.2 °C, and a viscosity (100 °C) of 4800 mPa·s. The bitumen chemical composition was 4.80% saturated, 45.29% aromatics, 31.30% resins, and 16.53% asphaltenes. The surfactant used for it formulation was an alkyl propylene diamine from long chain, N-Tallow-1,3-propyldiamine, activated at 50°C.The emulsions were formulated using tap water and adjusting their pH to 2-2.5.

The helix used is a turbine stirring rod with a helix diameter of 660 mm; with this helix the mixing material is suctioned from above and in the container an axial stream and a low shear force are generated, therefore, it is used for medium and high speeds

Analytical techniques

The emulsion average droplet size was measured with a laser diffractometer Malvern Mastersizer 2000. The results shown in this paper correspond to the average obtained from a single sample measured in triplicate. Viscosity was measured with a rotational viscosimeter model DV2T. The viscosimeter has a precision ±1.0% and a repetitivity ±0.2%.

Emulsion preparation

The High Internal Phase Ratio (HIPR) procedure was used for emulsion preparation[20]. This procedure requires the initial dispersion to be carried out at a packing fraction higher than critical, which corresponds to 0.74.This facilitates the formation of concentrated emulsions with a very narrow distribution of drop size, and small mean droplet diameter, d(0.5). According to this procedure, emulsions with a controlled final morphology can be manufactured.

The HIPR procedure is base in the following criteria:

- The emulsion is produced in an initial volume fraction, ø, 0.75 to 0.95. The volume fraction is the proportion of the bitumen respect the volume of surfactant, N-Tallow-1,3-propyldiamine diluted in water at pH=2±0.5 used in the manufacture of the emulsion.
- A high viscosity for the dispersed phase (bitumen) is used, 1-5000 Pa·s.
- The mixing rotational speed is low, 800-1200 rpm, working in laminar regime.
- The addition of the aqueous phase to the oily phase is performed adding the entire amount of water at once, with the helix stopped, and then the mixing process starts.

The emulsion obtained in the first few seconds is a phase inversion emulsion (W/O) changes very quickly to a direct emulsion (O/W) when in contact with the aqueous phase.Phase inversion is a process in which an emulsion changes its morphology from water-in-oil (W/O) to oil-in-water (O/W), or vice versa. If the emulsification process occurs correctly there should not be free surfactant remaining in the final product:

- The emulsion is obtained in a few seconds.
- Once the emulsion is formed, a viscoelastic paste, which is diluted in water to obtain the desired relationship bitumen/water, is obtained.
- The emulsions should be stored at the required temperature, 40-60°C.

The procedure to prepare the emulsions was the following: The necessary quantity of bitumen 50/70 Pen was heated up at 100°C±2°C. An aqueous solution of the surfactant to be used was prepared at different concentrations against bitumen, 1000-6000 ppm, pH was adjusted at 2±0.5 and was heated up to 40-50°C. The warm solution is added to the hot bituminous solution and is mixed between 1 to 15 min at 800-1300 rpm. Finally, the obtained emulsion is diluted adding warm water a(40-50°C) until a pH2±0.5 under gentle agitation to achieve the desired bituminous concentration. The obtained bitumen is stored at a temperature that ensures the adequate pumping and workability viscosity of the emulsion, but lower than 80°C in order to avoid boiling and breaking of the emulsion; therefore, the adequate storing temperature is between 40°C and 60°C.

RESULTS AND DISCUSSION

Bimodal emulsions droplet size distribution

To prepare bimodal emulsions it is necessary to manufacture first two monomodal emulsions with very controlled droplet size. This will require producing the emulsion with different ratios of initial dispersed phase volume fraction to control the size of final droplet. The monomodal emulsions were prepared according to Table 3 using an aqueous solution of long chain alkyl propylenediamine surfactant at a concentration of 10000 ppm on bitumen to obtain the emulsion with small average droplet size, hereinafter $d(0.5)_s$, and another one of large size, onwards $d(0.5)_l$. Once emulsions were obtained with the desired droplet size, they were diluted with water to give concentrations of 60, 70 and 80% wt./wt. It is important to highline we prepare six different emulsions, each one was manufactured at each corresponding bitumen ratio and diluted in water until the finial emulsion concentration desired, each sample is independent.

Table 3. *Droplet size and viscosity of the prepared emulsions*

Emulsion	Bitumen/Water [wt./wt.]	d(0.5) [μm]	Bitumen fraction	ν(50 rpm and 50 °C) [mPa·s]
1	60/40	0.811	95/5	270
2	60/40	4.042	85/15	36
3	70/30	1.134	95/5	12000
4	70/30	5.224	85/15	1850
5	80/20	0.763	95/5	*4340
6	80/20	8.864	85/15	*2360

*Measured with bitumen spindel 27 at 80°C

Table 4. *Viscosity of bimodal emulsions obtained using different emulsion fractions*

Emulsion	Ratio $d(0.5)_s$	Ratio $d(0.5)_l$	ν(50 rpm and 50 °C) [mPa·s]
A	1	0	12000
B	2	1	8000
C	3	1	6500
D	1	1	1200
E	1	2	283
F	1	3	800
G	0	1	1850

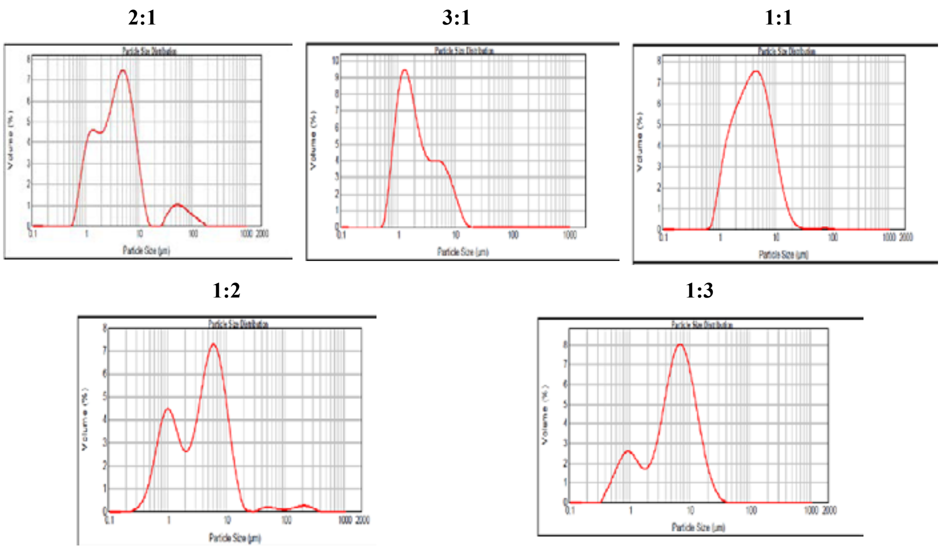

Figure 4 *Bimodal emulsions particle size distribution*

Different proportion of emulsions 3 and 4, with a concentration of residual bitumen of 70% and a small size droplet of approximately 1 µm and large one next to 5 µm, were mixed to get a bimodal emulsion (Table 4) in order to obtain the best emulsion mix ratio as function of viscosity decrease.Table 4 shows that there is a direct relationship between the proportion of each of the emulsions used and the viscosity of the bimodal final emulsion. As the proportion of large size emulsion d $(0.5)_l$ increases, the viscosity of the mix decreases. The viscosity of the emulsion A (small droplet size) is 12000 mPa·s, while the viscosity of the emulsion G (large droplet size) is 1850 mPa·s. When small and large droplet size emulsions are equitable mixed (emulsion D), the viscosity is decreased down to 1200 mPa·s. We have mixed the large and small droplet size emulsion in different proportions and the lowest viscosity is reached when the large droplet size is mixed with the small droplet size at a proportion of (1:2). The granulometric analysis of the different bimodal emulsions is presented in Figure 4.

Viscosity measurement

70% bitumen concentration of monomodal and bimodal emulsion

The viscosity of the emulsions formulated previously, (Table 4), was measured[15]. Figure 5 shows the viscosity of the monomodal emulsion with the small particle diameter size, $d(0.5)_s$, A, the viscosity of the monomodal emulsion with the largest particle diameter size, d $(0.5)_l$, G, and the bimodal emulsion prepared mixing one part of emulsion A with two parts of emulsion G, emulsion E. The viscosity of the bimodal emulsion is about five times lower than their homologous monomodal emulsion. At 60 °C and 25 rpm, the viscosity of the small droplets size emulsion is 1800 mPa·s, that of large droplets size emulsion is 1000 mPa·s, while the viscosity of the bimodal emulsion is 400 mPa·s.

Moreover, in Figure 5 the viscosity of bitumen with penetration 50/70 has been added as reference; a viscosity of 265 mPa·s at 150 °C. Since it is a Newtonian liquid, its viscosity does not change with the shear rate, therefore its viscosity is constant with time. Therefore, the viscosity of a bimodal emulsion with 70% residual bitumen, formulated as B50/70, has the same viscosity at 60 °C and 50 rpm than the virgin bitumen at 150 °C.

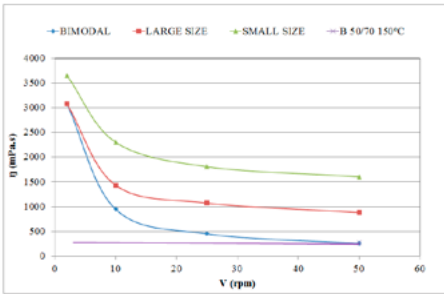

Figure 5. *Viscosity of monomodal emulsions (large and small size) and bimodal emulsion at different rpm*

Figure 6 represents the viscosity (at 60 °C and 50 rpm) of the produced emulsions vs the droplet diameter size. If the 4 µm emulsion would be monomodal, its viscosity would be around 1200 mPa·s, but as said above, being a bimodal emulsion has a viscosity five times smaller, with corresponds to 250 mPa·s.

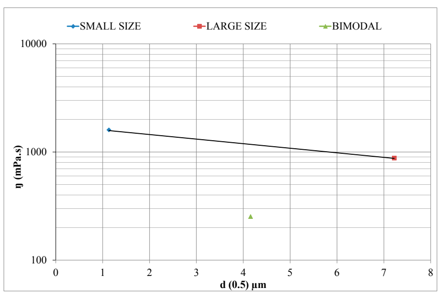

Figure 6. *Viscosity of monomodal emulsions (large and small size) and bimodal emulsion as function of diameter size*

80% bitumen concentration of monomodal and bimodal emulsion

Considering the good results obtained in the previous section, the behaviour of the bimodal emulsion developed with 80% residual bitumen was also studied. The viscosity at 80 ºC of the $d(0.5)_l$ monomodal emulsion with average droplet size 8.8 µm was determined together with the $d(0.5)_s$ monomodal emulsion with average droplet size 0.7 µm and the bimodal emulsion obtained when mixing them both with a proportion 1/2. The results obtained are presented in Figure 7.

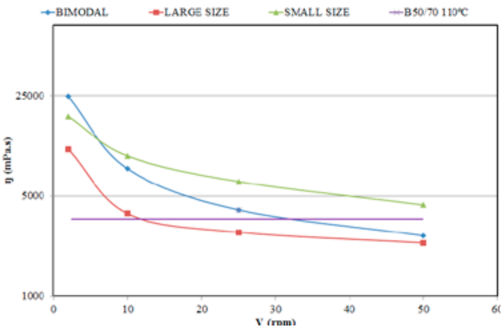

Figure 7. *Viscosity of monomodal emulsion $d(0.5)_P$, monomodal emulsion $d(0.5)_S$, and bimodal emulsion with 80% residual bitumen*

Figure 7 shows that the viscosity of the bimodal emulsion (4010 mPa·s at 80 ºC and 25 rpm) is between that of the big size emulsion (2800 mPa·s) and that of the small size emulsion (6320 mPa·s). Moreover, the viscosity of the bimodal emulsion is 1.5 lower than that of the small size emulsion, $d(0.5)_s$. Similarly to in the previous section, the viscosity of a virgin bitumen B50/70 at 110 ºC is included in the figure. With the same reasoning as before, it can be concluded that the bimodal emulsion with 80% residual bitumen has the same viscosity at 80 ºC and 25 rpm than the bitumen 50/70 at 110 ºC, 4000 mPa·s. The decrease in the viscosity in function of the droplet size at 80 ºC and 50 rpm can be seen in Figure 8. If the 4 µm emulsion would be monomodal, its viscosity would be close to 3500 mPa·s, but being bimodal its viscosity is 2650 mPa·s, a viscosity 1.5 times lower than expected as monomodal.

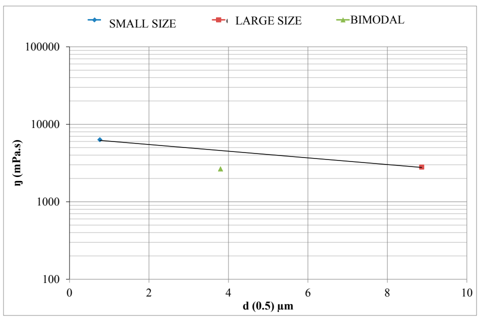

Figure 8. *Viscosity as function of the droplet size for a monomodal emulsion $d(0.5)_P$, monomodal emulsion $d(0.5)_S$, and bimodal emulsion with 80% residual bitumen*

Influence of the bitumen concentration in viscosity

The influence of the bitumen concentration in the bimodal emulsions viscosity, prepared mixing a ratio 1/2 of monomodal emulsions with of average droplet size of 1 µm and 5 µm respectively, is shown in Figure 9. The figure presents the viscosity at 60 ºC and 25 rpm for monomodal and bimodal emulsions with equivalent average droplet size at different bitumen concentrations. The figure shows that when the bitumen concentration increases, the viscosity also increases exponentially, but at a much lower rate for bimodal emulsions. The reduction of the viscosity of bimodal emulsions is much more significant when the residual bitumen is 70% or higher; in lower concentrations viscosity does not decrease significantly.

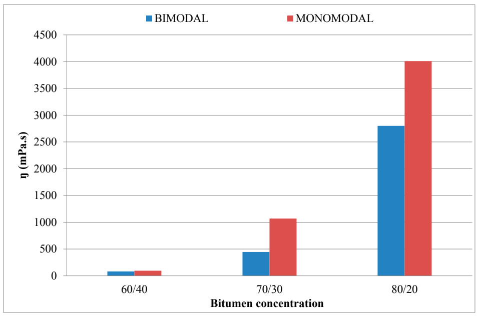

Figure 9. *Viscosity as function of bitumen concentration for monomodal and bimodal emulsions measured at 60ºC and 25 rpm*

CONCLUSIONS

Bimodal emulsions are characterized by having two different and controlled droplet size and distribution. The formation of new controlled droplet size emulsion was possible by using the HIPR method. The emulsion viscosities are exponentially increased when the bitumen concentration is increased. The best bimodal emulsion formulation as a result of lowest viscosity is reached when the large droplet size is mixed with the small droplet size at a proportion of (1:2). The viscosity of a 70% bitumen concentration of bimodal emulsion is about five times lower than their homologous monomodal emulsion. At 60 ºC and 25 rpm, the viscosity of the small droplets size emulsion is 1800 mPa·s, that of large droplets size emulsion is 1000 mPa·s, while the viscosity of the bimodal emulsion is 400 mPa·s. Therefore, the viscosity of a bimodal emulsion with 70% residual bitumen, formulated at B50/70, has the same viscosity at 60 ºC and 50 rpm than the virgin bitumen at 150 ºC.

For emulsions with 80% of residual bitumen the viscosity does not decrease as much as in those with 70% concentration. The viscosity of the bimodal emulsion is found to be between the viscosity of a big size emulsion and that of a low size viscosity. Actually, the viscosity of the bimodal emulsion is 1.5 lower than that of the low size viscosity.

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