Changes in Rubber Due to its Interaction with Bitumen when Producing Asphalt Rubber

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Abstract

The negative impact of the used tires residues can be reduced by reusing their rubber as a constituent of asphalt rubber (AR) mixtures, thus contributing for a sustainable development of road infrastructures. However, the increasing demands on the durability of pavements require a deeper knowledge about the physicochemical changes of the AR binders. The main objective of this research is to characterize the influence of bitumen in the rubber morphology and the changes in the density of bitumen, rubber and AR during its production. Four base bitumens interacted with crumb rubber in order to produce AR binders, which were then separated by using a modified "basket drainage method". The changes in rubber were studied through microscopy, swelling and depolymerization tests. It was concluded that i) the

rubber particles swelled 250% their weight, but only increased 2.5% their equivalent diameter; ii) rubber particles can swell till saturation after interacting with softer bitumens; iii) re-vulcanization and re-polymerization among the rubber particles can eventually occur.

KEYWORDS: Asphalt rubber, Microscopy, Densities, Rubber morphology, Swelling.

Introduction

Rubber from wasted tires is a material with a highly valuable constituent: vulcanized natural and synthetic rubber. Therefore, the introduction of crumb rubber in the production of asphalt rubber (AR) mixtures for road pavements should be considered as a sustainable technology which transforms an unwanted residue into a new bituminous mixture highly resistant to fatigue and fracture. However, the increasing demands concerning the durability of pavements lead to the need of a profound knowledge in the changes of the constituents of the AR binders.

Thus, the main objective of this paper is to characterize the influence of the type of bitumen on the rubber morphology during the AR binder production process, namely by evaluating the influence of different base bitumens on the rubber size and volume, and by assessing the changes that occur in the density of the bitumens, rubber and AR binders during the digestion time.

A large range of bitumens of the same origin and batch were used to produce AR binders, thus being possible assess some advantages of using less conventional base bitumens with very low and very high penetration grades (respectively, B10/20 and B150/200). All other AR production parameters (bitumen source, blending temperature/time and mixing/shearing method) were purposely prefixed in order to reduce the variability of the results. Therefore, four base bitumens interacted with crumb rubber in order to produce AR binders. The changes in the AR density were monitored and the rubber particles and the residual bitumen were separated by using a modified "basket drainage method". The changes in the rubber particles were studied through optical microscopy analysis, swelling and depolymerisation tests. This paper presents a new approach to evaluate the AR binders produced with diverse base bitumens and to study of their effect on the rubber morphology that controls the AR production process.

Literature review on bitumen-rubber interaction

Healthy economies require an appropriate transportation system, in which roadways are an essential part. Therefore, the construction and maintenance of road pavements should be long lasting and have a significant impact on the economic vitality of a nation. The primary reasons for the deteriorated conditions of roads include the increase of traffic, poor asphalt binder quality resulting from high-tech refining processes and climatic changes. Improved construction processes will secure the solution to these challenges. It is necessary to understand the fundamental behaviour and properties of roads before starting to develop advanced construction processes (Glover, 2007).

Frequently, the materials used in asphalt pavements are not sufficiently characterized, mainly concerning the changes that occur because of their mutual interaction at a microscopic scale. Thus, it is essential to develop the knowledge about the interaction between the constituents of bituminous materials used in flexible pavements by carrying out their characterization at a microscopic level, so as to understand their macroscopic structural behaviour. This additional study becomes more significant for modified or unconventional mixtures due to their complexity (e.g. AR). In fact, beyond the traditional constituents of the bituminous pavement layers, the use of crumb rubber recycled from used tires should be studied as a form of environmental protection and as a pavement performance enhancer.

When crumb rubber is blended with bitumen at high temperatures (wet process) to produce a modified binder, the two materials interact once the bitumen components migrate into the rubber causing it to swell. Initially, the bitumen-rubber interaction is a non-chemical reaction, where the rubber particles are swollen by the absorption of the aromatic oils of bitumen (Bahia and Davies, 1995). However, the base bitumen should be carefully selected to ensure that the content of light fractions of bitumen is high enough at the end of the curing process (Ould-Henia and Dumont, 2006). Bouldin et al. (1990) indicated that softer bitumens would be more compatible with rubber polymers and crumb rubber modification would be more effective than with stiffer bitumens.

The absorption of bitumen components by the rubber inevitably depletes the bitumen of the absorbed components and, consequently, modifies its properties by making it stiffer and more brittle (Green and Tolonen, 1977; Singleton et al., 2000; Artamendi et al., 2002; Airey et al., 2003). Furthermore, the rubber particles may also suffer some form of degradation (mainly devulcanization and depolymerization) when they are mixed with bitumen at high temperatures for prolonged periods of time (Green and Tolonen, 1977; Billiter et al., 1997b, Zanzotto and Kennepohl, 1996). The extent of swelling and degradation depends on the nature of the rubber, the chemical composition of bitumen and the mixing conditions of time, temperature and degree of agitation (Green and Tolonen, 1977; Huang and Pauli, 2008). Moreover, these processes will determine the mechanical properties of the crumb rubber modified binders (Abdelrahman and Carpenter, 1999). The asphalt rubber binders are very asphalt-dependent: lower contents of saturates and asphaltenes improve the asphalt capacity to dissolve rubber (Billiter et al., 1997a) and bitumens with low aromatic oil contents produce an asphalt rubber product with poor adhesive properties (Huff and Vallerga, 1979).

A re-vulcanization phenomenon may occur when mixing bitumen with rubber. The rubber vulcanization requires the use of sulphur and other agents, which may not react completely during this process. When rubber is mixed with hot bitumen, the vulcanization process will be reactivated and may continue for some time, depending on the interaction temperature (Green and Tolonen, 1977) and on the rubber volume fraction.

The size of rubber particles used to produce AR plays an important role in the final properties of the binder, with evident implication on pavement performance. Oliver (1981) concluded that elastic recovery of the asphalt-rubber binders tends to increase as the rubber particle size decreases. Chehovits et al. (1982) showed that coarser particles create a mix that is more sensitive to rubber concentration or bitumen grade. Frobel et al. (1978) concluded that finer rubber particles result in higher ductility than larger particles, and Lalwani et al. (1982) showed that toughness increases as particle size decreases.

Besides the changes in the morphology of the rubber particles, it is possible to observe variations in their density. Bitumen density also changes during the AR production. On one hand, before the introduction of rubber particles, bitumen is heated and its density tends to decrease linearly at 7.2×10^{-4} g/cm^3/ °C (Mochinaga et al., 2006; Basu et al., 1996). On the other hand, during the AR production at 180°C, the bitumen density decreases due to the volatilization and diffusion of the lighter fractions of bitumen into the rubber.

Furthermore, the density of bitumen during AR production can also change through the dissolution of extender oils, carbon black and other rubber components in the bitumen. This can occur because the extender oils and the carbon black are very compatible with bitumen. The extender oils are defined as any petroleum processed oil used in the manufacture of synthetic rubber applied in tire production (Cheremisinoff, 1996; Dick, 2003). In fact, the standard ASTM D 2007-03 is used to analyse these oils and other petroleum oils, such as bitumen. The carbon black used in the production of tire rubber is obtained by incomplete combustion of petroleum residues, being used as filler and giving the black colour to the tires (Arroyo et al, 2003). When rubber is milled, the carbon black is exposed, and in contact with hot bitumen it can become suspended on it. Additional amounts of carbon black are available as rubber particles split and de-vulcanize during AR production.

Asphalt rubber production, separation and characterisation

Bitumen and crumb rubber selection

Bitumen samples

Asphalt rubber properties are very dependent on the used bitumen and they change during the AR production time. Special attention was taken during the selection of the bitumens to be used in this work in order to control the variables to be studied. Therefore, all the bitumen samples were obtained from the same distillation column, since bitumen characteristics are very dependent on the petroleum sources and their processing (Lesueur, 2009). The source of bitumen was maintained in order to isolate the main variable studied in this work, i.e. the pen grade of the base bitumen. Thus, four commercial bitumens with different pen grades were chosen to evaluate their influence in the rubber morphology, namely bitumens 10/20 (A), 40/50 (E), 60/70 (I) and 150/200 (M).

Crumb rubber samples

The crumb rubber used in this work was produced by the cryogenic process and, according to the supplier, was obtained by the grinding of 30% of truck tires and 70% of car tires. The selected crumb rubber sizes (0.18 to 0.60 mm - sieves ASTM #80 and #30) fall within the grading envelope specified in Portugal and represent the AR mixtures typically produced and applied in Portuguese roads.

The supplied crumb rubber was sieved so as to reject a few particles unlikely retained in sieve ASTM #20 (0.850 mm) and to select only the fraction retained in sieve ASTM #40 (0.425 mm) (the finest rubber particles were rejected so that it would be feasible to use the "basket drainage method"). Then, the crumb rubber sieved in the laboratory was washed with toluene and dried in an oven at 135°C. After cleaning the rubber particles, they were observed and measured by using an optical microscope. The soluble percentage (ASTM D 6814-02) and density (apparent and bulk density - AG:PT/T144) of crumb rubber was also determined.

Production and separation of the asphalt-rubber binder

The method used to produce AR and collect the desired samples of AR, of recovered swelled rubber and of residual bitumen was the "basket drainage method" (Rahman, 2004). The asphalt rubber production facility is constituted by several equipments, presented in Figure 1, assembled in a laboratory ventilation chamber.

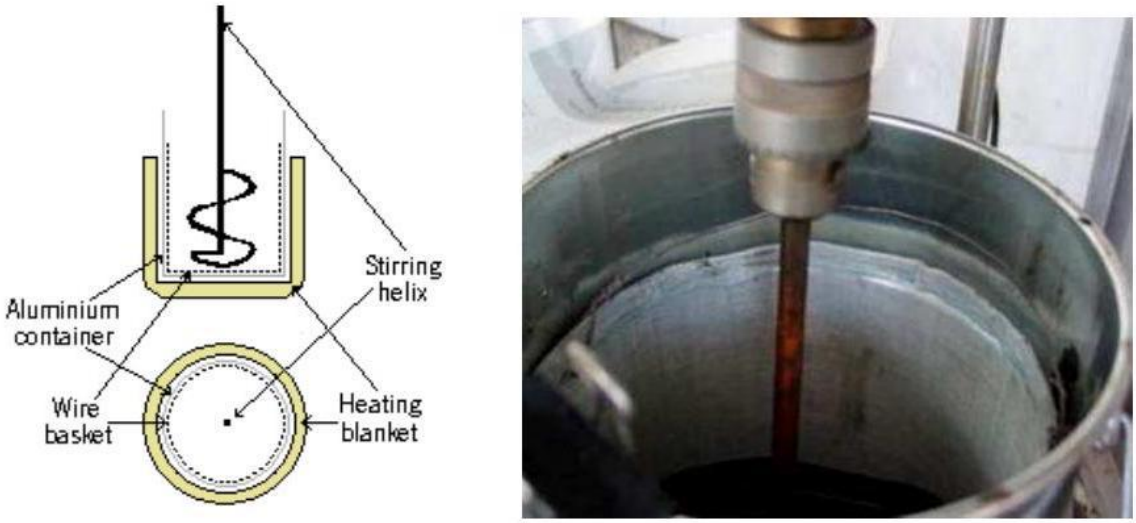

Figure 1. Scheme and photo of the asphalt rubber production facility

The wire basket used in the AR production facility was manufactured with a wire mesh, which was previously observed in an optical microscope (Figure 2) to measure its average opening dimension (#0.370 mm). The microscope was able to draw an idealized picture of the mesh in order to assess the referred opening dimension, by using a method of image analysis (Leica Quantimet 550).

Figure 2. Optical microscopy photo and drawing of the wire mesh used to make the basket

The process used to produce and collect the several samples of AR, of recovered swelled rubber and of residual bitumen consisted of heating of 1 kg of each base bitumen at 180 °C (collecting a sample). Then, 21%(w/w) of crumb rubber were added to the bitumen, and the resulting AR binder was continuously heated at 180°C for 60 minutes (digestion time), while stirring the binder at 230rot/min (Figure 1). A sample of the produced asphalt rubber (AR) was collected and finally, the wire basket with the AR binder was suspended in an oven at 180 °C for 15 minutes, so as to separate its constituents (Figure 3) and collect a sample of the residual bitumen (Res) (Figure 4).

Figure 3. Separation between the crumb rubber and the residual bitumen of the *AR*

Density determination during AR production

Aiming at assessing the variation of the apparent density of the AR binder at the selected production temperature (180°C), the density was measured every 5 minutes during the AR production. Even though some standard tests methods (e.g. those using densimeters) were found in the literature to be suitable to measure the density of bituminous binders (ASTM D3142-05, ASTM D 1298-99, prEN 15326), they
were not appropriate at the selected production conditions (the density should be measured almost continuously at 180°C).

Figure 4. Residual bitumen and recovered rubber after separation

Then, another approach about new technological devices suited to measure the apparent density of the binders also proved to be fruitless, because these devices are not able to evaluate the production conditions continuously. Therefore, the methodology selected for density assessment was based on the definition of density, i.e. by measuring the mass/volume of the binder during the production of the AR.

Technique

In this work, simple experimental equipment was developed to assist on the measurement of the mass and volume of the binder during the AR production. First, a measuring device made of a platform with two scales attached (Figure 5) was made. Then, the container used to produce the AR binders (with and without the basket) was filled with different and known volumes of liquid, assessing the corresponding height with the measuring device. Thus, two calibration lines (with and without the basket) were obtained relating the volume of liquid in the container with the average height measured in the scales of the measuring device. Finally, the density of AR was assessed every 5 minutes, by weighting all the AR production facility (W_{PF}), i.e., the heating blanket (W_{HB}), the container (W_{CT}), the basket (W_{BK}) and the AR binder (W_{AR}), and by measuring indirectly the volume of AR binder (V_{AR}) in the container with the measuring device. The density was the ratio between the measured values of weight and volume of the AR binder. During this procedure the AR production facility was placed on a balance and the system horizontality was confirmed using a "spirit level" installed in the measuring device (Figure 5).

The evolution of the density of the base/residual bitumen during AR production was determined using the same technique. However, the measurements (weight and volume) were carried out only in the residual bitumen left in the container after removing the basket with the rubber. The evolution of the rubber density was calculated based on the measured values of the residual bitumen and AR densities at the different interaction times.

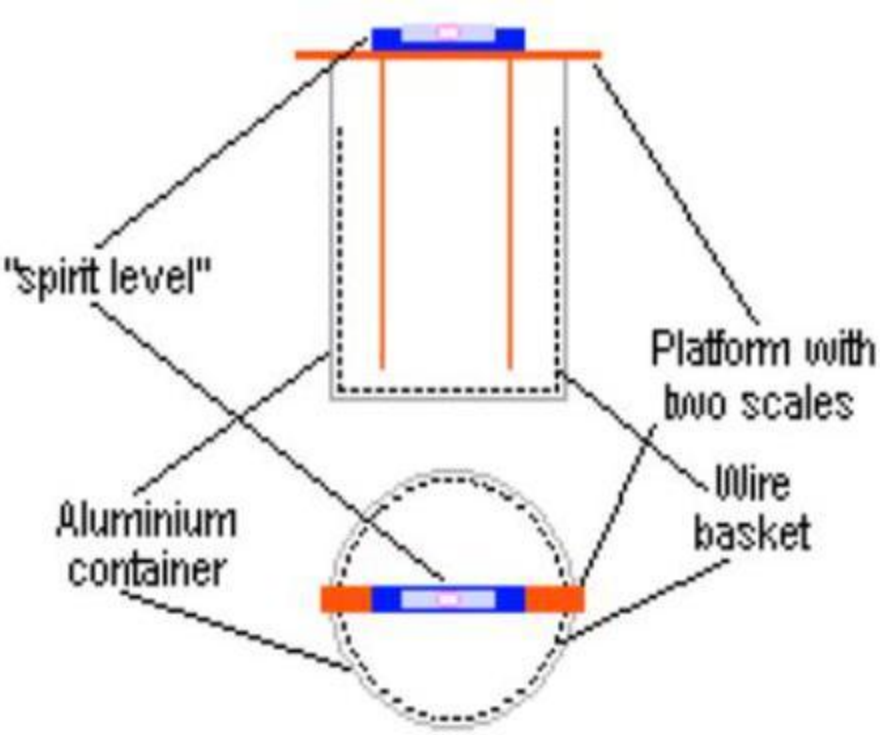

Figure 5. Scheme of the AR production device used for density assessment

Calculations

The apparent density of AR(D_{AR}) was calculated according to Equation [1], being the ratio between the measured values of its weight (W_{AR}) and volume (V_{AR}).

$$D_{AR}(g/\mathrm{cm}^3) = \frac{W_{AR}(g)}{V_{AR}(\mathrm{cm}^3)} = \frac{W_{PF} - W_{HB} - W_{CT} - W_{BK}(g)}{V_{AR}(\mathrm{cm}^3)} \quad (1)$$

Recovery and analysis of AR rubber particles

Recovery of the rubber particles from the *AR*

In order to prepare the recovered rubber particles for microscopic observations, 2.0 g of recovered rubber were put in a container with approximately 200 mL of toluene, slightly shaking the container until the rubber particles were totally dispersed. The resulting solution was filtered with a filter paper and washed again with toluene until the filtered solution became completely clean. Finally, the filter paper with the resulting recovered rubber was dried in an oven at 135°C and then analyzed by optical microscopy.

The preparation of the few rubber particles that passed through the wire basket (suspended in the residual bitumen) for microscopic analysis consisted of introducing 2.0 g of residual bitumen in a baker of 250 mL capacity and diluting the residual bitumen with small amounts of toluene while stirring the solution with a glass rod. The resulting solution was filtered with a filter paper and washed again with toluene until the filtered solution became completely clean. Finally, the filter paper with the resulting

filtered rubber was dried in an oven at 135°C and the clean filtered particles were analyzed by optical microscopy.

The amount of rubber in the residual bitumen was determined by using the standard solubility test method EN 12592. According to this standard method, the sample must have 2 ± 1 g. Therefore, the recovered and filtered rubber samples for microscopy analysis were also obtained by using standard EN 12592, repeating the procedure several times (if necessary) until the adequate number of rubber particles were obtained (about 150 in this study, according to standard ISO 9276).

Analysis of the rubber particles used in the AR production

Rubber apparent density

The apparent density of the original crumb rubber was assessed according to standard ASTM D 792-08. Approximately 2.0 g of crumb rubber were weighted in an analytical balance. Then, a sieve with an opening dimension lower than the size of the smallest rubber particles was selected and weighted (dry and in the isopropyl alcohol). Finally, the rubber particles were sealed and weighted, with the sieve, in the isopropyl alcohol. The apparent density of the used crumb rubber was calculated using Equation [2].

$$\rho_{\mathrm{a}} = 0.0012 + \left(m_{ds} \times \rho_{ip}\right)/[0.99983 \times (m_{sll} - m_{sl})] \quad (2)$$

Where:
ρ_{a} - Apparent density of the crumb rubber (g/cm^3);
m_{ds} - Mass of the dry sample of crumb rubber (g);
ρ_{ip} - Density of the isopropyl alcohol (g/cm^3);
m_{ssl} - Mass of the sealed sample of crumb rubber in isopropyl alcohol (g);
msl - Mass of the sieve in isopropyl alcohol (g).

Rubber bulk density

The sample of rubber previously weighted was boiled and stirred to release all the air and then the volume occupied by the boiled crumb rubber was assessed. This analytical procedure is described in the standard test AG:PT/T144.

Percentage of devulcanization

The crumb rubber solubility was assessed according to ASTM D 6814-02 standard, in order to indirectly evaluate the depolymerization potential of the studied rubber after interacting with bitumen. The solvents used in this test were toluene and cyclehexane.

Microscopy analysis of the rubber particles recovered and filtered from *AR*

The washed and dried rubber particles were analysed by optical microscopy using an Olympus BH-2 microscope and a magnification of 100x (10x × 10x). The rubber particle size was quantified using a method of image analysis (Leica

Quantimet 550). The results were obtained after studying typically 150 rubber particles (ISO 9276; Mercus, 2009; Scarlett, 2006).

Results and discussion

Screening of the changes in the density of the studied materials

During the production of the AR binders, the density of base bitumen, rubber and AR changes significantly. The study of the variations of the material density, throughout the AR production process, is very important to adequately design the production equipments and to understand the interactions between the bitumen and the rubber particles. The variation of the densities of the bitumen, rubber and AR binders, considering the four evaluated commercial base bitumens, is graphically represented in Figures 6, 7, 8 and 9.

The lines presented in Figures 6 to 9 were drawn to support the examination of the overall tendency of the individual results taken every 5 minutes. The lines presented in Figure 6 were obtained by linear regression of the bitumen results. In Figures 7 and 8 it was impossible to adjust the experimental results with usual numerical regression lines. However, the first 15 minutes (roughly) of digestion can be adjusted with quadratic polynomial regression lines, and the subsequent time can be adjusted with linear regression lines. Thus, the trend lines presented were drawn by connecting these to regression lines. Figure 9 summarizes, in the same graphic, the results of the three materials (bitumen, AR and rubber) previously presented in Figures 6 to 8.

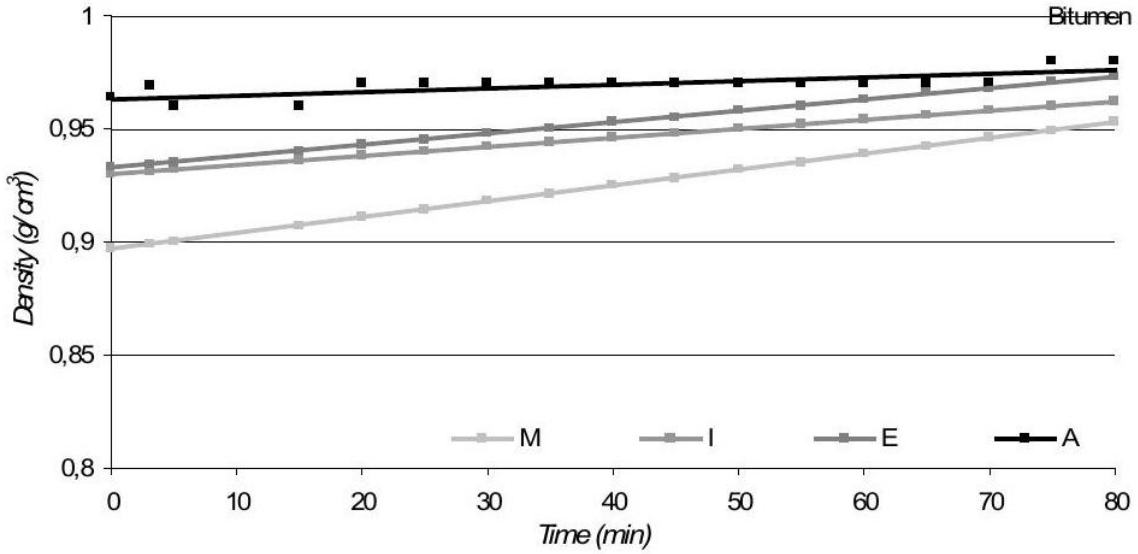

Figure 6. Screening of the evolution of the density of bitumen during the production of asphalt rubber

The values presented were measured at 180°C. At this temperature the density of bitumen is lower than at ambient temperature. In these bitumens the lowest density was 0.89 and refers to the softer bitumen (M – 150/200) before interacting with rubber.

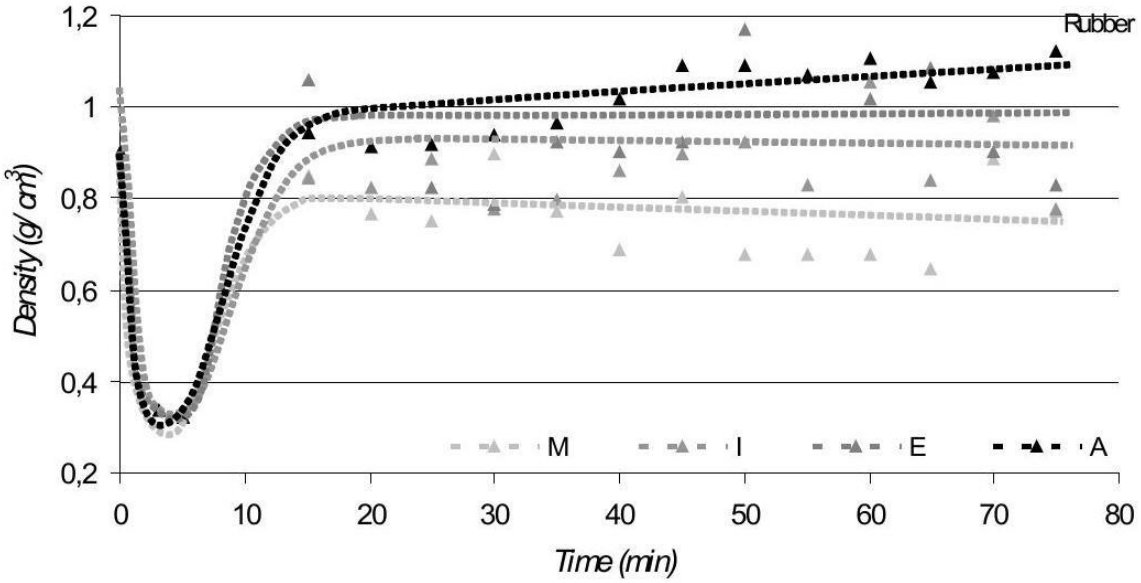

Figure 7. Screening of the evolution of the density of rubber during the production of asphalt rubber

The AR binders are primarily composed by base bitumen and crumb rubber. During the interaction period (digestion), several phenomena occur and some are independent of the interaction between the constituent materials:

- Bitumen becomes denser and harder due to volatilization after being heated and stirred for more than 60 minutes (Figure 6);
- Crumb rubber contains a large quantity of air and moisture in and among their particles. When heated, air and water expand their volume (thus reducing the rubber's density), before being replaced by the liquid bitumen (Figure 7).

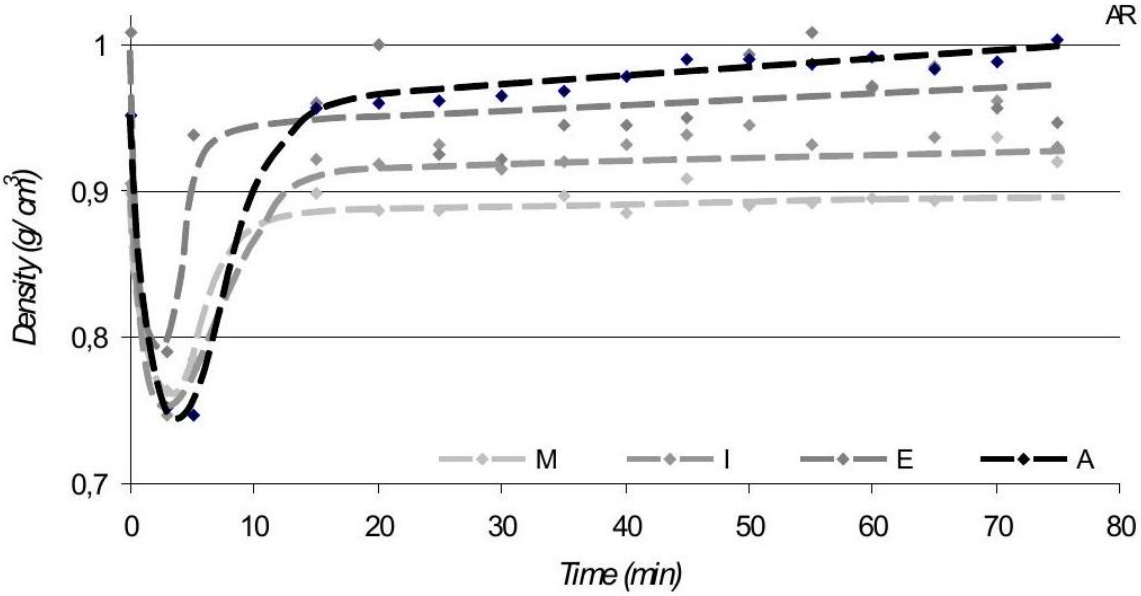

Figure 8. Screening of the evolution of the density of the asphalt rubber during its production

The study of the major reduction in the density for rubber and AR binder at start of digestive process is a very interesting issue, because this significant increase in the volume occupied by the AR binder should have an important impact on the design of the AR production plants. In this work, it was only possible to show the maximum volume occupied by the AR binder and by rubber (minimum density). The reduction of AR or rubber density at the beginning of the AR production is mainly due to the sudden increase of rubber temperature after being added to the very hot bitumen, which causes a great increase in the volume of the rubber particles. Therefore, the extent of the density reduction depends on the rubber temperature, particle size and milling process, and on the storage conditions.

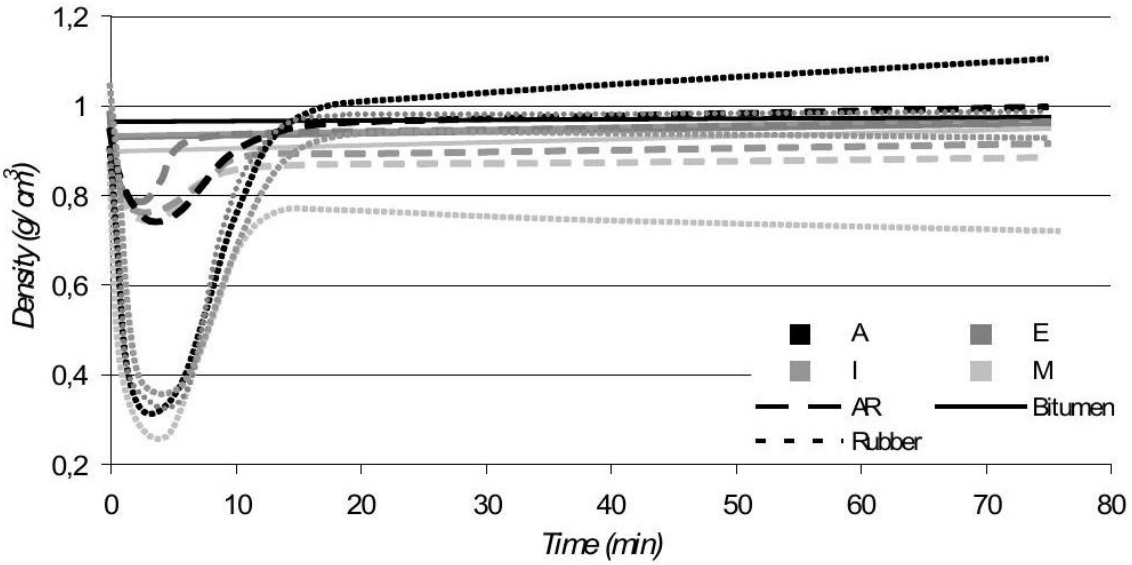

Figure 9. Screening of the evolution of the density of the materials during the production of asphalt rubber

During the rubber-bitumen interaction, other phenomena may also occur:

- Some components of the rubber, as extender oils, carbon black and other additives can be dissolved in the bitumen;
- The rubber particles swell, due to the diffusion of small molecules of the bitumen in the reticulated molecular structure of rubber;
- The molecules of bitumen diffused in rubber structure also induce a relaxation of the links between the rubber atoms, thus decreasing the rubber bulk density;
- The rubber particles saturated with bitumen molecules change into a brittle gel, which can split by stirring and heating (occasional depolymerization may occur).

The components of rubber that were dissolved in bitumen, combined with the absorption of the smallest molecules of the bitumen (that contributed to its fluidity and softness) by rubber, make the bitumen denser. Simultaneously, the density of bitumen increases due to heating (evaporation of its lighter molecules). Meanwhile, bitumen and

crumb rubber particles begin to interact and the different bitumens cause dissimilar evolutions in the rubber density. Actually, when rubber interacts with the hardest bitumen (A), its density increases (after the first 15 minutes of contact). At the end of the interaction time, the rubber density is higher than its apparent density ($0.9\ g/cm^3$), but lower than its bulk density ($1.21\ g/cm^3$). Nevertheless, when rubber interacts with the softer bitumen (M) the density of the rubber decreases over time and its final value is lower than the rubber apparent density (a similar, but less evident behaviour, was observed with base bitumen I). During the rubber interaction with base bitumen E, the density of the rubber particles remained very stable.

When analyzing all the materials, it was observed that the AR produced with base bitumen A was denser than the residual bitumen (bitumen after interaction with rubber), but the density of the swelled rubber particles is lower than the bulk density of the initial crumb rubber particles. This occurs due to the higher bulk density of the crumb rubber and insufficient quantity of small molecules in the harder base bitumen to further swell the rubber particles. The bulk density of the crumb rubber is largely higher than that of any other material used to produce the AR. The density of the recovered rubber particles from this AR($1.12\ g/cm^3$) is higher than the density of the residual bitumen. Thus, the densification of the bitumen due to the loss of the small maltenes is not balanced by the reduction of rubber density.

All other AR binders produced in this work presented densities lower than those of their residual bitumen, and the final densities of the softer residual bitumens (I and M) are even lower than those of the corresponding base bitumens. This happens because the smallest bitumen molecules deeply diffuse into the bulk rubber, causing it to swell while changing the crosslink density by depolymerisation and relaxation of the links between atoms, thus reducing the density of the rubber particles. Actually, when rubber interacts with softer bitumens, its final density is lower than the initial apparent density. However, despite the significant reduction in the apparent density of the rubber particles after interacting with softer bitumens, all studied AR binders increased their densities during the interaction phase. The balance between the significant reduction of the rubber density and the increase of the residual bitumen density results in an increase of the AR density, because the percentage of natural and polymeric rubber (not taking into account the bitumen molecules diffused in the swelled rubber) is clearly lower than that of the bitumen.

Study of the morphology of the crumb rubber particles

The importance of studying the morphology of rubber particles, before and after the interaction with bitumens of different chemical constitution, is based on two facts: (i) the morphology of the crumb rubber determines the form and extension of the interaction with bitumen and has a significant influence in the viscosity of the AR; (ii) bitumens with different constitution interact with rubber particles in diverse extension and rate, causing dissimilar changes in the rubber particles morphology.

Density of crumb rubber particles

The crumb rubber comprise small particles $\left(425 < \emptyset_{eq}\,(\mu m) < 850\right)$ that retain air and moisture among them. Moreover, rubber is a porous material containing air and moisture in the pores. The apparent density of this material can be determined:

- By the comparison between the volume (water displacement) and the weight of a sample (volume analysis);
- By the comparison between the weights of a sample before and after immersion in a liquid (weight analysis).

Apparent density

The apparent density of the crumb rubber could not be assessed by using the volume analysis in water because the density of the crumb rubber is lower than that of water. Thus, the rubber particles float in water, as presented in Figure 10a.

(a) Crumb rubber in water at 25 ºC

(b) Crumb rubber in water at 25 ºC after applying standard test AG:PT/T144

Figure 10. Assessment of the (a) apparent and (b) bulk density of the crumb rubber

Therefore, the apparent density of the rubber was determined by weight analysis, using a liquid with a density lower than that expected for rubber apparent density. The average value of the apparent density obtained in laboratory was 0.9 g/cm^3. The liquid used in the test was the isopropyl alcohol with a density of 0.783 g/cm^3, since it does not interact with rubber at the temperature and time of the test.

Bulk density

In order to assess the bulk density of the used crumb rubber, it was necessary to expel all the air in and among the rubber particles (Figure 10b). The average bulk density determined after repeated tests was 1.21 g/cm^3.

Percentage of devulcanization evaluated based on the crosslink density

The weight loss of the crumb rubber was 10.9% and 10.7% to toluene and cycle-hexane, respectively, meaning a low depolymerization potential. Beyond the depolymerization potential, the weight loss of the rubber can also be due to some soluble additives and fillers extracted by the solvents.

Form and size of the rubber particles

The rubber particles were observed by optical microscopy before and after the interaction with the different bitumens in order to assess their form and average size. The optical microscopy photos of the crumb rubber are presented in Figure 11.

The use of toluene to wash the rubber particles (when preparing the test samples) could change their dimensions by dissolving rubber constituents that were not vulcanized. However, the maximum mass change of rubber particles after being in contact with toluene (ASTM D 6814-02) was only 10%, i.e. toluene had a reduced influence on the microscopy results. Moreover, being the procedure equal for all rubber samples, even if it have slightly influenced the absolute results, it did not change their comparison (i.e. the influence of toluene was similar in all rubber samples). Therefore, the results of rubber morphology are valid, and the differences found after interaction with the studied bitumens are only dependent on them.

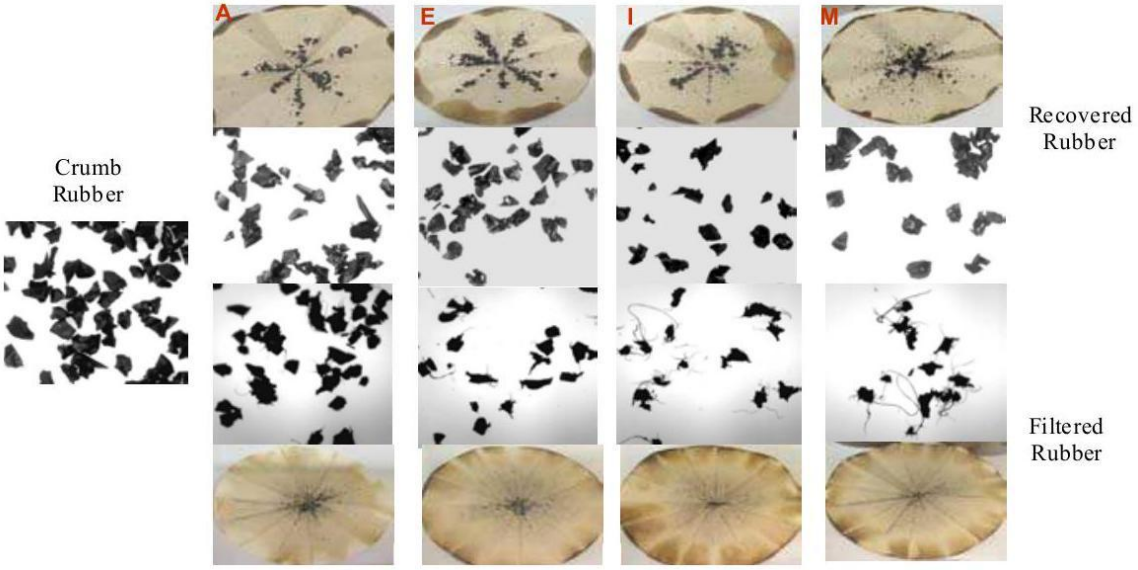

Figure 11. Optical microscopy and macroscopic photographs of crumb rubber before and after interacting with the four base bitumens

Before interacting with bitumen, rubber particles present different sizes and their form is irregular and angular, but their faces are almost plain (some appendixes increase their surface area). The changes in the crumb rubber morphology after interacting with the different bitumens (differences between the initial and recovered rubber particles) are evident for all the AR binders produced with the four studied bitumens. The recovered rubber particles differ in shape and size, whereas the initial crumb rubber particles are clearly more homogeneous. These changes are higher than 11%, and cannot only result from its solubility in the solvent constituents of bitumen (depolymerization and devulcanization changes may also occur).

By comparing the recovered rubber particles from AR binders produced with different bitumens, it was possible to observe that the interaction with softer bitumens (M) resulted in a higher variability in the shape and size of the rubber particles than with the

harder bitumens (A). This suggests that bitumen constitution has a significant influence in its interaction with the crumb rubber.

The clear evidence of the changes in the rubber particles morphology during the AR production can be seen in the microscopic photos of the rubber particles filtered from the residual bitumen. These photos confirm the reduction of the crumb rubber size during the AR production (i.e. some rubber particles were found in the residual bitumens, but the initial rubber particles could not pass through the wire basket).

The results indicate that the interaction of the crumb rubber particles with softer bitumens is clearly higher. Thus, the morphology of the rubber particles is clearly more influenced by these bitumens (apparently the rubber particles in contact with softer bitumens swell much more, splitting and releasing a great amount of very small elements recovered in the residual bitumen). The filtered rubber detected in the microscopy analysis is an obvious sign of the decrease in the concentration and size of the rubber particles in the residual bitumen, indicating a solubilisation of the discrete particles of rubber in the presence of very hot and soft bitumen.

The comparison between the several types of bitumen used to produce AR showed that the highest variations in the physical characteristics of the binder (AR compared with the base bitumens) are obtained with softer bitumens (Peralta et al., 2009a). This result is consistent with the microscopic evaluation of the most significant changes in the morphology of rubber particles when softer bitumens are used to produce AR binders. Thus, even using the 150/200 bitumen (M), which is not generally applied to produce AR or HMA mixtures, the experimental results showed that it presents the greatest interaction with the crumb rubber, thus being a good alternative to produce AR binders with final physical and rheological properties similar to those of the original 60/70 bitumen (I) (Peralta et al., 2009c).

Previously, Peralta (2009) and Peralta et al. (2009 b, c) presented a thorough study of the physical and rheological properties of the different base bitumens used to produce the current AR binders (including the evaluation of the recovered bitumens and the AR binders). The reported results were coherent with the data presented in this paper, since the physical and rheological properties of the AR binders produced with softer bitumens presented the highest changes after interacting with crumb rubber (which also had the highest morphological variation).

Even though the interactions of rubber particles with softer bitumens are clearly higher than with harder bitumens, the stability of the resulting AR binder is usually worse (e.g. the R&B temperature of AR binders produced with softer bitumens is lower than with harder bitumens). In fact, the possible appearance of rutting on pavements with AR binders produced with softer bitumens, despite the increased stiffness of the resulting residual bitumen after interaction with rubber, may be related with the amount of light fractions of bitumen absorbed by rubber. These fractions are largely formed by bitumen saturates, including waxes (Gawel et al., 2006), that may deform at high operating temperatures.

Changes on the morphology of the rubber particles after interacting with different base bitumens

The quantitative representation of the results obtained when analysing (Leica Quantimet 550) the microscopy images of the rubber particles is presented in Figures 12 to 14.

These Figures show the influence of the penetration grade of the base bitumen in the change of morphology of the rubber particles during the AR production. In fact, Figures 12 to 14 summarize the observations made in this part of the work, which allow a holistic understanding of the AR production process, considering the effect on rubber particles.

Initially, the equivalent diameter of the studied crumb rubber and that of the recovered and filtered rubber particles after interacting with the four base bitumens (i.e. the size/shape of recovered and filtered rubber) is presented in Figure 12.

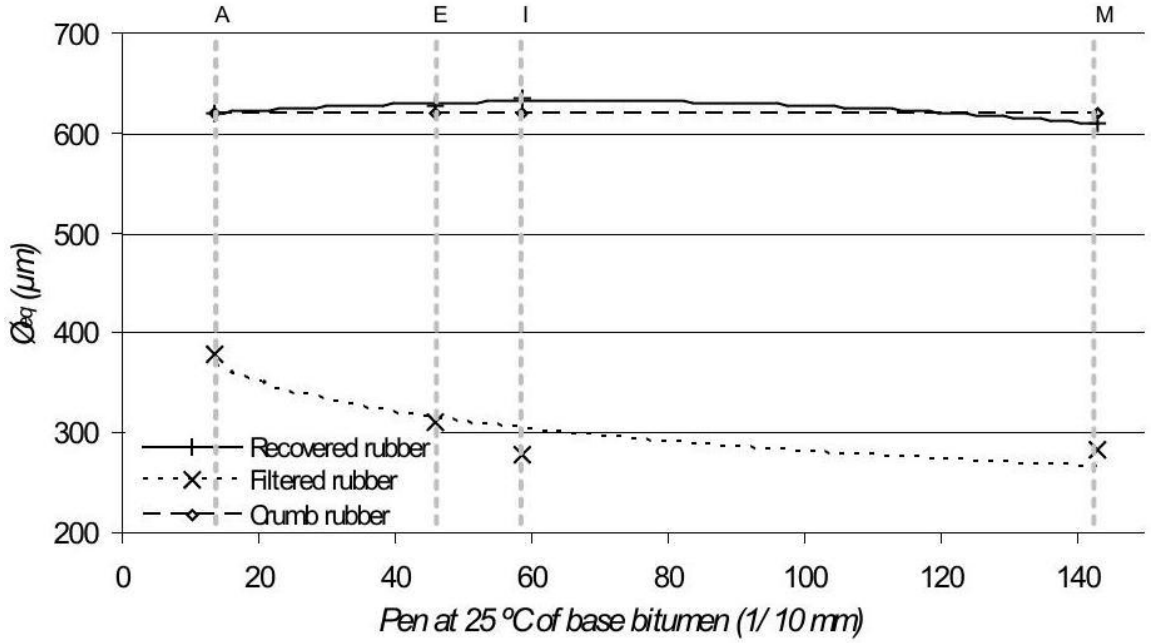

Figure 12. Size of the recovered rubber and filtered rubber particles after interacting with the four studied bitumens, compared to the added crumb rubber

The same crumb rubber was always used during the production process of the different studied AR binders, with an $\emptyset_{eq}$ of 620.10μ m. The added crumb rubber is represented in Figure 11 by a straight line (dashes) which is independent from the base bitumens.

At the end of the ARs production, the swelled rubber particles were recovered and their equivalent diameter assessed. The influence of base bitumen penetration in the evolution of the $\emptyset_{eq}$ of the rubber particles after interaction is described by a quadratic function. Therefore, a slight increase of the volume of the rubber particles is detected for base bitumens with a penetration lower than 70 dmm , but for softer bitumens the average size of the rubber particles decreases. Conversely, the size of the rubber particles filtered from the residual bitumen is considerably lower than that of the crumb rubber particles and varies significantly with the penetration of the used base bitumen. The relation between the size of the filtered rubber particles and the penetration of the base bitumen can be approached by a logarithmic trending line. The particles filtered from the residual bitumen A are the largest and those filtered from residual bitumen *M* the smallest.

Rubber swelling was assessed by using the "basket drainage method" (Airey et al., 2003) combined with the "sphere AR production simulator" method (Peralta et al., 2009b;

Peralta, 2009). The combination of the two methods allowed obtaining the variation of the rubber weight during the AR production. The percent variation of the rubber weight (Figure 13), which is a direct indication of the rubber swelling, was obtained by comparing the weight of the crumb rubber before and after the interaction with the four studied base bitumens.

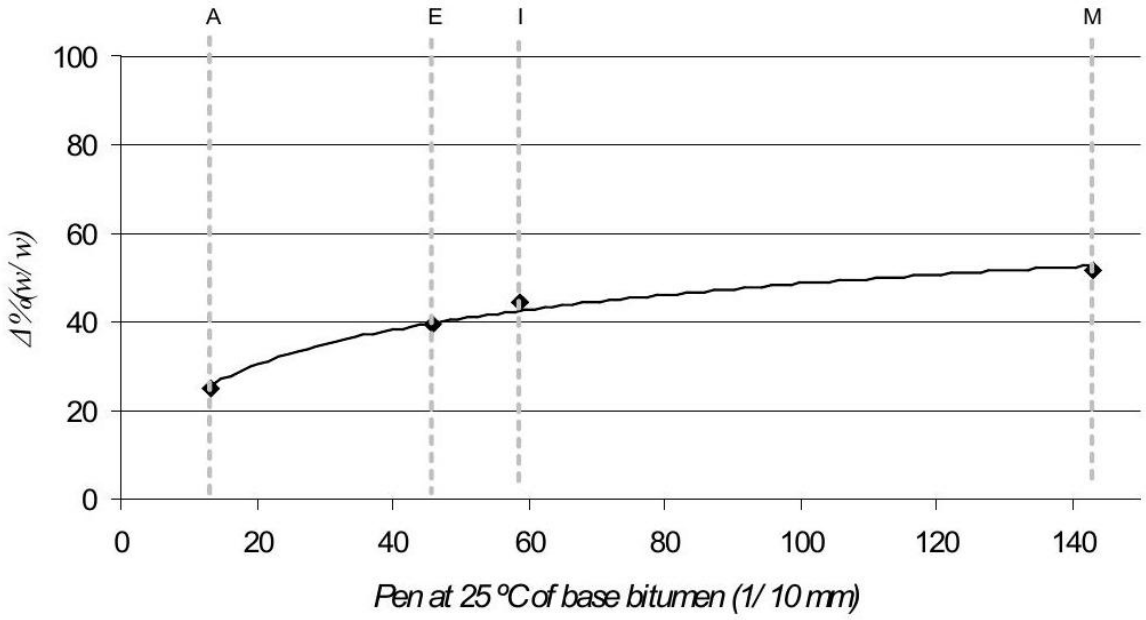

Figure 13. Percent variation of the weight of the swelled rubber particles, after interacting with the studied bitumens

The differential weight percentage between the added and the recovered rubber from each AR binder, i.e., the rubber swelling percentage, varies logarithmically in function of the penetration of the used base bitumen.

Rubber swelling increases with the penetration of the base bitumen, reaching a maximum value that corresponds to the saturation of the rubber particles. At this stage, the rubber particles have a gel type structure and the diffusion of bitumen molecules into the rubber reticules cannot continue. The stirring and the high temperatures used to produce AR cause the rupture of the particles, exposing the centre of each particle to the bitumen, thus maintaining the swelling process. Simultaneously, parts of the rubber particles with a gel structure are partly or completely depolymerised, depending on the concentration of light molecules in the bitumen. In fact, when the rubber swelling process is complete, splitting and degradation of gel rubber particles can occur in the AR binder. Therefore, it is evident that, over the AR production process, the relative importance of the rubber particles in the composition and in the behaviour of the AR binder increases.

The evolution of the rubber weight concentration in the AR and in the residual bitumen as a function of the penetration of the used base bitumen (Figure 14) was quantified and compared with the concentration of the crumb rubber at the beginning of the AR production process (21%w/w).

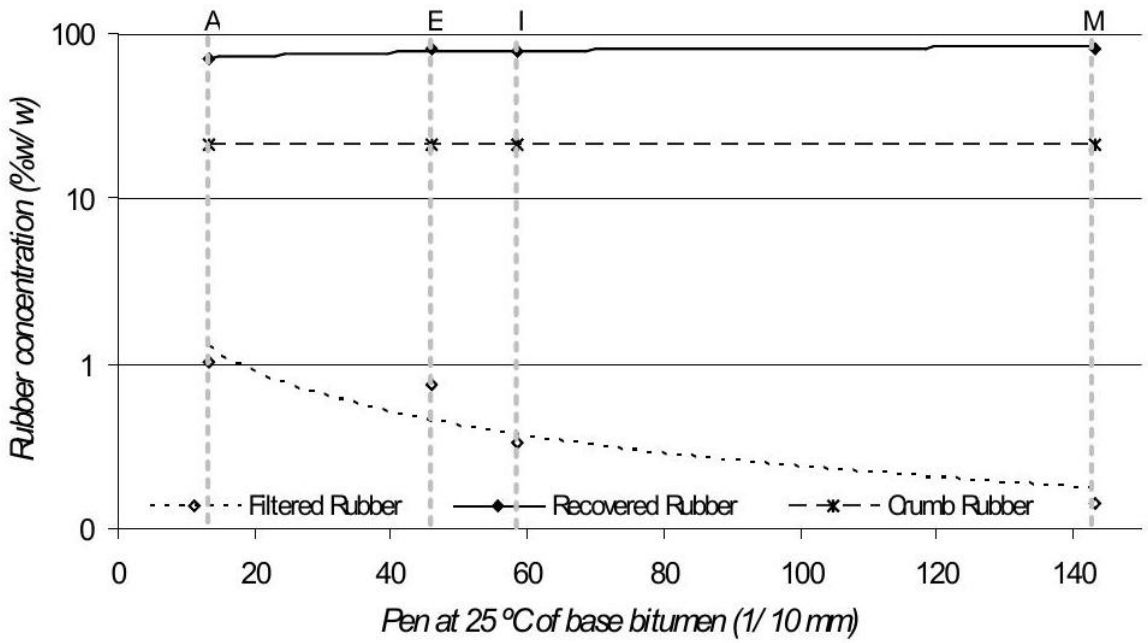

Figure 14. Weight percent of rubber particles in the base bitumen (added for AR production), in the asphalt rubber and in the residual bitumen

The logarithm of the rubber weight concentration in the initial base bitumen, in the final AR and in residual bitumen can be related with the penetration of base bitumen through a potential trending line. Comparing these results with those of rubber swelling (Figure 13), it was noticed that the increase of the differential between the initial and final weight concentration of crumb rubber is nearly the double of the rubber swelling percentage (for all base bitumens), thus confirming that the swelling phenomenon is caused by the absorption of parts of the bitumen.

The concentration of rubber particles in the AR binder is of major importance due to several reasons:

- The element that promotes the connection between the aggregates in AR mixtures is the residual bitumen, since the swelled rubber particles, by themselves, do not adhere to the aggregates. It was observed that the clean swelled rubber particles are not sticky and burn when heated on the absence of bitumen;
- The volume fraction of rubber in the AR binders produced in this work was always higher than 70%, being 82% for the AR produced with base bitumen M;
- In asphalt mixtures, the rubber particles can be seen as aggregates that partially hinder the contact (attrition) between mineral aggregates.

The change in the weight concentration of rubber particles is nearly independent of the base bitumen penetration. The increase in the rubber weight concentration was about 49% when bitumen A (10/20) was used to produce AR, and this value just grew up to about 61% when bitumen M (150/200) was used. The difference in the rubber concentration when producing AR with bitumens A and M is only of 12%. Since rubber particles reach the saturation after interact with bitumen, it is expected that, by using an

initial weight concentration of rubber of 21%, the final concentration of rubber will never exceed 82%(21% + 61%), independently of the base bitumen penetration.

The rubber weight concentration on the residual bitumen decreases when softer base bitumens are used to produce AR. This fact can result from the degradation of the rubber particles suspended in the softer residual bitumens. Moreover, when softer bitumens are used, rubber particles can swell to their saturation and, being the volume fraction of rubber considerable, re-vulcanization and re-polymerization of the rubber particles can occur, and the clusters formed by the assembly of rubber particles can have difficulties to pass through the wire basket.

Conclusions

The main conclusions that can be drawn from the results of this work are the following:

- During the AR binder production, the interaction of the crumb rubber particles with softer bitumens is clearly higher than with harder bitumens;
- Several morphological alterations on the crumb rubber were detected during the AR production and were related to the used base bitumen;
- The molecules of bitumen diffused in the rubber structure induce a relaxation of the links between the rubber atoms causing a decrease in the bulk density of rubber;
- The rubber particles saturated with bitumen molecules become a brittle gel that split by the action of stirring, heating and eventual depolymerization;
- By using an initial weight concentration of crumb rubber of 21.0%, the volume fraction of rubber in the ARs produced in this work was always higher than 70%, with a maximum value of 82% for the AR produced with base bitumen M;
- The particles filtered from residual bitumen A are the largest and the ones filtered from residual bitumen M are the smallest, due to a higher degradation of the rubber particles suspended in the softer bitumen;
- When AR binder is produced with softer bitumens, rubber particles can swell to their saturation and re-vulcanization and re-polymerization among the rubber particles can occur if the volume fraction of rubber particles is considerable;
- During the AR production the rubber particles swelled 250 to 300% their weight, respectively for the hardest ($A - 10/20$) and softest ($M - 150/200$) studied bitumens. However, the maximum increase in the equivalent diameter of the rubber particles was only 2.5% for bitumen 60/70.

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