

Article

# Storage Stability of Bimodal Emulsions vs. Monomodal Emulsions

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**Abstract:** Storage stability is a very important parameter that has to be considered in the formulation of asphalt emulsions. When monomodal emulsions are formulated, Stokes' law is fulfilled, therefore the higher the viscosity the less sedimentation, or the lower average droplet size the less sedimentation. But when bimodal emulsions are formulated, this rule does not apply. In this paper, two types of different emulsions are formulated: monomodal emulsions and bimodal emulsions. Bimodal emulsions are a combination of one large bitumen size and a small one. For this study, hard penetration bitumens were used, B35/50 and B15/25, because they are the most difficult bitumen to emulsify and, consequently, the worst sedimentation values are expected. Once the emulsions are manufactured, they are diluted to a bitumen rate concentration of 60% and 70%. Results show that bimodal emulsions, although having lower viscosity than their monomodal counterparts, have higher storage stability.

**Keywords:** bimodal emulsions; storage stability; bimodal viscosity values

## 1. Introduction

Emulsions are dispersed systems consisting of two immiscible liquids; one of them is the continuous phase, which contains the other liquid or internal phase, dispersed as small droplets. These systems are thermodynamically unstable and have a certain kinetic stability conferred by the presence of a surfactant absorbed on the oil/water interface.

Surfactants are chemical compounds with a surface activity which, when dissolved in a liquid, especially water, lowers its interfacial tension between the immiscible liquids, by preferential adsorption at the vapor/liquid surface or other interfaces, and facilitate dispersion of one liquid into the other [1,2].

Particle size and particle size distribution are important variables to consider and are controllable with formulation, raw materials, and the equipment used to manufacture the emulsion [3]. Many of the processes of breaking and curing are directly dependent on particle size and particle size distribution [4]. The importance of particle size in emulsions has been discussed in many papers [3–5]. It is a determinant of emulsion stability, coating, break rate, and cure rate. Methods to improve particle sizing of emulsions by formulation and adjustment of asphalt chemistry are described in the literature [5,6]. These methods usually involve improvement of the dispersing phase, doping of asphalt with surfactants, and tailoring asphalt composition and optimization of manufacturing conditions. The intention is to improve formation and dispersion of asphalt particles by the mill and stabilize the resulting emulsion [2].

The mean droplet size and the particle size distribution obtained can be controlled by changing the parameters of the formulation: rotational speed, mixing time, and surfactant type and concentration. The span of the drop size and the Sauter mean diameter become larger when the dispersed phase volume fraction becomes higher and the rotor speed becomes lower [3]. The type of surfactant used in the manufacture of the emulsion has a big effect on the speed of the breaking of an emulsion, so storage stability is one of the most important parameters to take into account in the formulation of bituminous emulsions. Bitumen in water emulsions are complex fluids. Their stability is governed by intermolecular forces, a result of a balance of repulsive and attractive forces. The formulator skillfully must understand and balance these forces such that the emulsion can be produced consistently, stored, pumped, transported, and applied by the practitioner in the field without experiencing any downtime in the operation. This difficult behavior could be reached, among other things, with a correct command of the formulation. If we want that the emulsion to have the same properties at the moment of application from the moment of manufacture, they have to be stable emulsions, or have good storage stability. The stability of the emulsion determines its appropriate use. Industrial manufacture of asphalt emulsion uses custom made equipment to provide thorough mixing capability to provide the fineness and stability of dispersion required to meet the desired asphalt emulsion properties. Once the asphalt emulsion has been manufactured for an application, tests must be conducted on the material to ensure it has the appropriate stability for storage and shipping. The weight of asphalt is very close to that of water, which helps in the ability of the asphalt to not settle to the bottom or cream to the top of the final product. Tests such as settlement and storage stability are done at 24 h and five days after manufacture to ensure the product maintains a good consistency [2].

The droplets of an emulsion are subjected to Brownian motion, which is the random motion observed in particles in a fluid (liquid or gas) as a result of collisions with the molecules of said fluid [4,5]. Brownian motion is an inherent movement in emulsions. The dispersed particles move inside the fluid. We must avoid, as far as possible, that this movement be abrupt or excessively fast, as an emulsion particle could be exchanged with another, fusing and resulting in larger droplet sizes. Industrial process, it is usual to pass the emulsion through a cooler in order to decrease Brownian motions. The stability of the emulsion will depend on how they interact with each other when encountered [2]. When the globules approach, due to the increase of concentration, by sedimentation if the increase of concentration is at the bottom, or creaming if the increase of concentration is at the top, the possibility of contact is much higher. Because of packaging or of friction between beads, some emulsifier molecules are removed from the surface and these unprotected areas are sensitive points to cause the emulsion to rupture [6,7].

During the storage of an emulsion, creaming or sedimentation takes place in a first step. Subsequently, flocculation occurs; it is characterized by the contact between globules, but they still are partially protected by the film of the emulsifier and, therefore, they maintain their shape. Then coalescence appears in what is already an irreversible process. After the first coalescence, these phenomena are accelerated resulting in the fracture and separation of the phases of the emulsion (Figure 1) [8,9]. The main factors that influence the storage stability of an emulsion are viscosity and average droplet size [2]. These two parameters are evaluated in this paper.

Bituminous emulsions form the basis for many paving applications in our asphalt industry, including driveway sealants, cold-pour crack sealants, and roofing emulsions or the recent development of half warm mix asphalt. Their rheological properties, such as viscosity, often dictate the uses for which they are suitable. For example, the viscoelastic properties of a slow setting versus a rapid-setting emulsion are different. We expect one day to be able to use rheological properties of bituminous emulsions to predict their success or failure in their respective applications. Even when rheological properties are not critical in the final product, they influence the workability of the emulsion as it is applied in the field [2].

Emulsion viscosity is a main test for the application of products. In a mixing application of dense graded aggregates, a thinner viscosity of emulsion is usually required. For an opengraded

application, a thicker emulsion is usually desired to get the appropriate film thickness. An asphalt emulsion used for bonding layers of asphalt needs to be thin enough to make a uniform layer and may need to be diluted with water to achieve the desired properties. For seal coating with aggregate chips, the emulsion needs to be thick enough to form the appropriate layer of emulsion for the size of chip while not forming drill marks or running off the road.

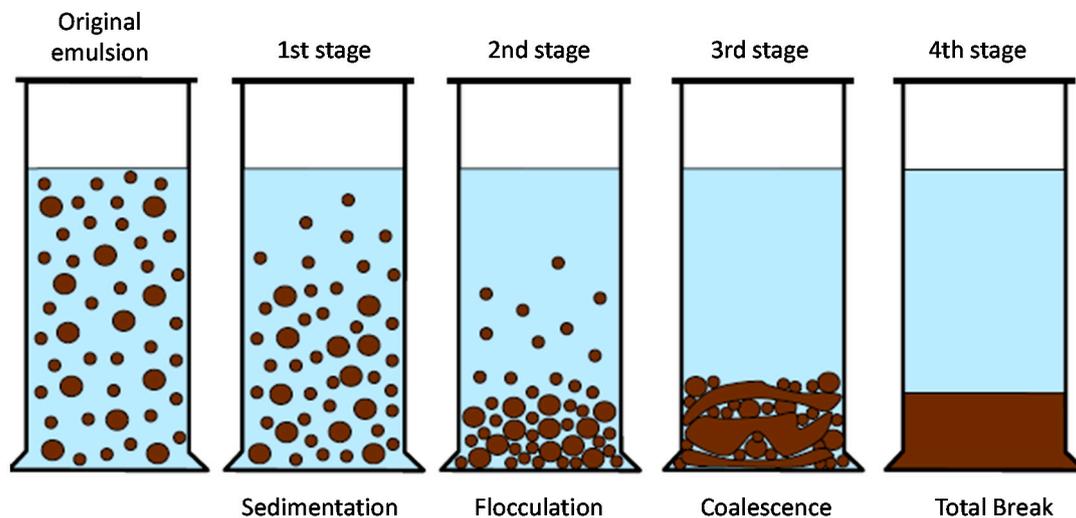


Figure 1. Storage stability evolution of an emulsion [8].

In order to measure the stability of the emulsions Stokes' law should be considered. Stokes' law evaluates sedimentation time as a function of mean particle size of the emulsion. In general, Stokes' law is valid in the movement of small spherical particles moving at low speeds but only for monomodal emulsions, as we will demonstrate in this paper [2,10–12].

If the particles are falling vertically into a viscous fluid due to their own weight, their falling rate or settling can be calculated by equating the frictional force with the apparent weight of the particle in the fluid. The speed of this phenomenon, still reversible, is governed by Stokes' law [13–16]:

$$V = \frac{2a^2(\rho - \rho_0)g}{9\eta} \quad (1)$$

where  $V$  is the particles falling rate,  $a$  is the globules ratio,  $\rho$  is the bitumen density,  $\rho_0$  is the water density,  $\eta$  is the emulsion viscosity, and  $g$  is acceleration.

According to the above equation, Stokes' law refers to the frictional force experienced by spherical objects moving in the interior of a viscous fluid in a lamellar regime with low Reynolds numbers, from which we can deduce that the sedimentation velocity is determined by two important factors: the mean droplet size and the viscosity of the emulsion. So, focusing on Stokes' law, the lower the average droplet size of the emulsion, the lower the sedimentation rate; and the more viscosity the emulsion has, the lower the sedimentation rate [17]. This rule is fulfilled as long as bimodal emulsions are not considered.

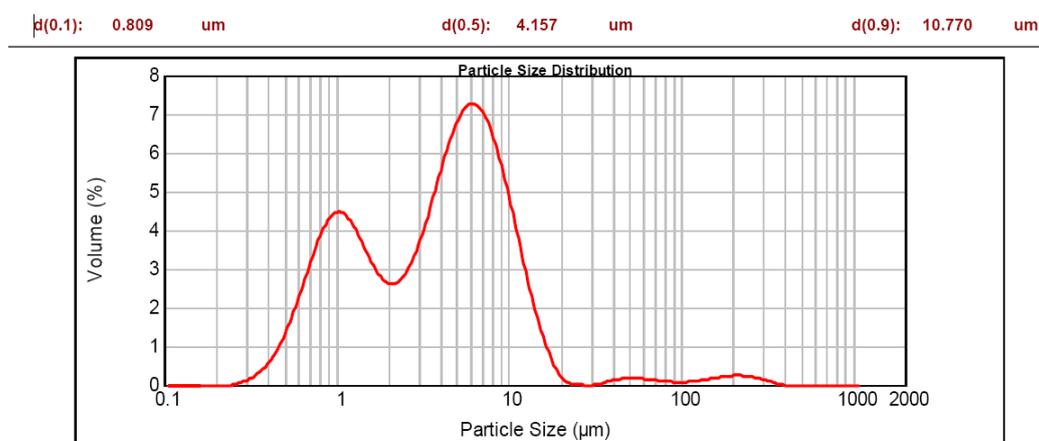
The viscosity of the emulsion is a very important parameter to take into account. As the viscosity increases, stability also increases, but if the viscosity is too high it will affect the workability. If the viscosity is too high, problems will appear when pumping it from the storage tank to the manufacturing plant, and the wrapping with aggregates will not be correct.

There are different procedures for preparing bitumen in water monomodal emulsions. The most widely used method in industrial processes is the one that uses colloid mills for its manufacture. This works with high temperatures, 140–170 °C, high pressures, 100–300 kPa, and/or high rotational speed, 5,000–10,000 rpm. In this process, emulsions are manufactured in a turbulent flow produced

by the colloid mill rotating at high speed of around  $105 \text{ s}^{-1}$ . Emulsification generally takes place at concentrations of the dispersed phase (bitumen) between 60–70 wt. %, or at a bitumen volume fraction of 0.6–0.7. Above this concentration the process is not efficient, since very large drop particles are obtained and emulsions have no storage stability. Moreover, the droplet size obtained by the traditional method is between 5–10 microns; small droplet sizes are very difficult to obtain [18,19]. Obviously, we could consider that the size of 5–10 microns is a small droplet size, but in this paper, we will further differentiate the necessity of different sizes. As we need a very small drop size to obtain a bimodal emulsion (around  $1 \mu\text{m}$ ), we decided to use small droplet size for the emulsion (around  $1 \mu\text{m}$ ) and large droplet size emulsions with 5–10 microns.

Another manufacturing system used to disperse two immiscible phases is the HIPR procedure (high internal phase ratio) [20]. This procedure involves a direct blend of a highly viscous phase, 1–5000 Pa·s, with a second phase immiscible with the first one and in the presence of at least one surfactant. It works with low shear, 500–1500 rpm, in laminar flow and very little time, producing a viscoelastic paste which can be subsequently diluted to the required concentration of the dispersed phase. With this system, it is possible to obtain monomodal emulsions with very narrow particle size distribution and small mean droplet size ( $d(0.5)_s$ , about  $1 \mu\text{m}$ ). Furthermore, this system can produce concentrated and highly concentrated bitumen emulsions of 70–95 wt. %. The droplet size of the emulsions produced by this procedure can be easily controlled by rotational speed, formulation parameters, or by the concentration of the dispersed phase used during manufacture [20,21].

Monomodal emulsions are characterized by one particle size distribution while bimodal emulsions are characterized by having two different and controlled droplet size and distributions. The optimal formulation contains a first small size of about  $1 \mu\text{m}$  and a second size of about  $5 \mu\text{m}$  with a proportion of  $\frac{1}{2}$ , respectively (Figure 2) [22–24].

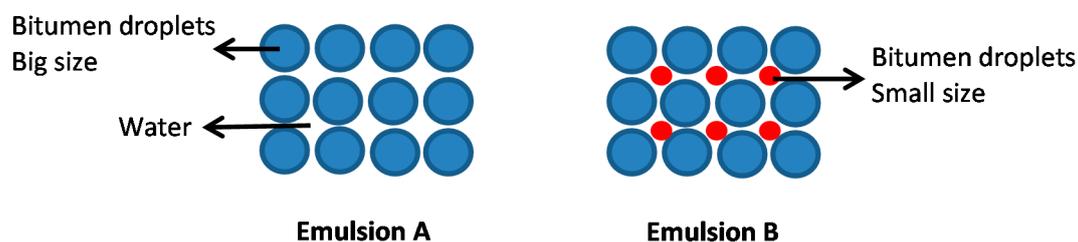


**Figure 2.** Representation of a bimodal bitumen emulsion particle size distribution.

The decrease in viscosity that can be observed in bimodal emulsions when compared to their equivalent monomodal emulsions can be attributed to the packing of the emulsion droplets. Viscosity reduction can be attained for different kinds of fine and coarse emulsion associations [22]. In bimodal emulsions, the small droplets try to place themselves in the empty voids of the cubic matrix generated by the distribution of the large droplets (Figure 3) [23,24]. Due to this different packing distribution, the droplet movement should be slower than in monomodal emulsions and, consequently, they have lowered sedimentation rates.

Due to this characteristic particle size distribution, the bimodal emulsions are characterized by having a lower viscosity than their monomodal homologues, but contrary to Stokes' law, they have higher storage stability and lower viscosity. The aim of this paper is to experimentally demonstrate this

last statement, formulating two different emulsions: monomodal emulsions and bimodal emulsions, and evaluating their viscosity and storage stability.



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

## 2. Materials and Method

### 2.1. Materials

For this study, 35/50 and 15/25 penetration grade bitumen were used. These two bitumens were selected because they are the most difficult bitumens to emulsify due to their hardness and, consequently, worst sedimentation values were expected [18,21]. Their main characteristics are shown in Table 1. Bitumen emulsions were formulated and stabilized with cationic commercial surfactants. In this paper, an *N*-alkyl propylene diamine long chain, *N*-Tallow-1,3-propyldiamine (S1), and a propylenic alkyl polyamine, ethanol,2,2'-[[3-[(2-hydroxyethyl)amino]propyl]imino]bis (S2), with medium/fast break and with alkyl propylene diamine long chain, were prepared at 50 °C. Surfactants were activated with acid solutions of hydrochloric acid adjusting their pH to 2.0–2.5. As emulsifiers are insoluble in water, it is necessary to convert them into salts so as to dissolve them in the dispersing phase [2].

**Table 1.** Physicochemical characteristics of used bitumens.

Characteristics	Standard	Units	15/25	35/50
Penetration	UNE-EN 1426:2007	0.1 mm	25	45
Softening temperature	UNE-EN 1427:2007	°C	61	52
Viscosity @ 100 °C	UNE-EN 13302	mPa·s	18,220	5450
Saturated	ASTM 4124	%	3.00	4.40
Aromatics	ASTM 4124	%	48.30	47.63
Resins	ASTM 4124	%	30.00	34.82
Asphaltenes	ASTM 4124	%	17.00	16.53

### 2.2. Emulsion Preparation

The method used for emulsion preparation was the high internal phase ratio (HIPR), described in the introduction. This method facilitates obtaining emulsions with very narrow droplet size and distribution [25,26]. The criteria governing the HIPR method are:

- The emulsion is produced with an initial volume fraction,  $\phi$ , between 0.75 and 0.95.
- The dispersed phase has high viscosity, 1–5000 Pa·s at 100 °C.
- A low mixing rate is used, between 800 and 1200 rpm (laminar regime).
- The addition of the aqueous phase in the oily phase is done altogether in one step.
- The emulsion produced in is an inversion emulsion which changes very quickly to a direct emulsion with contact of the aqueous phase.
- The emulsion is obtained within a few seconds.
- Once the emulsion is formed we obtain a viscoelastic paste that could be diluted in water to achieve the required bitumen/water relation.

- The emulsions should be stored at temperature between 40–60 °C.

To prepare bimodal emulsions, it is necessary to first manufacture two separately monomodal emulsions with very controlled droplet size. This will require producing the emulsion separately to be mixed before, with different ratios of initial dispersed phase volume fraction to control the final size of droplet [24,25]. To prepare bitumen emulsions with the same base materials but different particle size, we vary the volume ratio of bitumen/soap phase at the moment of emulsification. The ratio of bitumen/soap phase used was: 95/5 for small droplet size, and 85/5 for large droplet size. The monomodal emulsions were prepared mixing the necessary quantity of bitumen 35/50 or 15/25 penetration grade bitumen heated up at  $100 \pm 2$  °C with an aqueous solution of long chain alkyl propylenediamine surfactant at a concentration of 10,000 ppm on bitumen, heated up to 40–50 °C adjusted at a pH of  $2 \pm 0.5$ , by the addition of 6–10 gr HCl in the soap phase, to obtain the emulsion with small average droplet size, hereinafter  $d(0.5)_s$ , and 6750 ppm for the large size emulsion, onwards  $d(0.5)_l$ . Once emulsions were obtained after mixing between 1–15 min at 800–1300 rpm, they were diluted with water to give concentrations studied in this paper, 60, 70% wt./wt. The conditions used are summarized in Table 2. We evaluated these two different concentrations because as the concentration of bitumen increases, the expected viscosity will also increase, and the storage stability should improve. To obtain the best bimodal emulsion formulation, and as result of the lowest viscosity, the large droplet size should be mixed with the small droplet size at a proportion of (1:2) [24].

**Table 2.** Physicochemical characteristics to produce the different emulsions.

Characteristics	$d(0.5)_s$	$d(0.5)_l$
Emulsifier	Propylene alkyl diamine	Propylene alkyl diamine
Acid weight (gr)	10	6
Soap temperature (°C)	48	46
Bitumen temperature (°C)	100	100
Mixing speed (rpm)	1200	850
Mixing time (min)	15	15

In industrial processes, we think it could be possible to manufacture bimodal emulsions with the same emulsion plant used to produce monomodal emulsion. It will be so easy to alternate the manufacture of a large particle size with the small particle size and make a soft agitation in the storage tank in order to obtain the bimodal emulsion.

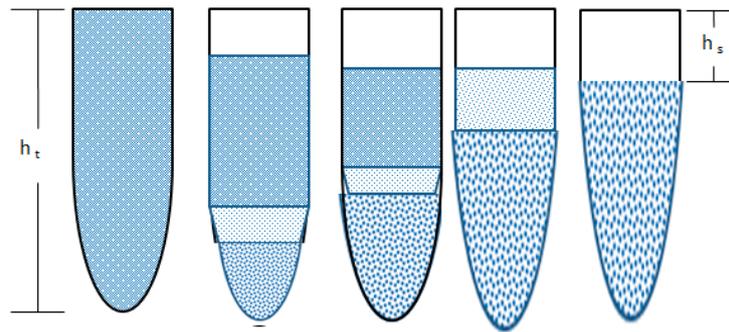
### 2.3. Particle Size Measurement

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 three measures for each sample. The average values have around 1% systematic error and a standard deviation of  $\pm 0.001$   $\mu\text{m}$ . Measurements were carried out at ambient temperature.

### 2.4. Emulsion Sedimentation Analysis

The effect of sedimentation of the emulsions over time was studied. As discussed earlier in the introduction, Equation (1) shows that as viscosity decreases when sedimentation increases [8]. In monomodal emulsions, this equation is perfectly fulfilled, however, the rheological behavior of bimodal emulsions is different and they are characterized by having a viscosity of less than equal concentration of monomodal emulsion [24].

To evaluate the sedimentation rate of both monomodal and bimodal emulsions, the emulsion sample was introduced into 13 mL sedimentation tubes, closed with screw cap, and left standing at room temperature for several days. The samples are observed to precipitate over time and precipitation was recorded in the different samples. Sedimentation can be measured as the height difference between the supernatant phase,  $h_s$ , and the initial phase,  $h_t$ , after a given time (Figure 4).



**Figure 4.** Process to measure emulsions sedimentation based on UNE-EN 12847.  $h_s$  is the supernatant phase and  $h_t$  is the initial phase.

### 2.5. Viscosity Measurement

To complete the measurements, the viscosity of the different emulsions was tested. The measures were made with a rotational viscosimeter model DV2T which has precision  $\pm 1.0\%$  and a repetitivity  $\pm 0.2\%$ . The attachment used to make the measurements was a cylinder SC4-21. They were carried out at  $60\text{ }^\circ\text{C}$  and 50 rpm.

## 3. Results

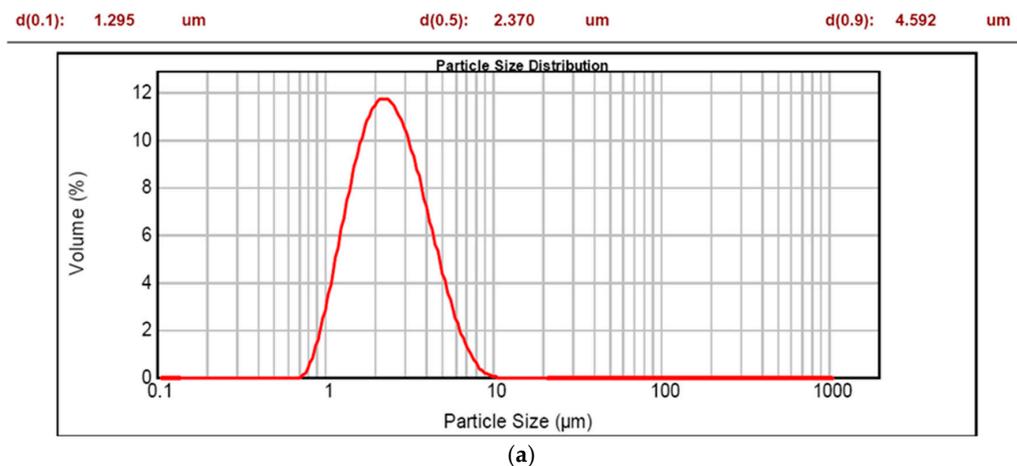
### 3.1. Particle Size Distribution

As discussed in Section 2.2, to prepare bimodal emulsions, it is necessary to first manufacture two monomodal emulsions with very controlled droplet size. The optimal formulation contains a first emulsion of about  $1\text{ }\mu\text{m}$  particle size distribution, hereinafter small size emulsion  $d(0.5)_s$ , and a second one of about  $5\text{ }\mu\text{m}$ , hereinafter large size emulsion,  $d(0.5)_l$ . Once we had these manufactured, we mix them with a proportion of 1/2.

First of all, the average droplet size of the monomodal with smaller size was measured, then, that of larger size, and finally, the bimodal emulsion (obtained with the mixture of the two previous ones).

The average droplet size obtained after the manufacture of the emulsions of 60 wt. % concentration, formulated with a B35/50 penetration grade, is presented in Figure 5, and for 70 wt. % concentration in Figure 6. Finally, the average droplet size of 70 wt. % emulsions for B15/25 is presented in Figure 7.

Notice that the average droplet size analyses have around 1% systematic which corresponds to a standard deviation of  $\pm 0.002\text{ }\mu\text{m}$ .



**Figure 5.** Cont.

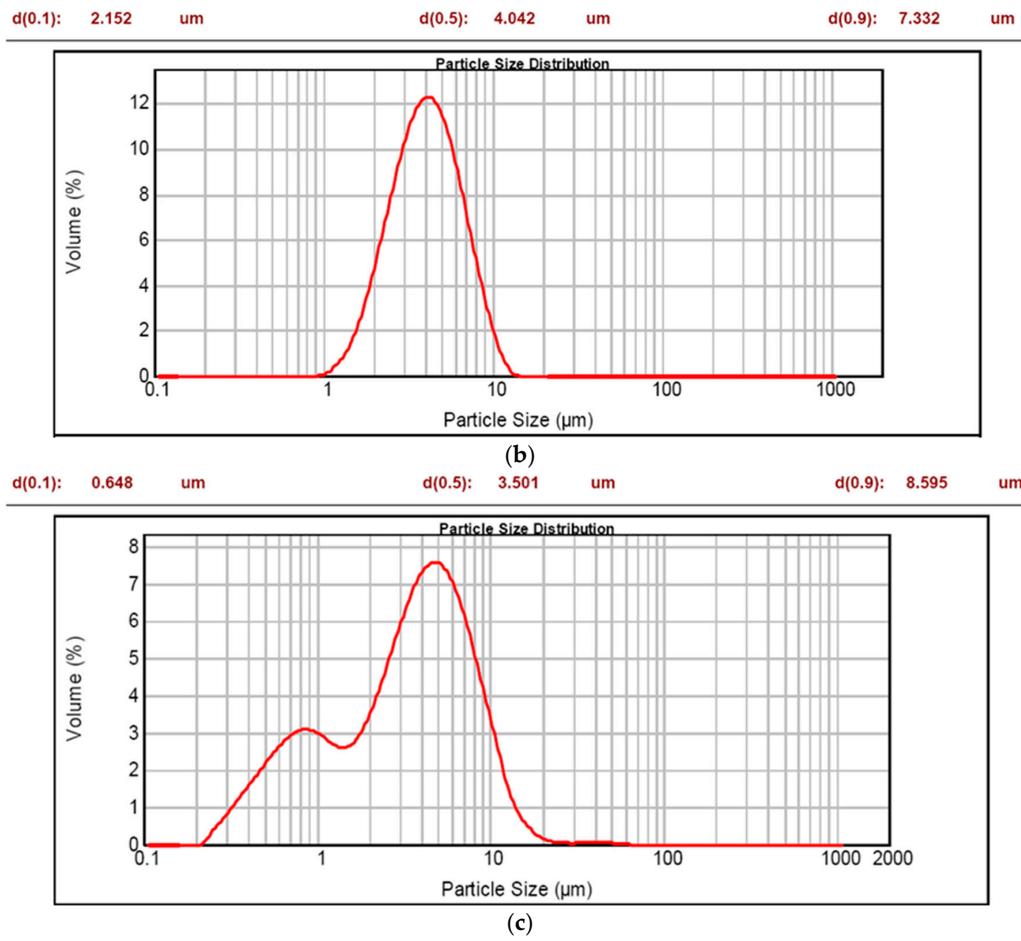


Figure 5. Particle size distribution for a 60 wt. % B35/50 for (a)  $d(0.5)_s$ , (b)  $d(0.5)_l$ , and (c) bimodal emulsion.

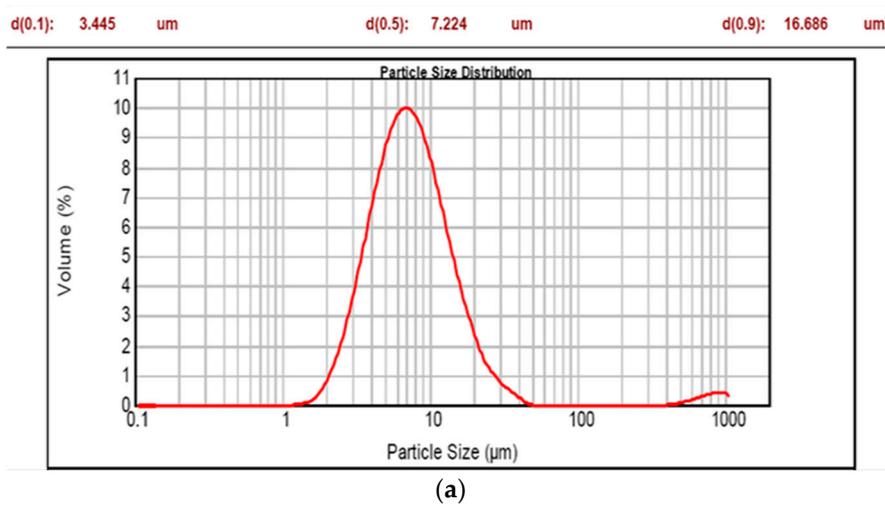


Figure 6. Cont.

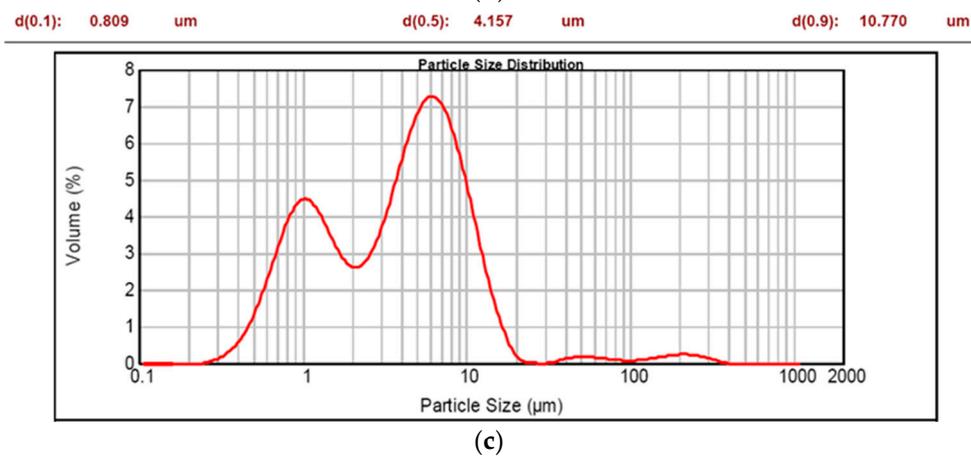
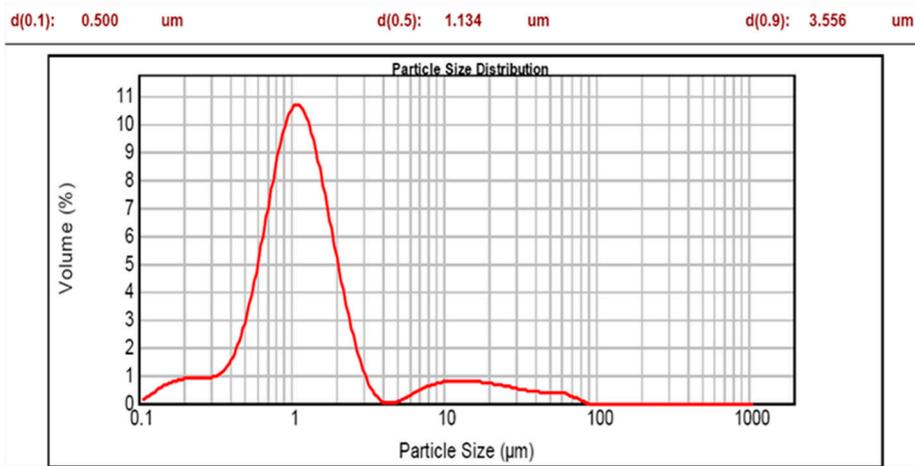


Figure 6. Particle size distribution for a 70 wt. % B35/50 for (a)  $d(0.5)_s$ , (b)  $d(0.5)_l$ , and (c) bimodal emulsion.

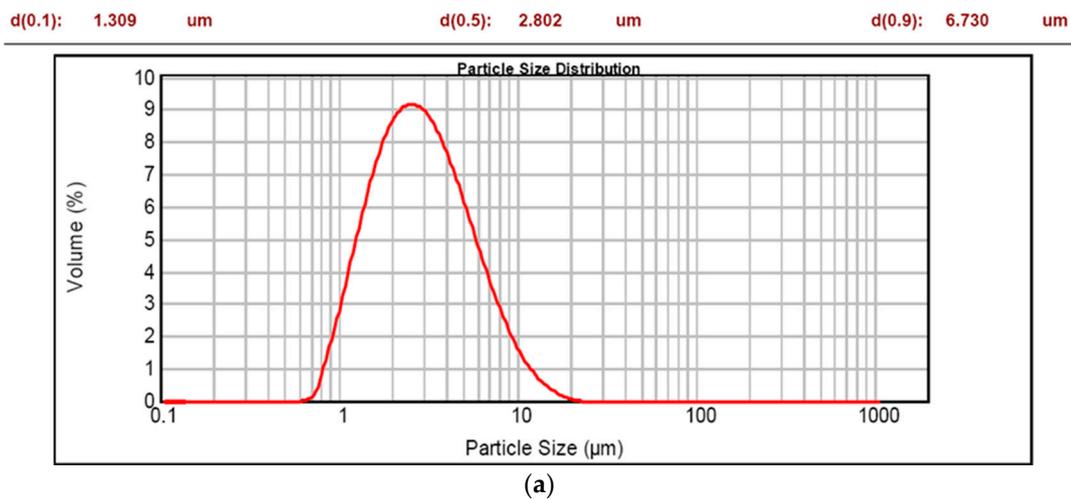
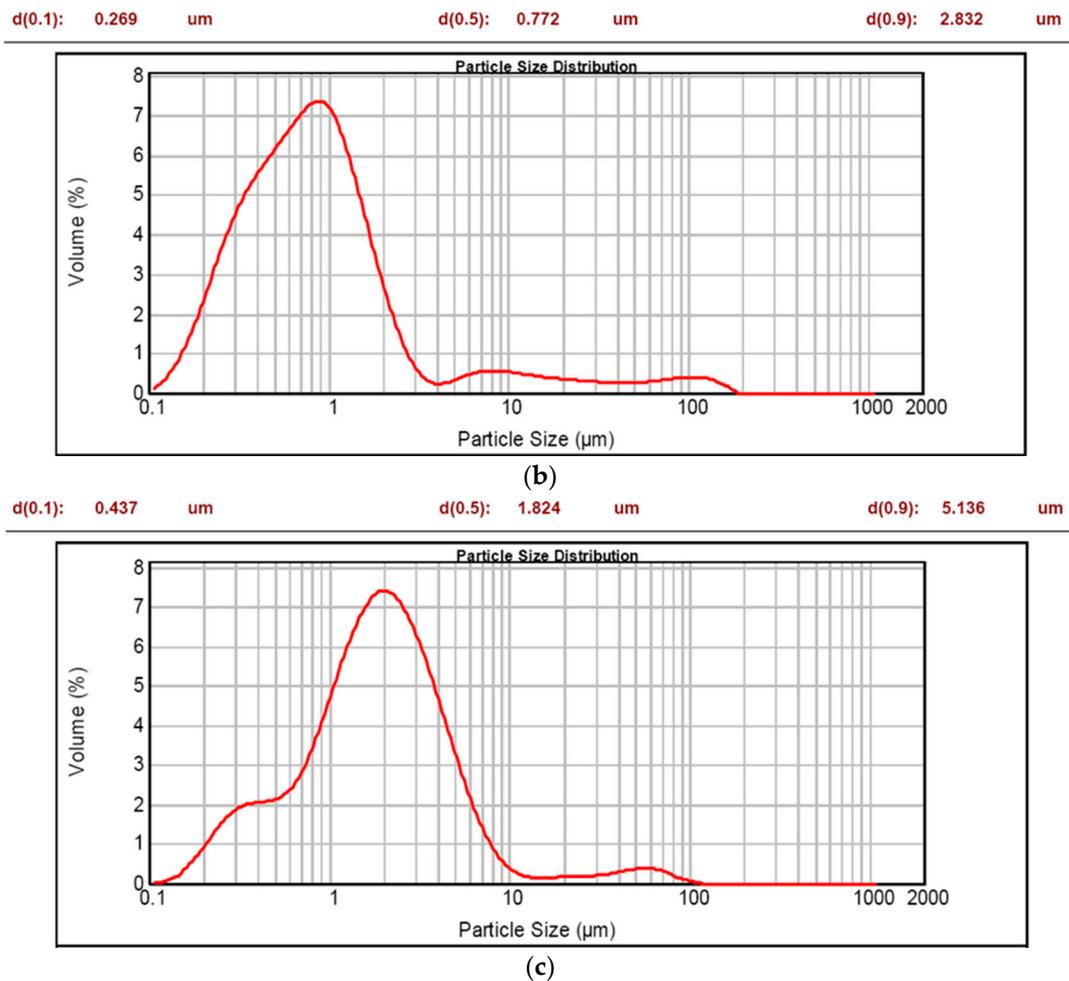


Figure 7. Cont.

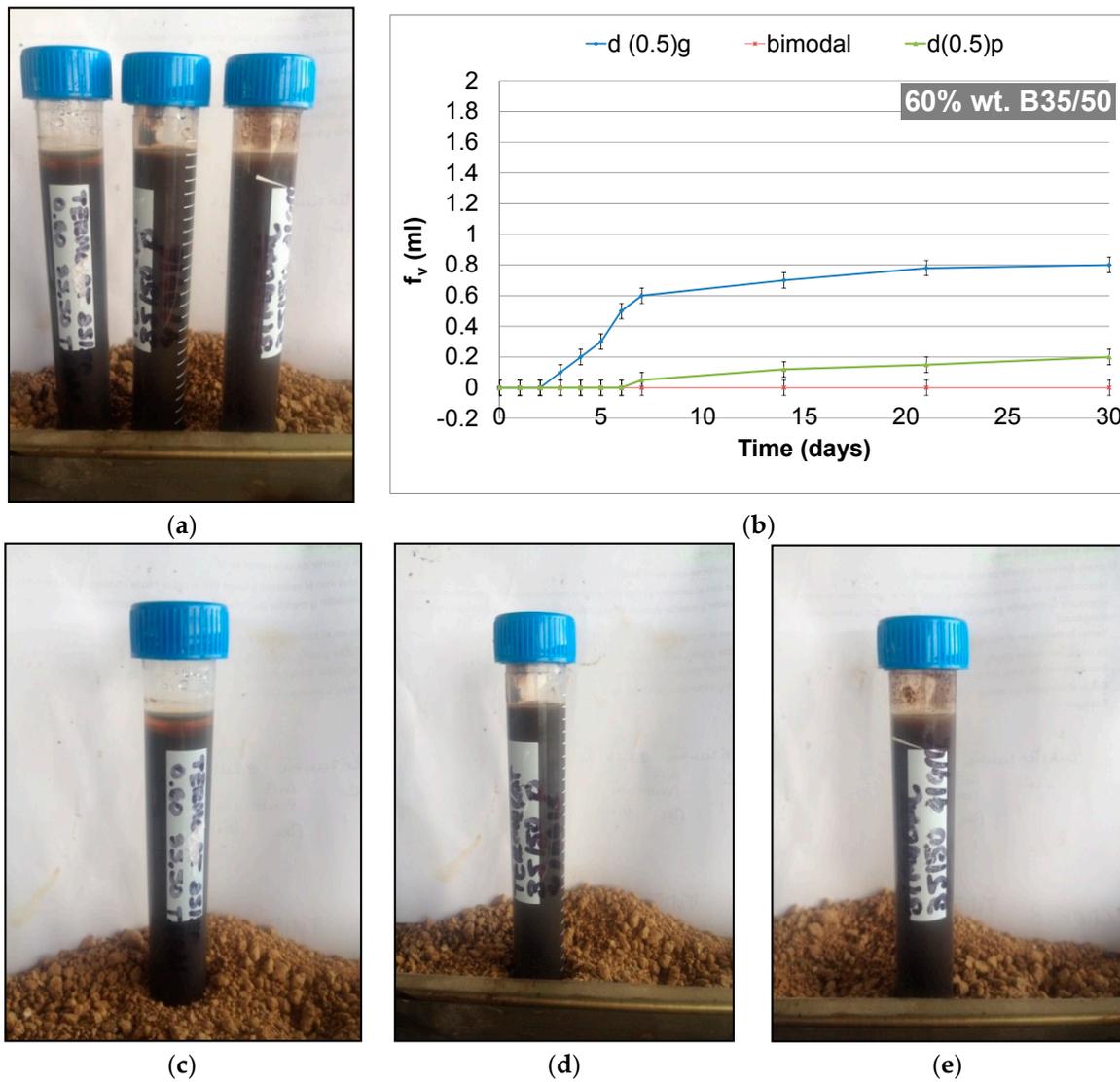


**Figure 7.** Particle size distribution for a 70 wt. % B15/25 for (a)  $d(0.5)_s$ , (b)  $d(0.5)_l$ , and (c) bimodal emulsion.

### 3.2. Emulsion Sedimentation

Three different groups of emulsions were manufactured combining concentration of 60 wt. % and 70 wt. % residual bitumen and B35/50 and B15/25 penetration grade bitumen, following the manufacturing protocol established in Section 2.2. In three cases, one monomodal emulsion of small controlled particle size, one monomodal emulsion of large particle controlled size, and a third bimodal emulsion mixing the previous two in a controlled rate of 1/2 small/large particle size were manufactured.

The first emulsion manufactured is a 60 wt. % bitumen emulsion formulated with a B35/50 penetration grade bitumen. Results obtained are shown in Figure 8. It can be seen that after one month since its manufacture the small-sized monomodal emulsion ( $d(0.5)_s$ ) settled slightly with supernatant starting from day 14. In contrast, the monomodal emulsion of large size ( $d(0.5)_l$ ) has a supernatant of 0.8 mL after one month from its manufacture. The viscosity results obtained are summarized in Table 3.



**Figure 8.** Emulsions of 60 wt. % B35/50: (a) global vision; (b) sedimentation curve; (c) monomodal  $d(0.5)_j$ ; (d) monomodal  $d(0.5)_s$ ; (e) bimodal emulsion.

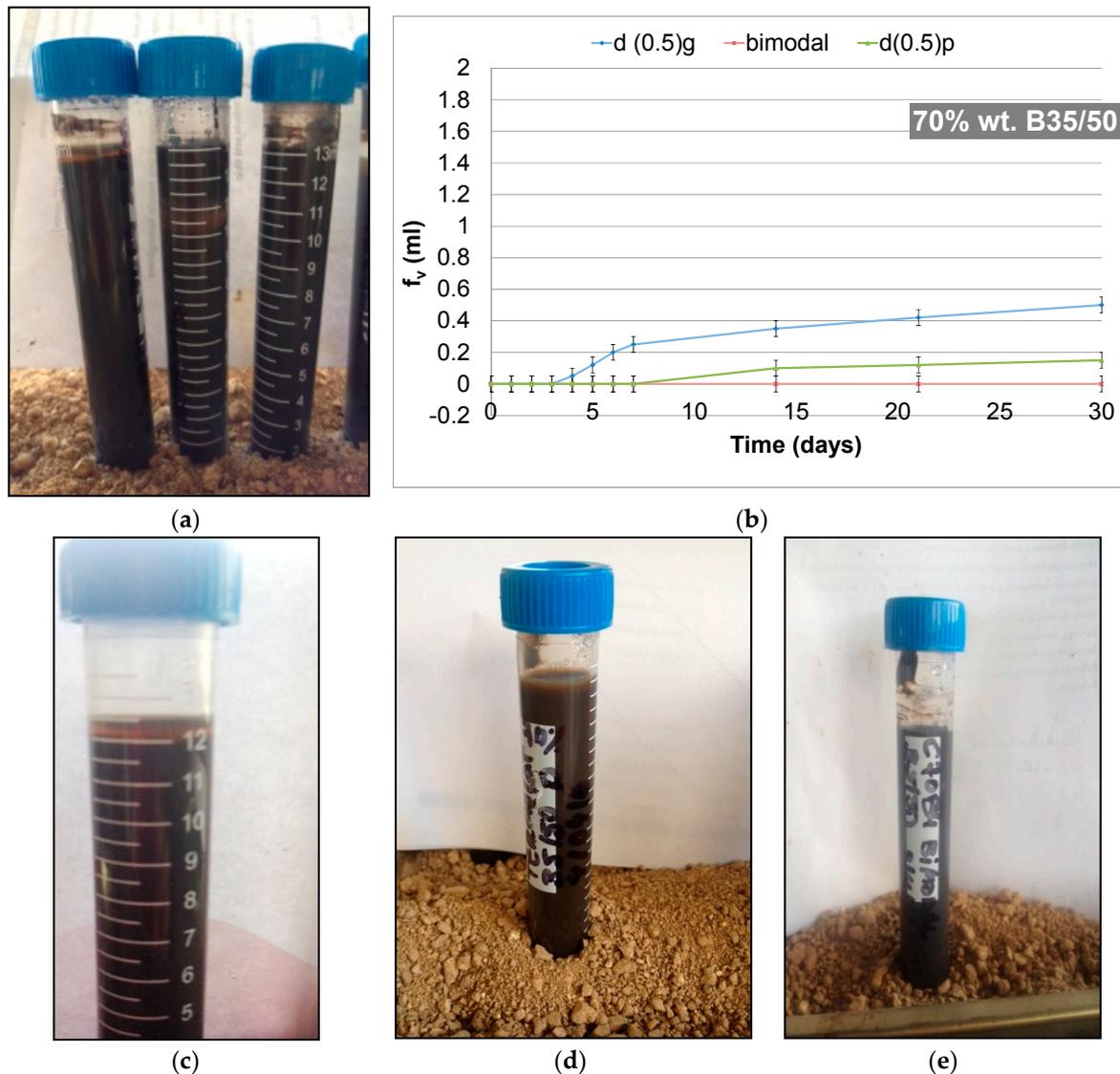
**Table 3.** Viscosity measurement for the different prepared samples.

60 °C 50 rpm	Emulsion Concentration	Bitumen	$d(0.5)_l$	$d(0.5)_s$	$d(0.5)_{bimodal}$
1	60	35/50	376	878	262
2	70	35/50	878	1805	253
3	60	15/25	37.25	253	24.75

Although the bimodal emulsion has a viscosity lower than the emulsion of large size, 262 mPa·s in front of 376 mPa·s, it does not present supernatant after one month from its manufacture, which is more similar to the emulsion of small sizes [20,25].

Three new emulsions were made where the residual bitumen concentration was increased to 70% residual bitumen. The bitumen used was the same as in the previous case, a B35/50. The first emulsion was a monomodal emulsion,  $d(0.5)_s$ , and the second emulsion a monomodal,  $d(0.5)_l$ , resulting in a bimodal emulsion from the mixture of 1/2 of the above two. Ten mL of emulsion was introduced into

three closed sedimentation tubes and left to stand at room temperature. The supernatant was read as the volume fraction,  $f_v$ , at different times. Results are shown in Figure 9.

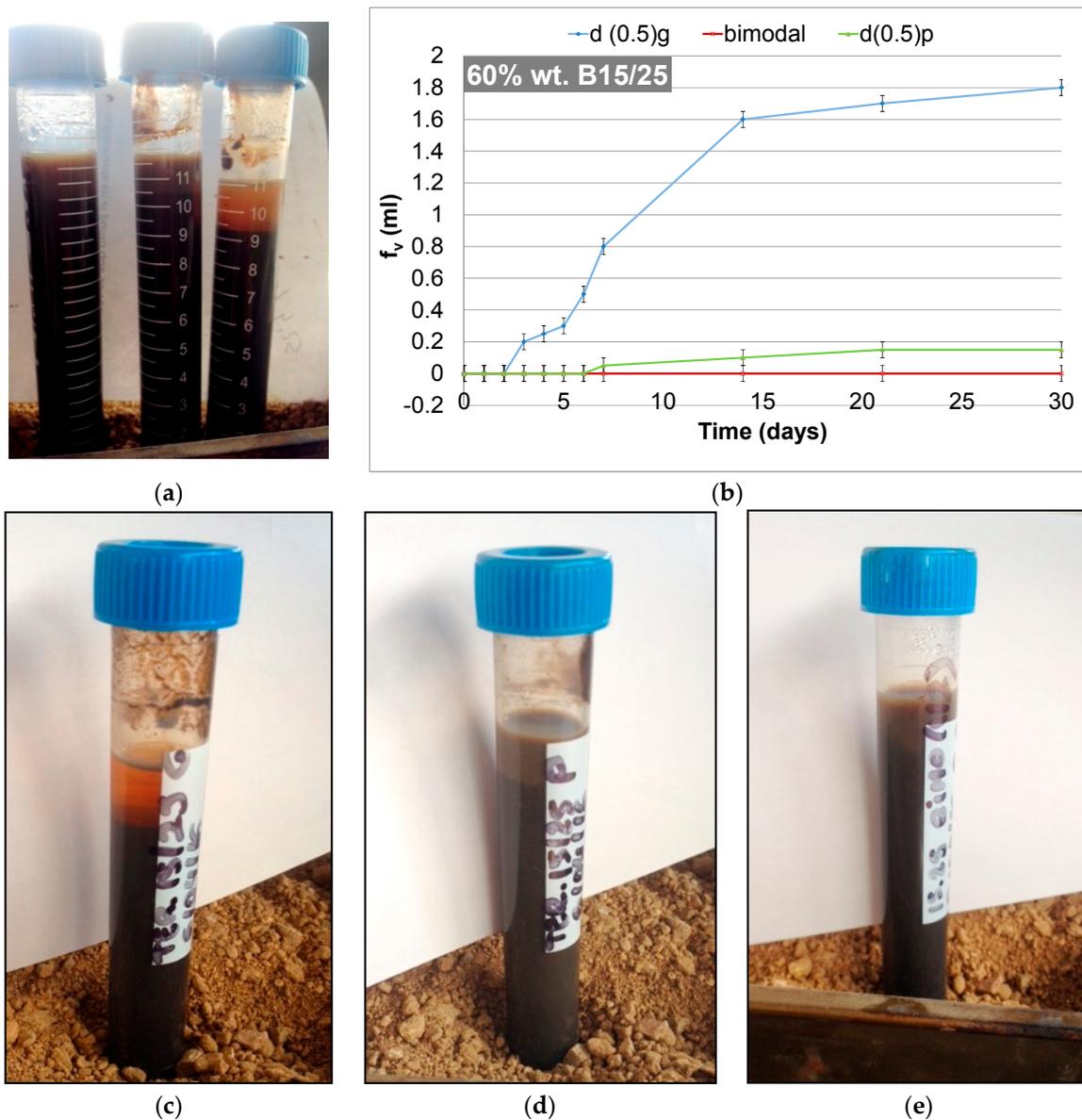


**Figure 9.** Emulsions of 70 wt. % B35/50: (a) global vision; (b) sedimentation curve; (c) monomodal  $d(0.5)_l$ ; (d) monomodal  $d(0.5)_s$ ; (e) bimodal emulsion.

In the monomodal emulsion of large size,  $d(0.5)_l$ , there was a slight sedimentation, 0.5 mL, after a month of storage; while the monomodal emulsion of small size,  $d(0.5)_s$ , practically had no sedimentation and only a light supernatant was observed from day 14; and finally, the bimodal emulsion corresponding to the mixture of the two above at ratio 1/2, did not have a supernatant after a month of its manufacture. Therefore, the bimodal emulsion was more stable for storage than the monomodal emulsion of large size, although it had lower viscosity (at 60 °C and 50 rpm the bimodal emulsion had a viscosity of 253 mPa·s, while the monomodal emulsion of large size had a viscosity of 878 mPa·s).

In view of the excellent results obtained, it was decided to test the behavior of these emulsions by varying the starting bitumen, using harder penetrating bitumen, that is more unfavorable for its manufacture. The 60 wt. % emulsions were made again but using a harder bitumen, B15/25. The emulsions of this hard residue are of great interest in the world of paving, although both their

difficulty to be manufactured and their little stability for storage are well-known. Results are shown in Figure 10.



**Figure 10.** Emulsions of 60 wt. % B15/25: (a) global vision; (b) sedimentation curve; (c) monomodal d(0.5)<sub>l</sub>; (d) monomodal d(0.5)<sub>s</sub>; (e) bimodal emulsion.

Results show that it is effectively an emulsion with a high sedimentation rate. Emulsion of big size, d(0.5)<sub>l</sub>, presents high sedimentation after one month of storage, the supernatant was almost 2 mL after this time. In contrast, the emulsion of small size, d(0.5)<sub>s</sub>, and the bimodal emulsion did not present clear sedimentation. In the emulsion of small size, a light supernatant of less than 0.1 mL appeared after the 14 days; this supernatant had a more turbid color, but there was no real sedimentation. This turbid supernatant also appeared in the bimodal emulsion, although less distinct than in the previous case.

In this case, the viscosity of the bimodal emulsion at 60 °C and 50 rpm was 24.75 mPa·s, while the viscosity of the emulsion of big size was 37.25 mPa·s. Therefore, the viscosity variation was not so

important, but the difference in the sedimentation values was, which is much more favorable for the case of the bimodal emulsion.

#### 4. Conclusions

The sedimentation of an emulsion is directly related to the concentration of residual bitumen and the viscosity of the emulsion. As shown in equation 1, there is a lower average drop size, lower settling velocity, and, at higher residual bitumen concentration, lower settling velocity. Stokes' law refers to the frictional force experienced by spherical objects moving within a viscous fluid in a lamellar regime of low Reynolds numbers. This equation is fulfilled as long as the spherical particles moving through the sine of the viscous fluid are not configured to form a bimodal distribution.

Bimodal emulsions are characterized by having two different and controlled droplet size and distribution. The optimal formulation contains a first small size of about 1  $\mu\text{m}$  and a second size of about 5  $\mu\text{m}$  with a proportion of 1/2, respectively. The decrease in viscosity that can be observed in bimodal emulsions when compared to their equivalent monomodal emulsions can be a consecution of the distribution of the different droplets in the matrix of the emulsion. Small particle size droplets could occupy the gaps between the large droplets and promote the decrease of viscosity [24].

The viscosity of the bimodal emulsion of 60 wt. % with a B35/50 penetration grade bitumen was 262 mPa.s, while when we use B15/25, the viscosity obtained was 24.75 for the same bitumen concentration of 60 wt. %. It seems that the penetration grade bitumen has greater influence on the viscosity value of bimodal emulsions than the final bitumen concentration, since, when we measured the viscosity of the bimodal emulsion 60 wt. % with B35/50 penetration grade bitumen was 262, while when the concentration is 70 wt. % the viscosity is almost the same, 253. It seems that the bitumen concentration does not influence the final viscosity. The bitumen penetration grade is more important.

Storage stability is a very important parameter that has to be considered in the formulation of asphalt emulsions. The stability of the emulsion determines its appropriate use. The main factors that influence the storage stability of an emulsion are viscosity and average droplet size. Focusing on Stokes' law, the lower the average droplet size of the emulsion, the lower the sedimentation rate; and the more viscosity the emulsion has, the lower the sedimentation rate. In the present paper, we have observed that this rule is fulfilled as long as bimodal emulsions are not considered. The storage stability of bimodal emulsions is much higher than their monomodal counterparts, even though they have a lower viscosity than these.

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