Laboratory and field performances of grave emulsion manufactured using nanocellulose crystals as an asphalt-emulsion emulsifier

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The use of fewer chemical emulsifying agents in the manufacture of bituminous emulsions for cold asphalt mixtures can help promote sustainable development in the road-pavement industry. The viability of replacing commercial emulsifiers derived from chemical and petrochemical industries with nanocellulose is investigated in this study. This research aims to use an ecologically beneficial nanocellulose material for fostering a circular economy. To this end, different bitumen emulsions are manufactured at the laboratory level using nanocellulose crystals and nanocellulose fibres as the emulsifying agents. The bitumen emulsion manufactured with nanocellulose display better results, and it is used to study the grave-emulsion type GE-1. A control GE-1 manufactured with a commercial bitumen emulsion type C60B5 is also tested. Modified proctor tests are employed to obtain the optimal fluid content of grave emulsions; the optimum bitumen emulsion content is determined using an immersion-compression test. The compactability of GE-1 is analysed using a gyratory compactor. Finally, the moisture damage resistance (tensile strength ratio), stiffness (resilient modulus), and permanent deformation (repeated load axial test) are studied. A trial section is designed and constructed on a real scale for evaluating the performance of the new grave emulsion because of the successful performance on the laboratory scale. The cores are collected after one year and the stiffness is analysed. The results indicate that conventional emulsifying agents can be partially replaced with nanocellulose crystals in the manufacture of cationic slow-setting bituminous emulsions for grave emulsions.

Keywords: nanocellulose crystals; nanocellulose fibres; emulsifier; bitumen emulsion; grave emulsion; mechanical properties; trial section

1. Introduction

Bitumen can be emulsified into an oil–water (O/W) emulsion for pavement construction to decrease its viscosity; this makes it easier to use by avoiding the need to heat it (Asjadi et al., 2018). A bituminous emulsion is a dispersion of small droplets (0.1–20 μm) of a hydrocarbon binder that acts as a dispersed or discontinuous phase in a solution of water and an anionic, cationic, non-ionic, or amphoteric emulsifying agent (continuous or dispersing phase) (ATEB, 2018). Emulsifiers are surfactants or tensioactive agents that facilitate the production of stable bitumen emulsions. Cationic emulsifiers are considered universal for creating bitumen emulsions for road paving applications (Abdullin and Emelyanycheva, 2020). They are composed of fatty amines and derivatives, alkyl-amide polyamines, lignin derivatives, or resin acids (Mercado and Fuentes-Pumarejo, 2016), and they originate from chemical or petrochemical industries. However, some examples of the successful use of bio-based substances as cationic emulsifiers have been reported. For example, Mallawarachchi et al. (2016) successfully used chitosan from waste fish and crabs as cationic bitumen emulsifiers. Zhao et al. (2021) dehydrated and condensed biomass residue to create imidazoline for use as a cationic bitumen emulsifier. Yuliestan et al. (2022) used bio-based surfactants that comprised three types of chemically modified lignin, and they found that cationic kraft lignin successfully stabilised oil-in-water emulsions containing 60% bitumen at surfactant concentrations ranging from 0.25 to 0.75%. Further, Levenard et al. (2022) used bio-based polymers as emulsifiers for bitumen emulsions with 50% bitumen.

Most surfactants are distinguished by the presence of two distinct molecular components: a fatty, lipophilic, or apolar portion with a strong affinity for bitumen and a hydrophilic or polar portion with a strong attraction to water. This dual characteristic allows the surfactant to be located at the bitumen–water interface as the polar component is in the water and the lipophilic component is incorporated into the bitumen (ATEB, 2018). Further, there are Pickering emulsions in which solid particles stabilise the emulsion (Fujisawa et al., 2017).

In pavement engineering, few studies focused on the use of solid particles as emulsified agents. Ataeian (2022) analysed the use of pristine and modified nanocellulose crystals (CNC) in Pickering asphalt emulsions. Chen and Li (2021) used SiO_2 nanoparticles successfully to obtain bitumen emulsions with improved stability, penetration, and a softening point of the residual binder. Nanosilicate particles were used by Li et al. (2019).

The European Union presented an Action Plan to promote Circular Economy in 2020: '*to achieving climate neutrality by 2050 and decoupling economic growth from resource use*' (European Commission, 2020). Lignocellulosic biomass, which is a high potential, low cost, and highly available raw material (González et al., 2020), is considered under this scenario. Lignocellulosic materials are composed of cellulose, hemicellulose, and lignin (Hendriks and Zeeman, 2009). Among these three natural products, cellulose is the most abundant biopolymer on the Earth, and it displays both amorphous and crystalline phases (Sonker et al., 2016).

In the road pavement construction sector, cellulose fibres have been extensively used in the manufacture of stone matrix asphalt mixtures (Putman and Amirkhanian, 2004) and open-graded and gap-graded mixtures for mitigating asphalt draindown and enhancing the mechanical performance of the mixtures (Eskandarsefat et al., 2019). Some researchers also tested cellulose ash as a filler to successfully control the aging of bituminous mixtures (Movilla-Quesada et al., 2017). In addition, sodium carboxymethylcellulose, which is a compound derived from cellulose, was successfully used to improve the settlement and stratification of the cement asphalt mastic (Lu et al., 2009) and to manufacture more stable bitumen emulsions (Hou et al., 2019)

The use of nanomaterials as bitumen modifiers is one of the most advanced developments in the field of nanotechnology in the road pavement construction sector. Considerable research has focused on the use of these materials as bitumen modifiers. For example, some authors have reported enhanced performance of bitumen modified with nanomaterials achieving better rutting performance (Yao et al., 2012), higher fatigue life (Yao et al., 2012; Akbari and Modarres, 2020; Bhat and Mir, 2020), improved fracture properties (Pirmohammad et al., 2020), higher shear deformation resistance, improved elastic behaviour (Zhu et al., 2017), improved moisture damage resistance (Hamedi, 2017; Razavi and Kavussi, 2020), and lower aging effects (Crucho et al., 2019). Enhancements in the modified asphalt properties promoted by nanomaterials are greater than those of other modifying methods (Fang et al., 2013); the quantum effect of nanoparticles helps in this process (Johnson, 2020).

Further, there are several types of nanomaterials. Fang et al. (2013) collected several examples where nanolayered silicates, nano SiO_2, nano TiO_2, nano $CaCO_3$, and nano Fe_3O_4 were used. Nano Al_2O_3 (Hamedi, 2017), nano-ZnO (Zhu et al., 2017; Zhang et al., 2020), nanoclays (Martinho and Farinha, 2019; Johnson, 2020), and graphene (Wu and Tahri, 2019) have also been used. However, nanocellulose is not used extensively as a bitumen modifier (Johnson et al., 2021). Johnson and Hashemian (2021) demonstrated that bitumen modification using 1% (by weight) CNC led to mixtures with lower thermal susceptibility and higher shear modulus. Johnson et al. (2021) reported that the use of bitumen modified with nanocellulose led to mixtures with improved cracking resistance at intermediate in-service temperatures.

For the last 40 years, microcellulose has been used in the food industry as an emulsion stabiliser (Krawczyk et al., 2009). CNC and nanocellulose fibres (CNF) can also act as Pickering (solid) stabilisers in oil-in-water emulsions, which help avoid droplet coalescence (Fujisawa et al., 2017; Mikkonen, 2020). However, in the road construction sector, the use of CNC and/or CNF as stabilisers or emulsifying agents for bitumen emulsions is yet to be fully investigated. Thus, as indicated previously, only one study on the use of CNC as emulsifiers has been conducted so far (Ataeian, 2022).

This study explores the highly novel use of nanocellulose as an emulsifying agent in the manufacture of bituminous emulsions for cold asphalt mixture-type grave emulsions.

2. Aims and scope

The present research aims to replace the commonly used commercial emulsifiers with nanocellulose, which is environmentally friendly and promotes a circular economy in road construction activity. To this end, and as shown in figure 1, several bituminous emulsions are manufactured at the laboratory level using CNC or CNF as the emulsifying agents. Further, a grave-emulsion type GE-1 is manufactured using nanocellulose bitumen emulsion, which yields a better performance. An analysis of the optimal dosage of the bituminous mixture is conducted using a visual test for pre-wetting water, a modified Proctor test for the fluid (pre-wetting water +bitumen emulsion), and an immersion-compression test for the bitumen emulsion. Further, a compactability analysis is conducted using the gyratory compactor. The moisture damage resistance is measured using an immersion-compression test and indirect tensile test. The resistance to permanent deformation and the stiffness are determined using a repeated load axial test and an indirect tensile stiffness modulus, respectively. The results are compared with those obtained for a grave-emulsion type GE-1 manufactured using a conventional commercial emulsion, C60B5 (control mixture). Finally, a pilot test section is built under real conditions with both grave emulsions; their performances are analysed over time.

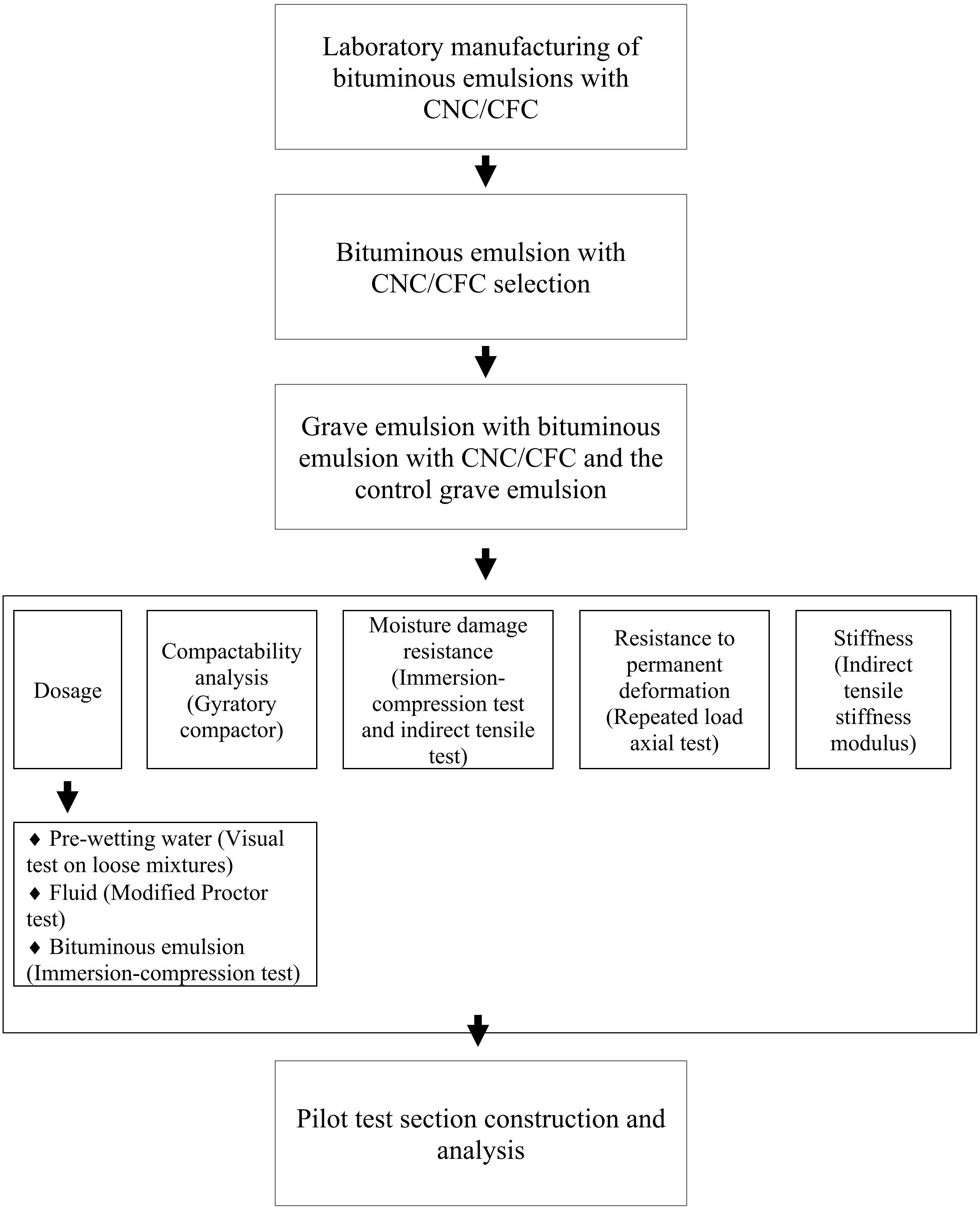

Figure 1. Research method algorithm

3. Materials and methods

Aggregates

Corneal, a siliceous aggregate used for road pavement construction in Spain, is used as a natural aggregate for manufacturing grave emulsions. According to EN 933-3 (AENOR, 2012b), the highest flakiness index (FI) is 24%. Following EN 933-5 (AENOR, 2005), 100% of the particles are crushed. The sand equivalent (SE) for the 0/2 mm fraction, which is determined as indicated in EN 933-8 (AENOR, 2016), is 61%. The Los Angeles (LA) coefficient determined according to EN 1097-2 (AENOR, 2010) is 14.2%. These results confirm that, the aggregate is suited to all categories of heavy traffic, according to the publication 'Grave-emulsion sheet' by the Technical Association of Bituminous Emulsions (ATEB) (n.d.) (Table 1). In other words, for T00–T4.

Table 1. Heavy traffic categories (ATEB, n.d)

Heavy traffic category	Annual average daily heavy traffic (AADHT) (vehicles/day)
T00	AADHT ≥ 4,000.
T0	4,000 > AADHT ≥ 2,000
T1	2,000 > AADHT ≥ 800
T2	800 > AADHT ≥ 200
T3	200 > AADHT ≥ 50
T4	AADHT < 50

Commercial bitumen emulsion

A cationic commercial bituminous emulsion (type C60B5 GE) is used as the control mixture because it is the most common for this type of application. The residual binder content, obtained according to the EN 1431 (AENOR, 2000) standard, is 59.8%, whereas the breakage index obtained following the EN 13075-1 (AENOR, 2017) standard is 214; this confirms that it is a slow-setting bitumen emulsion.

Bitumen

Commercial bitumen type B160/220 is used for the manufacture of the bitumen emulsion. This bitumen achieves penetration at 25 °C ranging from 160–220 tenths of millimetres.

Nanocellulose

There are three main types of nanocellulose: CNC, CNF, and bacterial nanocellulose (Abitol et al., 2016; Klemm et al., 2018). In the present study, CNC (figure 2a) and CNF (figure 2b) are used as partial substitutes for the chemical emulsifiers used in bitumen emulsion manufacturing.

According to the supplier, CNC has a particle size in the range 1–50 nm, an apparent density of 0.7 g/cm^3, and a specific surface area of 400 m^2/g. The CNF has a viscosity in water (2%) higher than 20,000 mPas, a conductivity (2%) lower than 500 µS/cm, a pH (2% in water) in the range 5–7, and a capacity of water retention that is higher or equal to that of 70 gH_2O/g; it is an anionic nanocellulose.

Figure 2. Two types of nanocellulose used in the present research: a) CNC and b) CNF.

Transmission electron microscopy (TEM) images of the CNC and CNF are obtained using a JEOL JEM-1010 instrument; this equipment has a thermionic electron gun with a tungsten filament and an acceleration voltage of 100 kV that allows obtaining conventional transmission images of dark and light fields with a resolution of 0.35 nm. The microscope is equipped with a MegaView II camera to capture images.

The TEM images indicate that both the CNC (figure 3a) and CNF (figure 3b) display nanoscale dimensions. Further, the morphological differences between the two types of nanocellulose are clearly observable in the TEM micrographs. The TEM micrograph of the CNC (figure 3a) shows uniformly dispersed rod-like nanocrystals; that of the CNF shows elongated nanofibrils.

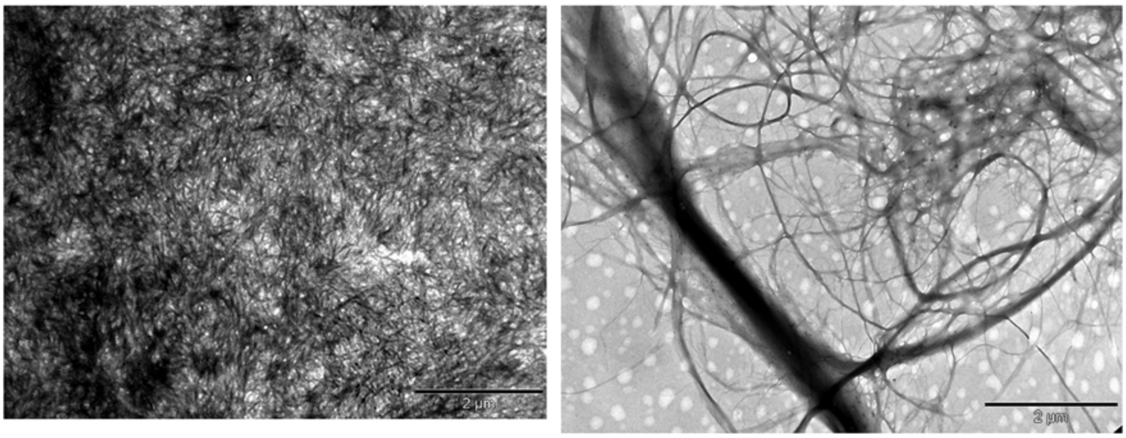

Figure 3. TEM micrographs of the nanocellulose used in the present research: a) CNC and b) CNF.

CNF resulted in an unstable bituminous emulsion, and therefore, despite repeated trials with both CNC and CNF, the latter is abandoned. Although cationic emulsions are desired in both CNC and CNF, anionic emulsions are produced when nanocellulose is used to replace 100% of the commercial emulsifier. This can be attributed to the anionic nature of the nanocellulose used. In this scenario, a combination of the CNC and a commercial emulsifier is required.

Commercial emulsifier

A reference commercial emulsifier for slow-breaking emulsions is used in this study. This emulsifier is composed of an inorganic polymer with amino groups and surface active properties. According to the supplier, the recommended dosage is 2.5% to 4.0%.

Bitumen emulsion manufacturing at a laboratory scale

A colloid mill is used to manufacture emulsions by partial replacing the chemical emulsifying agent with nanocellulose.

The required amount of heated (120 °C) B160/200 cells is weighed to manufacture the bitumen emulsion. Then, the dispersing phase (water and emulsifier agent including CNC) is decided. To this end, the required amount of water and emulsifier are weighed and mixed at 60 °C with a magnetic stirrer at 500 rpm. Then, the pH is adjusted by adding hydrochloric acid (HCl) until a pH lower than 7 is obtained. Subsequently, the colloid mill is conditioned at 80 °C. Once everything is acclimatised to the working temperature, the dispersing phase is introduced into the colloidal mill, which operates at 3,000 rpm. Next, heated bitumen is added gradually so that the thickness of the flow did not exceed 6 mm in diameter during this operation. Finally, the outlet valve of the mill is opened to allow the bituminous emulsion to flow through the colloid mill once the asphalt emulsion is manufactured.

Grave emulsion

Grave-emulsion type GE-1 (ATEB, n.d.) is selected for this study. The grain-size distribution of the cold bituminous mixture is shown in figure 4. Further, figure 4 shows the fit of the GE-1 among the upper and lower limits indicated by ATEB (n.d.). GE-1 has a nominal maximum aggregate size of 20 mm.

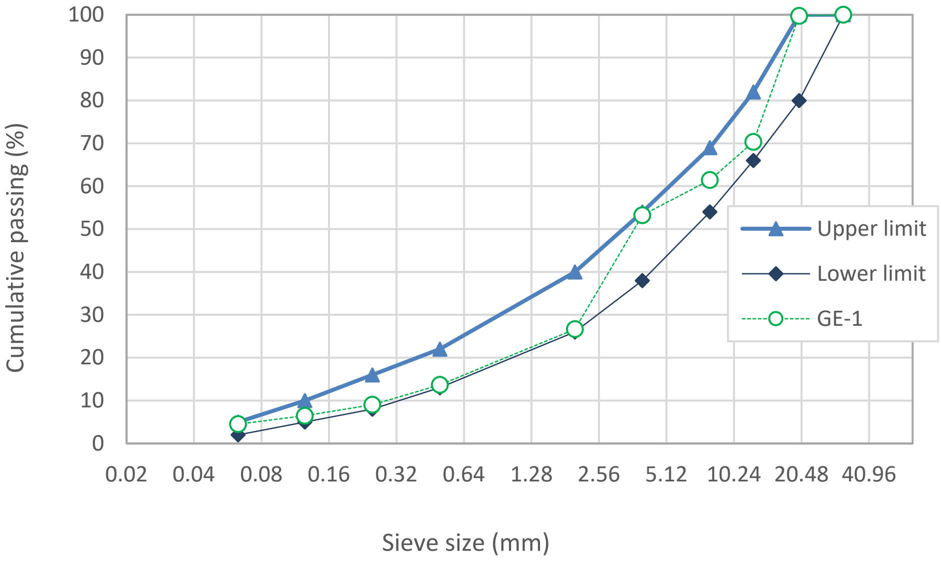

Figure 4. Grain size distribution of the grave-emulsion type GE-1.

Laboratory analysis

Pre-wetting water

Pre-wetting water is necessary for the correct dispersion of the emulsion during the mixing phase of the grave emulsion. The standard NLT-145 (Ministry of Public Works, 1995) is used to determine the water content. Loose mixtures of cold asphalt mixture type GE-1 are manufactured using 500 g of dry aggregate, pre-wetting water, and 5% bitumen emulsion by weight of the dry aggregate. 0%, 1%, 2%, and 3% pre-wetting water on the weight of the dry aggregate is added. A mechanical mixer is used for all trials. In all cases, a mixing time of 2 min is selected: 1 min for mixing the aggregate and pre-wetting water, and 1 min for mixing all mixture components.

This test was conducted with eight bitumen emulsions: the control emulsion and seven bitumen emulsions using nanocellulose (whose designation begins with “eNanocel”):

- Commercial bitumen emulsion C60B5 GE
- eNanocel-01: 0.4% CNC
- eNanocel-02: 1.2% CNC
- eNanocel-03: 0.6% CNC
- eNanocel-04: 0.8% CNC cationised at source with ethylenediamine
- eNanocel-05: 0.4% CNC cationised at source with ethylenediamine
- eNanocel-06: 0.4% CNC cationised with glycidyltrimethylammonium chloride (GTMAC)
- eNanocel-07: 0.4% CNC and 2% commercial emulsifier

Optimal fluid content: Modified Proctor test

A modified Proctor test was conducted following the EN-103501 standard (AENOR, 1994) to determine the maximum density of GE-1 and its optimum fluid (pre-wetting water plus bituminous emulsion) content for compaction.

Optimal emulsion content: Immersion-compression test

According to the ‘Grave-emulsion sheet’ (ATEB, n.d.), the optimal residual binder content in GE-1 should be selected through an immersion-compression test. The moisture damage resistance of the mixtures is analysed. Further, this test needs to be performed on cylindrical samples cured for three days in an oven at 50 °C.

For each residual binder content, 10 cylindrical specimens are manufactured as per NLT-162 (Ministry of Public Works, 2000). Five samples are immersed in water at 49 °C for 4 days, and the other five are maintained in air at room temperature. Later, both groups of samples are subjected to unconfined compression tests based on NLT-161 (Ministry of Public Works, 1998). The retained strength ratio (RSR) is determined as

$$RSR = \frac{UCS_{wet}}{UCS_{dry}} \times 100, \qquad (1)$$

where UCS_{wet} and UCS_{dry} represent the average compression strengths of the group immersed in water (MPa) and the group that was not submerged (MPa), respectively.

According to Spanish specifications (ATEB, n.d.), UCS_{wet}, UCS_{dry}, and RSR should comply with the values presented in Table 2 based on the heavy traffic category of the road on which GE-1 will be used.

Table 2. Specifications for the immersion-compression test.

Heavy traffic category	UCS_{dry} (MPa)	UCS_{wet} (MPa)	RSR (%)
T00, T0, T1, and T2	1.5	1.2	75
T3	1.2	1.0	60
T4	0.9	0.7	50

Compactability

The compactability of the mixture is analysed following the UNE-EN 12697-31 standard (AENOR, 2020) to obtain the most suitable number of turns to compact GE-1 with the gyratory compactor. Combining a rotational action with the vertical force that results from the mechanical head, the gyratory compactor is utilised to model and replicate real compaction conditions in highway paving operations.

To this end, the samples of the control mixture manufactured with a standard residual binder content are compacted by applying 500 turns of the rotary compactor under the following conditions:

- Consolidation pressure: 600 KPa
- Angle of internal rotation: 0.82°
- Rotation speed: <32 rpm
- 100-mm-diameter mould for cold asphalt mixes
- Cylindrical samples of 60 mm in height
- Compaction at room temperature

The following values are considered to determine the most appropriate number of turns.

- The ATEB Specifications for grave emulsions (ATEB, n.d.) indicate that it is necessary to reach at least 98% of the modified Proctor density for obtaining a good compaction of the sample.
- Similarly, it is considered appropriate to consider the value of the density obtained by Marshall compaction when applying 75 blows per face; it is a common laboratory compaction procedure for other types of mixtures.
- The number of gyrations obtained from the compaction analysis of the control mixture are applied to all tested mixtures and compared using the same compaction energy.

Moisture damage resistance

In addition to the immersion-compression test, the EN 12697-12 (AENOR, 2019) standard is also followed to evaluate the moisture damage resistance (stripping potential) of GE-1. According to this standard, ten cylindrical samples are manufactured using a gyratory compactor for each of the tested GE-1 mixtures. According to the ATEB (n.d.), the water sensitivity of GE-1 should be analysed by compacting the specimens with fewer turns than those selected by the compactability analysis; 67% of the selected turns are used. Once manufactured, the samples are cured for 3 days at 50 °C. The set is then subdivided into two subsets of five specimens each. The 'dry' subset is kept dry at room temperature, whereas the 'wet' subset is saturated and held in a water bath for three days at 40 °C. Next, both subsets are left at 15 °C for 2 h; the 'dry' subset in air and the 'wet' subset in water. Then, the medium tensile strengths of the 'dry' (ITS_D) and 'wet' (ITS_W) subsets are determined using a static press. The tensile strength ratio (TSR) is determined as

$$TSR = \frac{ITS_W}{ITS_D} \times 100. \tag{2}$$

For GE-1, the ATEB (n.d.) does not require a minimum TSR value. However, for other bituminous mixtures, it is a minimum TSR of 80% for base courses (MFOM, 2015) of road pavements.

Stiffness

The resilient modulus is obtained following EN 12697-26 Annex C (AENOR, 2012a) to analyse the stiffness of GE-1. A Cooper NU 14 servo-pneumatic universal testing machine, with a maximum loading capacity up to 14kN, is employed to perform an indirect tensile stiffness modulus test (ITSM). In this test, ten conditioning haversine pulses with a rise time of 124 ± 4 ms and a repetition period of 3 ± 0.1 s are applied along the vertical diameter of the cylindrical GE-1 sample. Five similar haversine test pulses are used, and the pulses are applied to two perpendicular diameters of a cylindrical specimen; the average stiffness of the two tested diameters is recorded as the stiffness modulus of the GE-1 specimen. Four samples are tested for each case. The average resilient modulus of the four samples is recorded.

The resilient modulus (M_R) for each specimen is obtained in a climatic chamber at 20 °C as

$$M_R = \frac{F.(\nu+0.27)}{zxh}, \tag{3}$$

where F, z, h, and ν represent the maximum repeated load (N) selected to produce a maximum horizontal strain of 0.005% of the sample diameter, horizontal elastic deformation (mm), thickness of the GE-1 cylindrical sample (mm), and Poisson’s ratio (a typical value of 0.35 was used (Huang, 1993)).

GE-1 has no requirements in terms of its resilient modulus. Therefore, this test is used only for comparison between the control GE-1 and GE-1 manufactured with an asphalt emulsion that used nanocellulose as an emulsifier.

Resistance to permanent deformation

In this study, a repeated load axial test (RLAT) is conducted without confinement to analyse the resistance of the GE-1 to permanent deformation in the Cooper NU 14 servo-pneumatic universal testing machine. According to DD 226:1996 (British Standard, 1996), cylindrical specimens compacted using a gyratory compactor are placed in a climate chamber overnight at 30 °C. Once the samples are conditioned at the test temperature, each specimen is placed between two load platens. A preload of 10 kPa axial stress for 600 ± 6 s is applied using a Cooper NU 14 universal testing machine. Each specimen is subjected to 5,400 load cycles; each load cycle comprises one axial square load pulse with a pulse width of 1 s, stress level of 100 ± 2 kPa, and rest period of 1 s. The axial permanent strain is calculated as

$$\varepsilon_{d(n,T)} = \frac{\Delta h}{h_0} \text{x} 100 \tag{3}$$

where $\varepsilon_{d(n,\,T)}$, h_0, and Δh represent the axial permanent strain (in $\mu\varepsilon$) after n load applications at temperature T (°C), initial distance between the two load platens (mm), and axial permanent deformation (mm), respectively.

4. Results and discussion

Pre-wetting water

Figure 5 shows the appearance of the loose mixture made with the control bitumen emulsion. Figure 6 shows the appearance of the loose mixture made with the bitumen emulsion with CNC, which led to better coating; this one is named ‘eNanocel-07’. The optimal pre-wetting water is 3% for both the control bitumen emulsion and the bitumen emulsion manufactured using nanocellulose (‘eNanocel-07’).

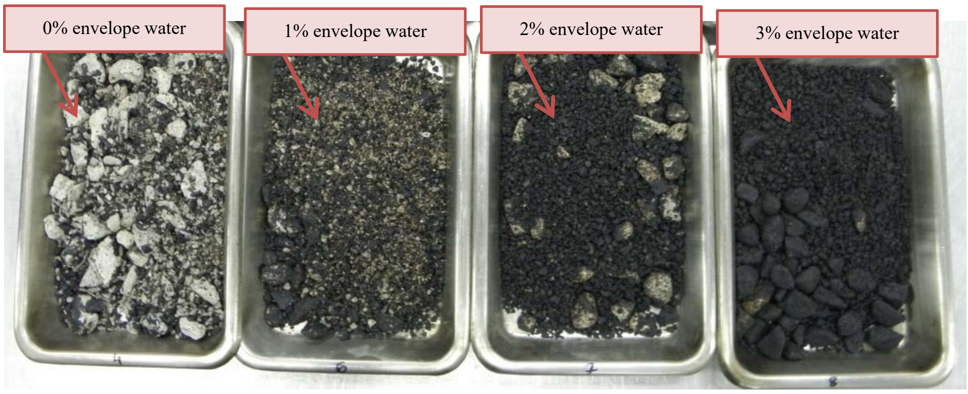

Figure 5. Appearance of loose mixtures, type GE-1, manufactured with 5% C60B5 (control bitumen emulsion) and 0%, 1%, 2%, and 3% pre-wetting water, after 2 min of mixing.

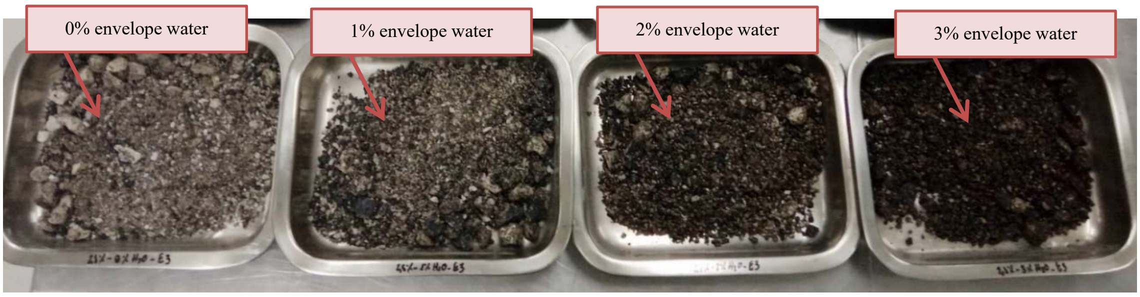

Figure 6. Appearance of loose mixtures, type GE-1, manufactured with 5% eNanocel-07 and 0%, 1%, 2%, and 3% pre-wetting water, after 2 min of mixing.

Optimal fluid content: Modified Proctor test

Figure 7 shows the dry density of the aggregates with respect to their moisture content. The optimal modified Proctor water content for the aggregate is 5% by weight of the dry aggregate; i.e. the optimal fluid (water and bitumen emulsion) content is 5%. Further, figure 7 shows that the maximum dry density of the GE-1 aggregate is 2.228 Mg/m^3.

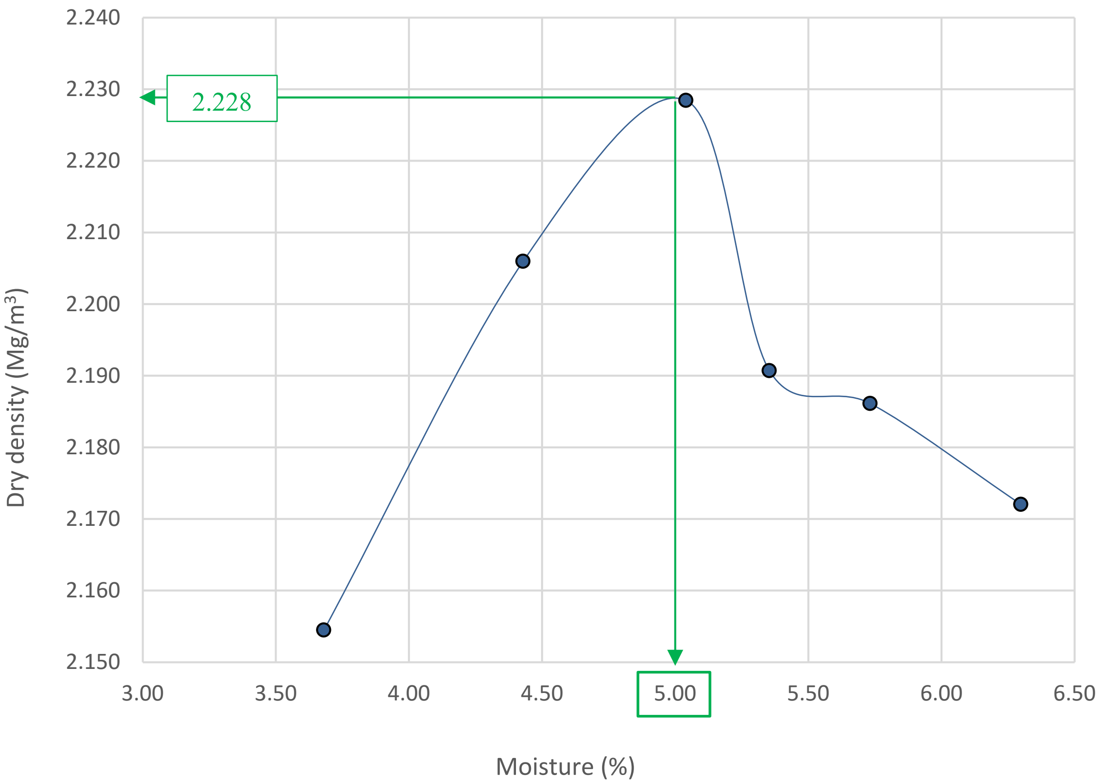

Figure 7. Dry density versus moisture content for the natural aggregate with the grain size distribution of GE-1.

Optimal emulsion content: Immersion-compression test

In all cases, 3.0% pre-wetting water is used for the control mixture and the mixtures made with the emulsion with nanocellulose. Mixing times of 2 min (1 min of mixing of the aggregate with the coating water + 1 min of mixing with the emulsion) are also used for all samples. Further, all specimens are subjected to a curing time of 3 d in an oven at 50 °C.

Both the control emulsion (C60B5) and different 'eNanocel' are used as binders. The four 'eNanocel' emulsions with the best results during the determination of the pre-wetting water are selected:

- eNanocel-03: 0.6% CNC
- eNanocel-04: 0.8% CNC cationised at the source with ethylenediamine

- eNanocel-06: 0.4% CNC cationised with GTMAC
- eNanocel-07: 0.4% CNC and 2% commercial emulsifier

Three of the four selected ‘eNanocel’ used only CNC as the emulsifier; they are stable Pickering asphalt emulsions.

The control mixture, GE-1 manufactured with C60B5, is analysed first. Table 3 summarises the immersion-compression results for this mixture. The first residual binder content that led to GE-1 for T3 was 3.0%. The residual binder content can be excessive for achieving a higher heavy-traffic category. In fact, the residual binder content of a GE ranges from 3.8–4.8% (Charentais n.d.), and therefore, 3.0% was selected as the optimum residual binder content.

Table 3. Immersion-compression test results for the control mixture.

Residual binder content (%)	UCS_{dry} (MPa)	UCS_{wet} (MPa)	RSR (%)	Heavy traffic category
2.5	1.250	0.974	77.91	T4
3.0	**1.295**	**1.034**	**79.84**	**T3, T4**
3.5	1.239	1.121	90.52	T3, T4

An immersion-compression test was performed on the GE-1 manufactured with the four selected ‘eNanocel’ emulsions using the optimum residual binder content of the control mixture (3.0%). The results are presented in Table 4; the ‘eNanocel-07’ is the only ‘eNanocel’ bituminous emulsion that leads to GE-1 achieving the same heavy traffic category as the GE-1 manufactured using the control emulsion. Thus, this is selected as the most appropriate method. In this case, it was not a Pickering asphalt emulsion because a commercial emulsifier agent (with polar and apolar parts) was used, in addition to the CNC.

Table 4. Immersion-compression test results for the GE-1 manufactured with the selected ‘eNanocel’ bitumen emulsion with a 3.0% residual binder content.

Bitumen emulsion	UCS_{dry} (MPa)	UCS_{wet} (MPa)	RSR (%)	Heavy traffic category
eNanocel-03	1.20	0.45	37.52	-
eNanocel-04	1.26	0.48	37.92	-
eNanocel-06	1.00	0.83	83,14	T4
eNanocel-07	**1.32**	**1.05**	**79.20**	**T3, T4**

The immersion-compression test was performed using different residual binder contents for GE-1 manufactured using ‘eNanocel-07’ as the bitumen emulsion. The results are presented in Table 5. The 3.0% residual binder content is the minimum residual binder content that leads to the higher heavy traffic category. Thus, the optimum residual binder content is the same (3.0%) and the heavy traffic category achieved is also the same (T3, T4) for the control mixture and for the GE-1 manufactured using ‘eNanocel-07’ as the bitumen emulsion.

Table 5. Immersion-compression test results for the GE-1 manufactured with 'eNanocel-07' as the bitumen emulsion.

Residual binder content (%)	UCS_{dry} (MPa)	UCS_{wet} (MPa)	RSR (%)	Heavy traffic category
2.5	1.250	0.974	77.91	T4
3.0	**1.320**	**1.050**	**79.20**	**T3, T4**
3.5	1.239	1.121	90.47	T3, T4

Compactability

Figure 8 shows the geometric density of the GE-1 manufactured using 5.0% bitumen emulsion type C60B5 (3.0% residual binder content) and 3.0% pre-wetting water versus the number of turns of the gyratory compactor. Further, figure 8 shows the value of the modified Proctor maximum dry density (2.228 Mg/m^3), 98% modified Proctor maximum dry density (2.1834 Mg/m^3), and apparent density of the mixture obtained by applying the saturated surface dry (SSD) procedure on Marshall samples compacted with 75 blows per face (2.1815 Mg/m^3), figure 8 shows that the Marshall SSD density and maximum 98% of the modified Proctor maximum dry density are very similar; therefore, selecting the number of turns to achieve 98% of the modified Proctor maximum dry density can lead to similar results when selecting the number of turns to reproduce the Marshall SSD density. In addition, figure 8 shows that a minimum specified value of 98% modified Proctor maximum dry density is achieved for 55 turns of the gyratory compactor, and 100% is achieved for 105 turns. Compacting with an average number of turns (80 turns of the gyratory compactor) is considered the most suitable value for all tested mixtures, to be on the safe side.

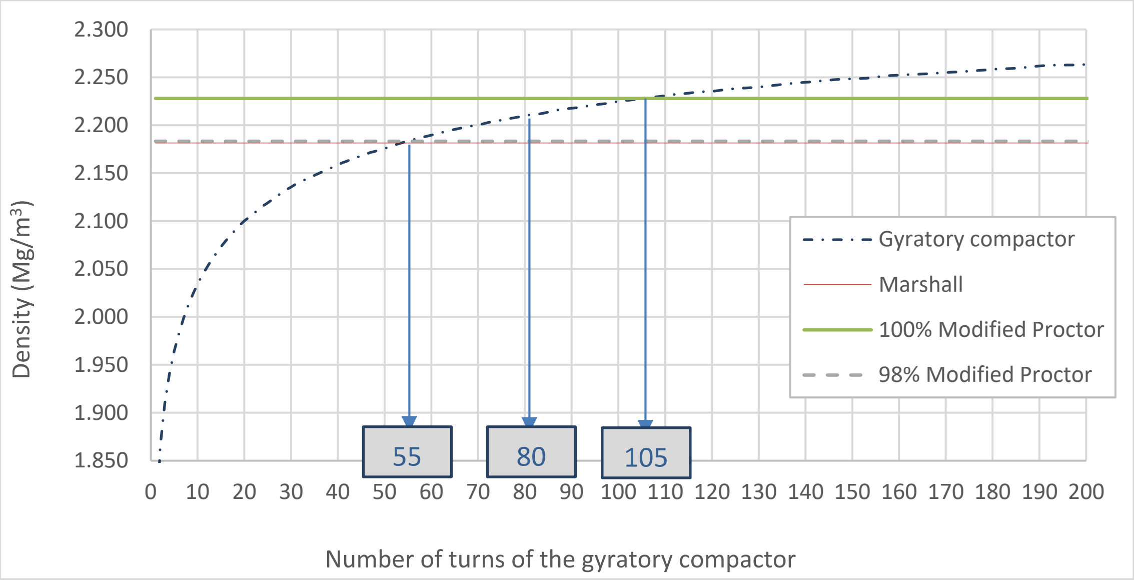

Figure 8. Density of GE-1 versus the number of turns of the gyratory compactor.

Moisture damage resistance

A moisture damage resistance analysis was performed for the control GE-1 and GE-1 manufactured with the selected ‘eNanocel-07’ as the bitumen emulsion. In both cases, the grave-emulsion samples were manufactured with the optimum residual binder content (3.0%), optimum pre-wetting water content (3.0%), and 55 turns of the gyratory compactor (67% of the 80 previously selected turns), as prescribed by the ATEB (n.d.), and after 3 days of curing at 50 °C.

The results of the moisture damage resistance analysis are shown in figure 9.

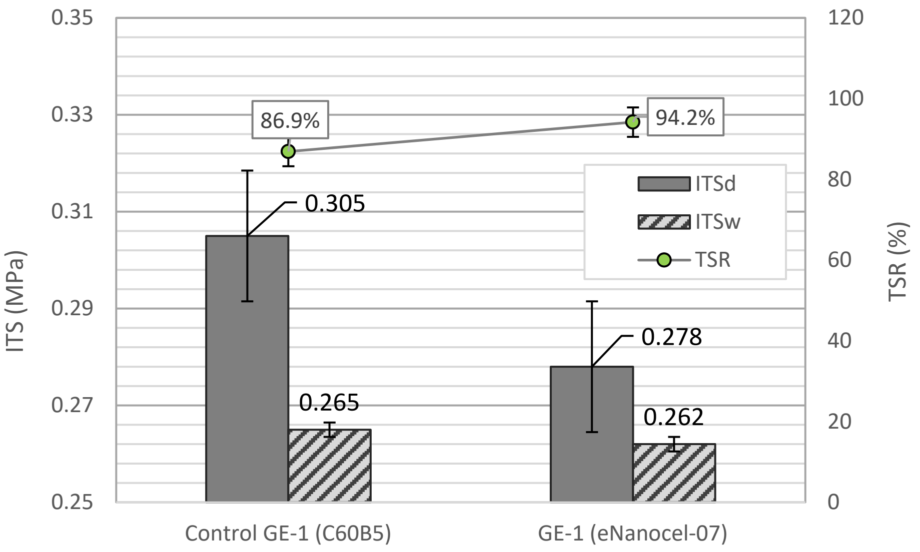

Figure 9. Moisture damage resistance results for the tested GE-1.

Figure 9 shows that the dry strength of the control GE-1 is slightly higher (8.85% higher) than that of the GE-1 with the 'eNanocel-07'. However, the wet strength is the same in both cases. Thus, the TSR of the GE-1 with 'eNanocel-07' is higher than the TSR of the control GE-1 (8.4% higher); this is indicative of the better water sensitivity of mixtures made with 'eNanocel-07'. This result contrasts with the one obtained in the immersion-compression test because the RSR obtained in the immersion-compression results are very similar in both cases. The deeper static compaction suffered by specimens during the immersion-compression test is responsible for the more homogeneous performance of both mixtures in this test.

Stiffness

The resilient modulus is determined for the control GE-1 and for the GE-1 made using 'eNanocel-07' as the bitumen emulsion, at their optimum residual binder (3.0%) and water content (3.0%), and with 80 turns of the gyratory compactor. Both cold asphalt mixtures were cured for 3 d at 50 °C before testing. For the control GE-1, a resilient modulus of 630 MPa was obtained, whereas for GE-1 with ‘eNanocel-07’, the resilient modulus was 293 MPa.

Low values of the resilient modulus are associated with poor resistance to permanent deformation, whereas high values of the resilient modulus are associated with brittle mixtures (FHWA, 2016). The high resilient modulus difference suggests that the mixture made with ‘eNanocel-07’ requires a longer curing time to allow the mixture to develop its stiffness. Therefore, the resilient moduli at 4, 5, 6, and 7 d of curing time in the oven at 50 °C were determined for both GE-1. The results are presented in Table 6.

Table 6. Resilient modulus (in MPa) after 3, 4, 5, 6, and 7 days of curing time in the oven at 50ºC.

	Curing time in the oven				
Type of GE-1	3 days	4 days	5 days	6 days	7 days
Control GE-1	630	535.4	520.8	465.3	464.9
GE-1 with “eNanocel-07”	293	368.2	428.8	505.1	528.0

Table 6 indicates that the resilient modulus for the control GE-1 decreases with curing time, and for 6 and 7 days of curing time, it stabilises. However, the resilient modulus for GE-1 manufactured with ‘eNanocel-07’ increases with curing time in the oven; i.e. GE-1 manufactured using ‘eNanocel-07’ required more curing time in the oven. Six days seems an adequate number of days because an increase of 25.65% is produced from days 3 to 4 of curing time; from days 4 to 5, the increase is 16.46%; from days 5 to 6, the increase is 17.81%; and from days 6 to 7, only a 4.59% increase is achieved.

Resistance to permanent deformation

Figure 10 shows the permanent deformation results for the RLAT test conducted on the control GE-1 and GE-1 manufactured with ‘eNanocel-07’ as a bitumen emulsion and cured for three days at 50 °C in an oven. The results are the average of the results obtained for four specimens in each case.

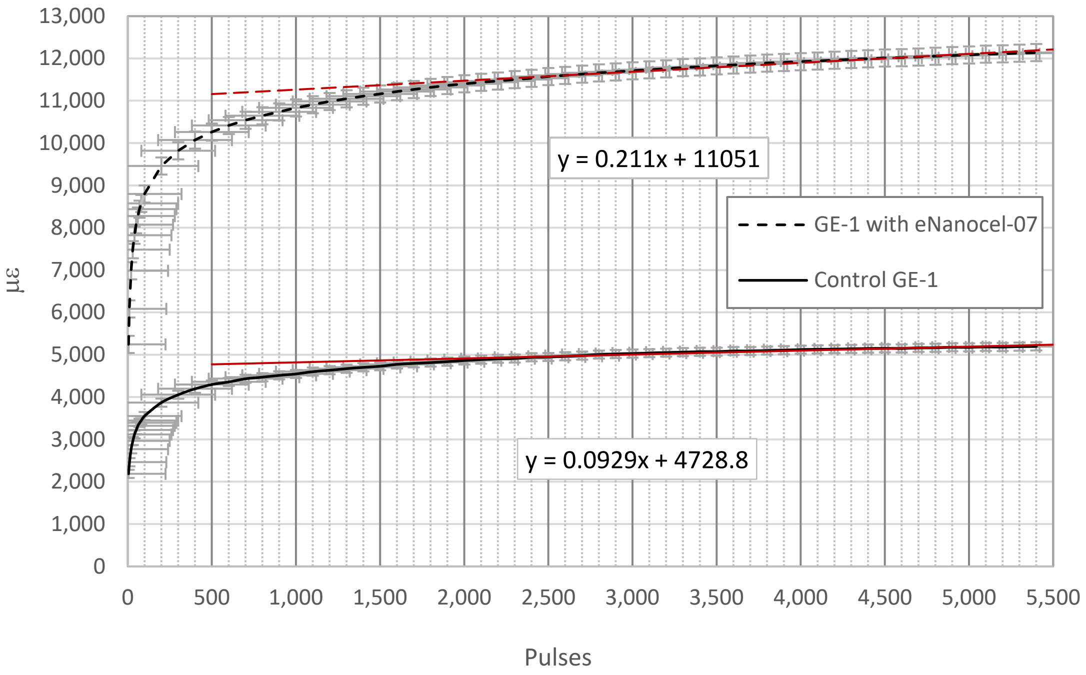

Figure 10. RLAT results. Axial microstrain versus the number of pulses for the control GE-1 and GE-1 manufactured using ‘eNanocel-07’ as the bitumen emulsion.

Figure 10 indicates that only primary and secondary stages are developed for the two tested mixtures. The tertiary stage and turning point are not achieved in either case. Further, figure 10 also shows that GE-1 manufactured with ‘eNanocel-07’ displays a higher initial microstrain because of the higher initial post-compaction suffered by this mixture. Early in the service life of this mixture, it could increase the risk of permanent deformation, especially because of heavy vehicle transit. The slope of the secondary stage is higher (21.1%) than that of the control mixture (9.29%); this result is in accordance with the results of the resilient modulus because a higher resilient modulus is associated with a higher resistance to permanent deformation.

Bitumen emulsion and GE-1 manufacturing at the plant

The industrial-scale manufacture of the asphalt emulsion 'eNanocel-07' required a minimum production of 2,000 kg per batch to guarantee adequate performance and correct operation of the equipment used. The quantities presented in Table 7 are followed by their dosage in an industrial-scale plant.

Table 7. Quantities (in kg) employed to manufacture 2,000 kg of 'eNanocel-07'

Aqueous or continuous phase				Discontinuous phase
Water	Commercial emulsifier	CNC nanocellulose emulsifier	Defoamer	B160/220
752.0	40.0	8.0	0.8	1,200.0

First, it is necessary to prepare aqueous or continuous phases. To this end, all products used in the preparation of this phase (Table 7) are mixed in an industrial mixer at a temperature of 60 °C. Once the nanocellulose completely dissolved in the mixture, the acidity of the entire system was adjusted by adding HCl until a pH of 2.6 was achieved. Once the aqueous phase was prepared, it was stored in a tank at a temperature of 60 °C.

After manufacturing the aqueous phase, it was mixed with the discontinuous phase (bitumen) using an industrial colloid mill at 3,000 rpm. The mill was preheated to 80 °C to avoid a sudden drop in temperature at the time of mixing; this helped avoid the breakage of the emulsion during its manufacturing process.

The stored aqueous phase was first added to the colloid mill to proceed with mixing the aqueous phase with bitumen. Subsequently, bitumen heated to 140 °C was added gradually. Additionally, and as is usual in these cases, the theoretical dosage of the emulsion was corrected by adding a commercial additive called 'whitespirit' to ensure that the emulsion did not break in the process. Good practice standards indicate that for every 8,000 kg of emulsion produced, it is necessary to add 680 kg of this specific additive; thus, 309.1 kg of whitespirit was used in this case. Throughout the process, the emulsion outlet temperature did not exceed 90 °C. Once the manufacture of the 'eNanocel-07' was finished, the product was loaded into a tanker truck and transported to the asphalt plant.

A mobile plant of the Fabremasa brand, model MZF-3, with two hoppers and a production capacity of 180 tons per hour for cold mixes was used for the manufacture of GE-1 (both control and GE-1 manufactured with 'eNanocel-07').

Trial section

Description

In the present investigation, a trial section 50 m in length and 3 m in width was constructed in Allariz (Galicia, Spain) in November 2020. The section selected was 311-2 (ATEB, n.d.), and it consisted of a 20 cm subbase of natural gravel, 20 cm base of artificial gravel, another 12 cm base of GE-1, 7 cm binder layer of AC 22 bin 50/70 D, and surface course of 5 cm of AC 16 surf 50/70 D. The control GE-1 was used as a base layer in the first 25 m of the section. In the next 25 m, the construction of the same section was performed using GE-1 manufactured with 'eNanocel-07' as the base layer (Figure 11), instead of using the conventional one.

Figure 11. Construction of the base layer of GE-1 manufactured with ‘eNanocel-07’.

Test on samples

During the construction of the test section, samples of both grave emulsions (control and eNanocel-07) manufactured at the plant were collected in situ to check their characteristics. The compression strength of the samples was obtained according to NLT-161 (Ministry of Public Works, 1998); the results are presented in Table 8. The differences between these results and those obtained in the laboratory highlight the differences between small- and large-scale manufacturing.

Table 8. Immersion-compression test results for the grave emulsions manufactured in the plant

Type of grave emulsion	UCS_{dry} (MPa)	UCS_{wet} (MPa)	RSR (%)	Heavy traffic category
Control GE-1	2.86	2.08	72.9	T3, T4
GE-1 with eNanocel-07	4.39	2.94	66.8	T3, T4

Test on cores

Two months after the construction of the test section, it was impossible to obtain cores because of the lack of cohesion between the grave emulsion. Due to the nature of the mixture and the region's frequent rain, it was foreseen. Further, it was more difficult to obtain cores on the grave emulsion manufactured with eNanocel-07 because of the lack of maturation of this mixture. Therefore, cores were collected one year after the construction of the trial section. For both control GE-1 and GE-1 manufactured with eNanocel-07, the resilient modulus of the cores was obtained according to Annex C of EN 12697-26 at 20 °C (AENOR, 2012a); the results are presented in Table 9. The resilient modulus for the case of the grave emulsion made with nanocellulose as an emulsifying agent is 159.7% higher than that of the control grave emulsion. Although the maturation is slower, considerably higher stiffness values are reached in the case of GE-1 with eNanocel-07, which confirms the results obtained in the laboratory.

Table 9. Resilient modulus of the grave-emulsion cores

Type of grave emulsion	Resilient modulus (MPa)
Control GE-1	941.7
GE-1 with eNanocel-07	2,445.5

5. Conclusions

This study explored the feasibility of using nanocellulose as an emulsifying agent for bitumen emulsions to manufacture cold asphalt mixtures. Laboratory and trial section analyses were performed, and the main findings are summarised below.

1. The use of nanocellulose as a substitute for chemical emulsifying agents in the manufacture of bituminous emulsions led to the formation of anionic bituminous emulsions.
2. It was not possible to manufacture a stable bituminous emulsion using nanocellulose fibres (CNFs).
3. Part of the conventional emulsifying agents could be replaced with CNC in the manufacture of cationic slow-setting bituminous emulsions to be used in the manufacture of cold asphalt mixtures, particularly grave-emulsion type GE-1.
4. ‘eNanocel-07’, which uses 0.4% CNC and 2% commercial emulsifier, a commercial bitumen type B160/220, water, and hydrochloric acid is found to be the best binder-aggregate coating.
5. Faster maturation is detected in the case of the control mixture compared to that of the grave emulsion manufactured with ‘eNanocel-07’. In the laboratory, the control mixture required an accelerated curing of 3 days at 50 °C in an oven, where GE made with ‘eNanocel-07’ required a minimum of 6 days at 50 °C in the oven. Visual observations suggested that the maturation of the control mixture was also faster in the test section. However, because the mixture is made for low traffic, a higher risk of permanent deformation is not expected.
6. When using CNC as the emulsifying agent, the accelerated laboratory curing protocol needs to be revised to compare the mechanical performance of the control mixture with that of the mixture made with bitumen emulsion with CNC as an emulsifying agent.
7. The laboratory small-scale manufacturing process differs from the industrial large-scale manufacturing process, which leads to differences in the performance of both the bitumen emulsion and mixtures. Therefore, in the case

of a novel bituminous emulsion, such as that analysed in the present study, it is highly recommended to perform both laboratory and field studies.

8. The GE made with ‘eNanocel-07’ clearly developed higher stiffness than the control mixture (159.7% higher after one year at the site) in the long term.
9. It's important to notice that despite the increased stiffness of the GE attained in the field, the road's surface showed no signs of reflective cracking.

The conclusions are based on limited laboratory and field research; therefore, further analyses are required. These encouraging results have inspired us to continue the investigation of the CNC as an emulsifying agent.

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Declaration of interest statement

There are no relevant financial or non-financial competing interests to report.

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