Moisture damage resistance of hot-mix asphalt made with paper industry wastes as filler

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Abstract

Certain paper industry wastes display high recycling potential. In this investigation, the feasibility of using green liquor dregs and biomass fly ash from the paper industry as filler in hot-mix asphalt (HMA) for road pavement construction is analysed. Particularly, the moisture damage resistance (i.e., water sensitivity) of an AC 22 base B50/70 G has been studied using the Indirect Tensile Strength Test at the Marshall mix design optimum asphalt content. The most important filler properties have been determined to study water resistance: filler water content, grain size distribution using light scattering analysis techniques, morphology using a scanning electron microscope (SEM), chemical and mineralogical composition using X-ray fluorescence (XRF) and X-ray diffraction (XRD) techniques, detrimental fines content using the methylene blue test and the stiffening effect of the filler in the mastic by determining the ring and ball (R&B) softening temperature and the bitumen penetration grade. Additionally, the Rolling Bottle method and Boiling Water tests have been conducted to analyse the asphalt-aggregate bond. A control filler (i.e., commercial limestone filler) was used to compare the results. Also the mechanical properties (stiffness and resistance to the permanent deformation) of the mixtures were studied. As a result, it can be concluded that dregs have poor water resistance. Additionally, fly ash displayed inadequate water resistance for HMA.

Keywords: paper industry waste; dregs; biomass fly ash; filler; hot-mix asphalt; water resistance.
1. Introduction

In recent decades, many investigations have been conducted into the use of wastes in road pavement layers, including the use of debris such as crumb rubber from tire waste (Oliveira et al., 2013), construction and demolition wastes (C&DW) (Pasandín et al., 2015), mixed recycled aggregate (Medina et al., 2014), reclaimed asphalt pavement (RAP) (Moghadas Nejad et al., 2014), coal waste (Modarres and Ayar, 2014), etc.

The paper industry generates large amounts of waste, that could cause severe environmental and ecological impacts (Zhang et al., 2015). In the European Union, 11 million tonnes of waste per year are produced, 70% of which comes from the paper recycling industry (Monte et al., 2009). Some of these wastes have great reutilization potential; as a result, in the last decade, some investigations into the use of this type of waste have been conducted, and most studied paper industry wastes in road construction (Modolo et al., 2010), the manufacture of ceramic materials (Warpechowski da Silva et al., 1998), interior coatings and acoustic bricks (Wolff et al., 2015), forestry and the horticulture (Cabral et al., 2008) and biogas production for the road transport sector (Larsson et al., 2015).

However, there is limited research on the use of paper industry waste in the manufacture of hot mix asphalt (HMA) for road pavement construction. In this regard, the research performed in Portugal by Modolo et al. (2010) is unique in that it analysed the possibility of using green liquor dregs as a partial substitute for natural aggregate. These researchers concluded that the dregs must be subjected to a pretreatment (drying at 105 °C and subsequent washing with distilled water at 70 °C for periods of 10 minutes) to ensure that the mixtures have suitable water resistance. Despite these good results, Modolo et al. (2010) also concluded that the high plasticity of dregs could cause an increase in the bitumen content of the mixture and consequently lead to mixtures susceptible to volumetric changes.

It is also important to note the existence of an international patent of the International Paper Company, invented by Mark C. Labart (1995) and entitled “USE OF SLAKER GRITS AND GREEN LIQUOR DREGS IN ASPHALT PAVING” (US 5407478 A). The patent describes the use of lime slaker grits and green liquor dregs as partial substitutes of the finer fraction of natural aggregate in the manufacture of HMA for a parking structure.
Only a few researchers have studied the feasibility of using biomass fly ashes as filler in bituminous mixtures. Nevertheless, none of them have investigated with biomass fly ashes from the paper industry. In this regard, Melotti et al. (2013) analyzed biomass ashes from 12 different power plants. They focused their study on the geometrical, physical and chemical properties of these ashes and suggested that most of them could be used as substitute for natural filler in bituminous mixtures. However, the mechanical and physical properties of bituminous mixtures made with biomass fly ashes were not analyzed.

In addition to aggregates and bitumen, filler (i.e., mineral powder with size passing the 0.063 mm sieve) is one of the primary compounds of HMA. The goal of this investigation is to analyse if two paper industry wastes (dregs and biomass fly ash) are suitable for use as filler material in HMA for base course materials in road pavement, with the aim of reducing waste disposal and saving raw materials, which contributes to sustainable development and cleaner production practices. This investigation focuses on moisture damage resistance of such mixtures by analysing water sensitivity resistance, asphalt-aggregate affinity and other properties of filler (water content, size distribution, geometry, chemical and mineralogical composition, detrimental fines content, stiffening effect) that could affect the HMA performance. Commercial limestone filler was used in the control mixture.

2. Materials and methods

2.1. Aggregates

Two types of typical commercial aggregates were used in this study to manufacture HMA: siliceous in the coarse fraction and limestone in the fine fraction. The properties of both aggregates were evaluated according to the Spanish General Technical Specifications for Roads, also known as PG-3 (MFOM, 2008). Table 1a shows the bulk specific gravity (ap), the water absorption (W24) (AENOR, 2014), the sand equivalent (SE) (AENOR, 2012b), the Los Angeles (LA) abrasion coefficient (AENOR, 2010) and the flakiness index (AENOR, 2012a). As shown in Table 1a, both aggregates complied with PG-3 as base course materials in roads in all heavy traffic categories.
2.2. Filler and bitumen

Two different wastes from the paper industry were analysed as filler in this study: dregs and biomass fly ash (figure 1). Dregs are inorganic wastes that do not decant in a green liquor clarifier during cellulose manufacture (Monte et al., 2009). Biomass fly ash is the sediment obtained from energy production (Monte et al., 2009). The bulk densities in toluene of dregs (0.5 g/cm$^3$) and biomass fly ash (0.5 g/cm$^3$) comply with the limits given by PG-3 for HMA (0.5 to 0.8 g/cm$^3$).

Additionally, typical commercial limestone filler was used for the control mixture (Figure 1a), which is composed of a natural calcium carbonate (CaCO$_3$ content higher than 97.1%) with a bulk density in toluene of 0.67 g/cm$^3$, which comply with the limits given for PG-3 for use as a mineral filler in HMA.

A penetration-grade bitumen B50/70 was selected for these experiments. Table 1b includes the primary rheological properties of this bitumen.

2.3. Filler characterization

Filler properties may affect the water resistance of the bituminous mixtures. In this regard some filler properties have been analysed:

- The water content of the three fillers was determined following the standard UNE-EN 1097-5 (AENOR, 2009).
- Light scattering analysis techniques (Saturn Digisizer II 5205) have been used to determine the size distribution of the three fillers.
- Fineness Modulus has been calculated as follows (Wang et al., 2011):

  $$F_M = \frac{P_{<5} + P_{5-10} + P_{10-20} + P_{20-30} + P_{30-50} + P_{50-75}}{100}$$  

  where $F_M =$ the Fineness Modulus (%) and $P_X =$ the cumulative percentage of filler retained on the sieve size $x$ μm by mass.
- A morphological study was performed using a scanning electron microscope (SEM). This analysis was conducted to make a qualitative evaluation of the geometric characteristics of the filler particles.
X-ray fluorescence spectroscopy (XRF) (Bruker S4 Pioneer Fluorescence Spectrometer) was used to determine the elemental composition of the three filler grains.

The material’s crystallography was also evaluated using the X-ray diffraction (XRD) method (Siemens D5000 X-ray diffractometer).

The Methylene Blue Test following UNE-EN 933-9 (AENOR, 2013) was performed to quantify the amount of harmful clays, iron hydroxides and organic matter present.

The penetration grade was determined following the UNE-EN 1426 (AENOR, 2007a), and the Ring and Ball (R&B) softening point was determined following UNE-EN 1427 (AENOR, 2007b).

### 2.4. Affinity

The asphalt-aggregate affinity analysis was performed using two tests: the Rolling Bottle method and the Boiling Water test. Both tests were applied to loose mixtures; thus, these tests are only useful to analyse the loss of adhesion but not the loss of cohesion.

UNE-EN 12697-11 (AENOR, 2012c) was followed during testing of the Rolling Bottle method. In this test, a sample of loose bituminous mixture is placed in a bottle with distilled water. Then, the bottle is rotated for 6 hours and then for an additional 18 hours. The percentage of bitumen that is not removed from the aggregate surface as a result of the rotation of the bottle is then estimated. There are no requirements for minimum bitumen coverage in this test; thus, the results are useful to compare samples.

ASTM D3625 (2005) was followed to perform the Boiling Water test. In this test, a sample of a loose mixture is placed in distilled water and heated at boiling for 10 minutes. Then, the percentage of asphalt that has not been detached from the aggregate surface as the result of the action of boiling water is determined. A minimum of 85%–90% of asphalt coverage is required in this test (Kiggundu and Roberts, 1988).

### 2.5. Marshall mix design method

The Marshall mix design procedure, as specified in NLT-159/86 (MOPT, 1992), was used in this investigation. To manufacture the HMA, the aggregate gradation, which was an AC 22 B50/70 base G (Table 2), was chosen in accordance with the limits given by PG-3 (MFOM,
In the Marshall mix design method, five series of three cylindrical samples (101.6 mm in diameter and 63.5 mm in height) were manufactured with bitumen contents of 3.25%, 3.75%, 4.25%, 4.75% and 5.25% by total weight of the aggregate. The laboratory mixing temperature was 160°C, and the compaction temperature was 150°C. Samples were compacted using a Marshall hammer with 75 blows per face. The optimum asphalt content (OAC) was selected inside the limits that produced the minimum void content in the mineral aggregate (VMA), and thus the minimum air void (Va) content. Additionally, Marshall flow (F) and Marshall stability (S) were selected in compliance with PG-3 specifications (Table 3).

2.6. Water resistance

UNE-EN 12697-12 (AENOR, 2006a) was used to evaluate the water resistance of the HMA made with filler dregs and filler biomass fly ash from the paper industry at the optimum Marshall bitumen content. A control mixture made with commercial limestone filler was also analysed at the optimum bitumen content. As stated above, an AC 22 base B50/70 (Table 2) was chosen to conduct the water resistance analysis.

In this test for each type of filler, a set of cylindrical samples was manufactured. It is also important to note that this test was conducted on compacted mixtures, and thus, the lack of cohesion may be analysed. Each set was subdivided into two subsets with the same number of specimens in each subset. One subset, known as the “dry subset,” was kept dry at room temperature, while the other subset, known as the “wet subset,” was saturated and held in a water bath for 3 days at 40°C. After that time, the two subsets were left a minimum of 2 hours at 15°C with the “dry subset” in air and the “wet subset” in water. The tensile strength ratios (TSR) of the specimens in each set were then determined as follows:

\[
\text{TSR} = \frac{\text{ITS}_W}{\text{ITS}_D} \times 100
\]

(2)

where TSR = the tensile strength ratio (%), ITS\_W = the average tensile strength of four conditioned (wet) specimens (MPa) and ITS\_D = the average tensile strength of four unconditioned (dry) specimens (MPa). TSR ≥ 80% is required by PG-3 specifications for an AC 22 base B50/70 G.
2.7. Mechanical properties

Stiffness and resistance to the permanent deformation have been studied in mixtures made with filler dregs and filler biomass fly ash at optimum asphalt content. Also a control mixture made with commercial limestone was analysed.

With the aim of investigating the stiffness, the resilient modulus ($M_R$) was measured in indirect tensile mode at 20ºC following the UNE-EN 12697-26 Annex C (AENOR, 2006b) using Cooper NU 14 testing machine.

The resistance to permanent deformation was evaluated using the repeated load axial test (RLAT) without confinement, following DD 226:1996 (BSI, 1996).

3. Results and Discussion

3.1. Filler characterization

Dreg particles trend to congregate (figure 1a). As shown in Table 4, this trend is probably due to their high natural water content, which is 2.6 times greater than that of fly ash and 57.1 times greater than that of commercial limestone filler. In addition, water content may affect the water sensitivity of the mixtures. In this regard, the European standard UNE-EN 13043 (AENOR, 2004) limits the water content of fillers for bituminous mixtures to not more than 1% by mass.

As shown in Table 4, it must be noted that dregs and fly ash exceed this value.

Figure 2 shows the gradation curve for the three tested fillers. As shown in Figure 2, the grain size distribution of all tested fillers comply with PG-3, which indicates that between 70% and 100% must be lower than 0.063 mm. Figure 2 also shows that commercial limestone is continuously graded, while dregs and biomass fly ash show a discontinuity between sizes from 0.15 μm to 5 μm. The Fineness Modulus for the dregs was 1.830, while the biomass fly ash showed a value of 3.688 and the commercial limestone a value of 3.763. Thereby, the dregs were the finest filler while the commercial limestone was the coarsest filler. It must be noted that filler activity is related to fineness in that a finer filler typically has a higher activity.

Selected SEM pictures of the three fillers are shown in Figure 1. As shown, the dregs formed in large cube shaped crystals (Figure 1c), which do not appear in the fly ash (Figure 1d) or in the commercial limestone filler (Figure 1e). It is important to note that geometric irregularity of
filler is associated with a higher surface activity (i.e., a higher capacity of adsorbing the bitumen binder by the filler particles) (Craus et al., 1978). Thus, filler geometric irregularities could lead to a decrease in effective bitumen (i.e., bitumen that remains free to coat the aggregates), which may affect the stripping resistance of HMA. In view of the SEM results, it is expected that the geometric irregularities of the dregs (i.e., the presence of sharp edges in the cube shaped grains) may reduce the water resistance of the mixture compared with other fillers. Additionally, it must be noted that dregs are agglomerated (Figure 1b), and agglomerations may be detrimental because make bitumen coating difficult.

Table 5 shows the chemical and mineralogical composition of the three tested fillers from the XRF and XRD test results. As shown in Table 5, dregs, biomass fly ash and commercial limestone show calcite and dolomite in its mineralogical composition. Calcite and dolomite generally have good bitumen adhesion (Bagampadde, 2004). Commercial limestone filler is primarily composed of calcite and, to a lesser extent, dolomite. Because calcite is water insoluble, it will not modify water penetration (Ishai and Craus, 1977), and thus, it is not expected that this compound will produce a chemical reaction that contributes to improve or worsen stripping potential. Conversely, the dregs and the biomass fly ash contain other mineralogical compounds in addition to calcite and dolomite. Dregs include thernardite, which is water soluble, and cesanite, which is marginally soluble in water. Thus, a poor stripping performance is expected for this filler. In the case of biomass fly ash, quartz was found in its composition, which is usually associated with poor adhesion (Bagampadde, 2004), along with soluble compounds such as halite or sylvite, which is associated with poor stripping performance. Fly ash also contains anhydrite, which may turn into gypsum when in contact with water, which is a deleterious HMA compound. However, it is interesting to note that fly ash also includes portlandite (i.e., hydrated lime) in its composition, which has known beneficial effects on HMA stripping potential (Little and Epps, 2001). Thus, based on these results, the mineralogical composition of fly ash may have positive or negative effects on the water resistance of the mixture.

For filler dregs, the methylene blue value was determined to be 2.2 g/kg, while that for biomass fly ash was 0.5 g/kg and that for commercial limestone filler was 1.0 g/kg. In both cases, the methylene blue values are near the lower limit of the methylene blue values range of the most common fillers (0-20) (Lesueur et al., 2013), indicating that there are no detrimental fines.
Table 1b shows the penetration grade and the R&B softening point temperature for the B50/70 material and the three tested mastics (B50/70+dregs, B50/70+biomass fly ash and B50/70 + commercial limestone filler). Among them, dregs and biomass fly ash have a lower penetration grades and higher R&B softening temperatures, and thus higher viscosities, which could make the coating process more difficult. This finding is corroborated by the finding that the mastic made with B50/70 and commercial limestone filler showed good workability, while the other two mastics were difficult to properly mix and introduce into the penetration grade and R&B softening point moulds.

It is important to note that chemical and physical properties of dregs and biomass fly ashes could vary from one batch to another and over time. In this regard, when using these waste materials as filler, regular sampling must be conducted.

3.2. Affinity

Figure 3a shows the results of the Rolling Bottle method. As shown, loose mixtures made with fly ash and dregs as filler showed better bitumen coverage results than those made with the commercial limestone filler. Among the two paper industry wastes, fly ash has better affinity performance; however, none of the three fillers displayed good affinity results (all results after 24 hours of rolling time are below 80%). These are surprising results because the commercial limestone filler is commonly used in Spain to improve the water sensitivity of hot-mix asphalt; thus, a higher affinity was expected.

Figure 3b shows the results of the Boiling Water test. As shown, fly ash again displays the best bitumen coverage results (95%); it is the only one of the tested fillers that achieves the minimum required bitumen coverage of 85% - 90%. However, the sequence of the second and third best materials differs from that obtained in the Rolling Bottle method. In this case, the commercial limestone filler is second best, while the dregs are the worst; however, neither complies with the minimum requirement, which, as said above, in the case of the commercial limestone filler is, in principle, surprising. In this regard, during technical literature review, an explanation for this performance has been found: commercial limestone filler is primarily compose of CaCO₃, which is water insoluble and thus produces an increase in the bitumen
viscosity but not physio-chemical changes in the bitumen-aggregate interface (Ishai and Craus, 1977), which contribute to improving affinity.

In both test (Figures 3a and 3b), using fly ash as filler produces the best bitumen coverage results. In addition, using commercial limestone as filler yields similar results in both tests. However, the lack of consistency between the results obtained with the dregs is surprising: in the Rolling Bottle test, the dregs showed satisfactory results, but in the Boiling Water test, using dregs as filler produced unsatisfactory results. The primary reason for these variations in performance can be found in the mechanisms that act during both tests. In this regard, it seems that the heat applied during the Boiling Water Test is being particularly detrimental for the dregs.

As shown in Table 4, to clarify these observations, the conductivity and pH were measured. Because conductivity increases with the amount of ions dissolved in water, it is clear that with the dregs, more solutions occur than when biomass fly ash or commercial limestone fillers are used. This effect can also be observed in the measured pH variations: the dregs’ pH values are more pronounced. Thus, it can be concluded that for the dregs, some compounds’ dissolutions are being highly accelerated due to the applied heat during the Boiling Water test.

3.3. Marshall mix design method
Results from the Marshal mix design method are shown in Table 3. As shown, the control mixture with an optimum asphalt content of 4.25% complies with PG-3 for heavy traffic categories T1 to T3. As shown in Table 3, the primary reason to not comply with the highest and lowest heavy traffic categories is excessive flow in the mixture.

3.4. Water resistance
Table 4 shows the TSR and ITS of the AC 22 base B50/70 G mixture made with 4.25% bitumen content, filler fly ash, dregs and commercial limestone. Table 4 also includes volumetric properties such as air voids (Vm) and voids in the mineral aggregate (VMA).

As shown, only mixtures made with commercial limestone as filler (i.e., the control mixture) reach the minimum TSR (80%) for base course HMA specified by PG-3. As was expected, the
dregs produced poor HMA water resistance; therefore, using dregs as filler produces poor HMA water sensitivity. Thus, using dregs as filler for hot mix asphalt should not be considered.

Unexpectedly, mixtures made with biomass fly ash as filler displayed TSR lower than the minimum required by PG-3. An explanation for this performance can be found in the fact that the optimum asphalt content was obtained for the control mixtures. For this reason, as shown in Table 6, this test was then conducted for mixtures made with biomass fly ash as filler and asphalt contents higher than the optimum asphalt content. Again, no compliance with PG-3 was found. These results may seem, in principle, contradictory to the results obtained from the tests conducted on the loose mixtures (i.e., the Rolling Bottle method and Boiling Water test). However, it seems clear that a lack of cohesion is primarily responsible of the poor performance against the action of water in mixtures made using biomass fly ash as filler. Moreover, it must be considered that the tests conducted on the loose mixtures were performed using siliceous aggregates. The fly ash’s mineralogical composition includes hydrated lime, which is particularly effective when used in wet siliceous aggregates.

3.5. Mechanical properties

There are no Spanish specifications for the acceptance of conventional mixtures in terms of resilient modulus, so it is useful to compare the results obtained for the different mixtures tested in this investigation. As shown in figure 4a, the resilient modulus values of the three tested mixtures were fairly similar. Mixtures made using dregs as filler exhibit a resilient modulus a 20.3% lower than that obtained for the control mixture, while mixtures made using biomass fly ash as filler exhibit a resilient modulus a 7.8% lower than that obtained for the control mixture. Therefore, mixtures made with dregs and biomass fly ash are less stiff than conventional ones.

Results of the RLAT indicate the rutting potential of the mixtures. Figure 4b shows the accumulated permanent axial strain values versus the number of loading cycles. Mixture made using dregs as filler exhibited permanent deformation levels at 1,800 cycles lower than that that control mixture exhibit. Mixture made using biomass fly ash as filler displayed permanent deformation levels at 1,800 cycles higher than those obtained for the control mixture. Nevertheless, the value obtained for the mixture using biomass fly ash as filler is lower than those typically obtained for conventional mixtures. For example, Aschuri et al. (2009) obtained values of approximately 13,000 με for conventional mixtures. As can be seen in figure 4b, all of
the studied mixtures had final axial permanent strain values lower than 7,000 µε. Also, as shown in figure 4b, after a given number of load applications (around 600), a linear relationship exists between the axial permanent strain and the number of load cycles. The slope of the line reflects the trend of axial deformation, such that larger slopes indicate less resistance to permanent deformation (Verhaeghe et al., 2007). In this regard, the control mixture displayed a slope between cycles 600 and 1,800 of 0.62 µε/cycle, while mixtures made with dregs (0.48 µε/cycle) and biomass fly ash (0.46 µε/cycle), displayed lower slopes. Thus, mixtures with dregs and fly ash as filler will perform well against rutting.

5. Conclusions

Mineral fillers are usually adhesion promoters. This study has attempted to provide a scientific explanation for why using dregs and biomass fly ash as filler does not follow this general trend and leads to hot-mix asphalt with a poor water resistance (significantly worse in the case of mixtures made with dregs as filler) despite displaying adequate mechanical properties (stiffness and permanent deformation). It appears that there is not only one reason that explains the poor performances found against the action of water. In this way, multiple factors have led to a loss of adhesion and cohesion of the mixtures. The high natural water content of dregs (4.1%) and fly ash (1.6%) and their high fineness could affect the bitumen-aggregate bond and enhance their activity. Moreover, the presence of cube-shaped crystals and agglomerations in the dregs may affect its stripping performance. Also, dregs include thermardite, which is water soluble, and cesanite, which is marginally soluble in water. Thus, a poor stripping performance is expected for this filler as a consequence of its chemical composition. Furthermore, the larger increase in the mastic viscosity when using dregs or fly ash can also be detrimental due to an increase in coating difficulty (i.e., worse workability).

Biomass fly ash includes hydrated lime in its composition; this compound is particularly beneficial when using wet siliceous aggregates. This conclusion indicates that biomass fly ash could be successfully used as filler in cold mix asphalt; thus, a new route of investigation has been opened as a consequence of the investigations described in this paper.
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