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Potential application of waste bivalve shells as recycled filler in porous asphalt concrete through rheo-mechanical analysis

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ABSTRACT

Bivalve farming annually generates millions of waste seashells as production by-products. Since seashells mainly consisted of calcium carbonate, they could be used in many construction products offering a sustainable alternative to virgin raw materials coming from mining processes. This research explores the possible use of three bio-fillers from mussel, oyster and clam shells as an effective replacement for limestone filler in porous asphalt concrete. The rheological and mechanical properties of bituminous mastics and mixtures were investigated. The rheological characterization of the three bituminous mastics did not highlight any substantial discrepancy between them and the control one. At the same time, no relevant differences were observed in the physical and mechanical properties of asphalt concretes. Based on the presented outcomes, the use of these experimental bio-fillers in open-graded mixtures can be considered as an eco-friendly alternative to reduce waste bivalve shells and their disposal.

1. Introduction

Seafood is a key ingredient and protein source in traditional cuisines of many populations. Against a backdrop of continuous growth of aquatic food consumption pro capita (from 9.0 kg in 1961 to 20.2 kg in 2020), the global aquaculture production has been expanding in the last three decades, while a nearly stable or slightly reduction of world's fisheries production. In fact, the expansion rate of fisheries has come to a halt thanks to, not only but mainly, more restrictive environment protection policies (Food and Agriculture Organization (FAO), 2022. The aquaculture is often considered a feasible solution against the aquatic ecosystem concerns related to fishing activities, and particularly to overfishing (Longo et al., 2019). Among all, the production of molluscs can provide several ecosystem benefits such as the control of anthropogenic CO_2, costal protection and bio-diversity maintenance (Morris et al., 2019). However, the worldwide aquaculture-related farming also contributes to the production of huge quantities of waste during their processes. Over a total production of 87.5 million tonnes (49.2%) of aquaculture products in 2020, 13 million tons of waste bivalves are produced every year and are usually dumped in open fields or in landfills (Food and Agriculture Organization (FAO), 2022; UBezerra et al., 2011). Due to the unregulated disposal, shell waste piles are present all around the world and cause harm to the environment in terms of visual pollution, area contamination and unpleasant smell (Summa et al., 2022; Yao et al., 2014). Also, the post-consumption of molluscs counts for a large disposal of shell residues (Summa et al., 2022).

Since bivalve shells (i.e. mussels, clams and oysters, etc.) mainly consist of calcium carbonate ($CaCO_3$), this waste may represent a suitable recycled mineral aggregate for several construction and building materials (He et al., 2023; Morris et al., 2019). In road pavement sector, the calcium carbonate is commonly present in the filler that is obtained by crushing natural and non-renewable basic rock as limestone (Nwaobakata and Cagwunwamba, 2012). The filler is the finest aggregate fraction of asphalt mixtures. At least the 70% wt. of its particles passes through the 0.063 mm sieve according to the EN 13043 standard. The filler is a mandatory constituent of the lithic skeleton of asphalt concrete that allows it to meet the required grading distribution. Being part of the aggregates, filler provides contact points between particles and it actively contributes to the volumetric properties and mechanical resistance of asphalt pavements. Moreover, the suspended filler particles within the bituminous binder (i.e. bituminous mastic) affects the rheological response of the final material (Kallas et al., 1961). The filler presence and interaction with bitumen leads to three different reinforcement mechanisms: volume-filling, physical and chemical and particle-interaction reinforcements (Buttlar et al., 1999). The overall increased stiffness of the resulting bituminous mastic was found to be

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affected by filler quantity and type, coming either from virgin or recycled materials, and hence, its rheo-mechanical characteristics, aging and water damage resistances. The latter includes particles shape, size distribution, agglomerates and degree of filler dispersion within the bituminous matrix (Antunes et al., 2019; Buttlar et al., 1999; Guo et al., 2021; Tan and Guo, 2014; Varveri et al., 2021). Due to the intrinsic variability and influence of filler at both binder and asphalt mixture scales, the rheo-mechanical investigations of alternative fillers coming from valuable wasted products is crucial to potentially assess their possible use as road construction materials. Particularly, the use of seashell fillers in road pavements represents a valorisation process of a biological waste, which may protect the environment while reducing the construction cost of infrastructures (Guo et al., 2021).

The growing global demand of sustainable solution and eco-friendly materials in the paving industry, has led to the use and integration of porous asphalt mixture with recycled materials including biowaste coming from the seafood farming (Choudhary et al., 2021; Rodríguez-Fernández et al., 2020). In a contest of environmental sustainability and minimization of urban impacts, porous asphalt concrete results to be the proper solution in the field of road construction materials (Afonso et al., 2017; Antunes et al., 2020). In the last few decades, the use of porous asphalt mix has been widespread worldwide thanks to its properties. Various studies underline that the main advantages of using this mixture are the capacity of manage the stormwater and the runoff, and the consequent possibility to refurbish the groundwater (Carmo et al., 2022; Vardanega, 2014). Furthermore, when porous asphalt concrete is used in an urban context, it is well demonstrated that it is capable to reduce the acoustic impact, absorbing traffic noise, and it is able to mitigate the urban heat island phenomenon due to its structure (Cao et al., 2018; Guan et al., 2021). Moreover, the trend in the field of road materials is to couple porous asphalt mixture with recycled materials or/and biowaste (Chen and Wong, 2013; De Pascale et al., 2023; Russo et al., 2022). The research is pushing forward to use different type of waste to replace the virgin aggregates composing the mixture, going from the use of reclaimed asphalt pavement and construction and demolition waste aggregates to the use of eggshells and seashells wastes (Carmo et al., 2022; Hu et al., 2019; Waisy Khalid and Ahmad AL-Hadad, 2023; Yang et al., 2021). For what concern the replacement of limestone filler, few studies have investigated the use of waste filler from different sources for the production of asphalt concrete in general (Sangiorgi et al., 2016; Topini et al., 2018). Even fewer studies focused their attention on the use of waste coming from bivalve shells as filler replacement in paving materials and even less when considering the porous asphalt concrete (Arabani et al., 2015; Sholichin and Ayunaning, 2019).

Therefore, the present research work takes place in this context, with the objective of verify the possible substitution in porous asphalt concrete of limestone filler with bio-fillers coming from mussel, oyster and clam shells.

2. Materials and methods

With the final aim of exploring the untapped potential of bivalve shell wastes from mussels, oyster and clams as a total replacement of limestone filler in porous asphalt concrete, four bituminous mastics and four corresponding open-graded asphalt mixtures were produced. The materials underwent a rheological, physical and mechanical characterizations. Since the asphalt mixes were composed of 88% of virgin mineral aggregates, 7 % of filler, 5 % of polymer modified bitumen (PmB) and 0.3% of cellulosic fibres, the four bituminous mastics were prepared considering the same filler-bitumen ratio and they were tested by means of Dynamic Shear Rheometer (DSR). The four bituminous mastics counted the control one (labelled PmB-L) with limestone filler and the experimental ones with bio-fillers (PmB-M, PmB-O and PmB-C for mussels, oysters and clams respectively).

The properties of the four porous asphalt mixes were evaluated in terms of air voids contents, vertical permeability, tensile resistance, stiffness and skid resistance. In addition, the water susceptibility of bituminous mastics and mixes were assessed. The mixtures were named PA-L (limestone filler), PA-M (mussels), PA-O (oysters) and PA-C (clams).

2.1. Materials

2.1.1. From bivalve shells to bio-fillers

The waste materials used in this study come from the shells of three different bivalves. The procedure for transforming the waste in a powdery material to be used as filler involved the following phases: (i) a manual cleaning of the shells, (ii) a subsequent drying phase in the oven at 400 °C to remove all the organic compound, (iii) and crushing and milling operations at the desired particle size suggested by the European standard EN 13043. A fulfilling analysis and explanation of the biofiller production is present and published in a preliminary study (Caroscio et al., 2024). The final fillers are presented in Fig. 1. Bio-fillers coming from a) M, b) O, c) C. and labelled as M, O, C for the material produced by the mussel, oyster and clam shells, respectively. The physical and chemical properties of the three bio-fillers and of the limestone (L) filler, which is the control material for this study are shown in Table 1.

2.1.2. Virgin aggregates

The lithic skeleton of the porous asphalt mixture consists of aggregates with different sizes. In the present study virgin coarse basalt aggregates and virgin sand were used. For developing the desired grading distribution of the mix three different sizes of the aggregates were employed: basalt aggregates with grading dimension ranging from 12 to 20 mm and from 4 to 10 mm, and sand with a size dimension in the range between 0 and 4 mm.

2.1.3. Bituminous binder

A polymer-modified bitumen (PmB) is commonly used for the production of porous asphalt mixtures. In this research, a commercial PmB 45/80-70 with Styrene-Butadiene-Styrene (SBS) modification was employed as base binder for the production of bituminous mastics and porous asphalt concretes. As reported in the technical specification of the selected PmB, it has a penetration value that ranges between 45 and 75 dmm at 25 °C (EN 1426) and a softening point higher than 70 °C (EN 1427).

2.2. Samples preparation

2.2.1. Bituminous mastics preparation

The filler-bitumen ratio of all bituminous binders was constant and equal to 1.4, which corresponded to 41.7% of PmB and the 58.3% of each filler. The aforementioned mass proportions of PmB and filler derived from the mix design of the porous asphalt concrete. In order to produce the bituminous mastics, the PmB was heated in an oven at 180 °C for 1 h 30′ before mixing it with the specific quantity of each filler. The mixing phase was performed on a heating plate by the use of a propeller mixer at 800 rpm for 8′. Then, samples with a circular shape were prepared pouring the bituminous binder and mastics. To avoid the settlement of filler particles at the bottom of the can, the mastics were manually stirred again before sampling procedure.

2.2.2. Porous asphalt samples preparation

The grading distribution of the four porous mixes was designed considering an Italian technical specification. By following the European standard EN 933-1, the size particle distribution of the virgin aggregates was analysed. The aggregates composition and gradation were the same for the three innovative mixtures and for the control mix produced with limestone filler. The amounts of PmB and fibres are the same for all the mixtures and correspond to 5% and 0.3% respectively. No further investigation was need for the characterization of the optimum of

Fig. 1. Bio-fillers coming from a) M, b) O, c) C.

Table 1
Bio-fillers chemical and mechanical properties.

Properties	Unit	Limestone filler	Bio-filler M	Bio-filler O	Bio-filler C
Particle density (EN 1097-7)	Mg/cm^3	2.70	2.68	2.63	2.64
Rigden voids (EN 1097-4)	%	41.0	33.3	35.1	34.8
Delta Ring & Ball (EN 13179-1)	°C	8.0	13.0	13.9	10.3
$CaCO_3$ content (EN 196-2)	%	98.0	90.3	98.3	94.8

bitumen since the properties of the fillers are similar and the assessment of the optimal dosage of bitumen for the virgin mixture was developed in previous studies. The obtained grading curve is presented in Fig. 2.

After optimizing the grading distribution of the mixes, 11 specimens for each mixture were prepared using a laboratory mixer based on a standardized procedure. The aggregates and bitumen were preheated in oven at a temperature of 170 °C for at least 4 h and less than 2 h, respectively. A total of 6 specimens were compacted with a gyratory compactor in accordance with the EN 12697-31 standard, applying 50 gyrations. These 6 samples had a diameter of 150 mm and were tested in terms of air voids, tensile strength, stiffness, vertical permeability and skid resistance. The remaining 5 samples were prepared in the same way but compacted by 2 × 50 blows using a Marshal compactor, following the European standard EN 12697-30, and underwent abrasion resistance test.

2.3. Test methods

The experimental program was set up to evaluate the rheological, mechanical, physical and functional properties of the four bituminous mastics and asphalt mixtures. An Anton Paar MCR 302 (Austria) DSR was used to study the rheological behavior of the produced mastics by using the following characterization tests:

- Frequency Sweep (FS) test at 10÷60°C (EN 14770);

The FS test allows the evaluation of the stress-strain responses of the bituminous mastics over a wide range of frequencies/temperatures. Preliminarily, the linear viscoelastic (LVE) range of the four mastics was determined by means of the Amplitude Sweep (AS) test and, then, the minimum value (i.e. 0.07%) was used as an input data of the FS test. During the AS tests the samples underwent an increasing strain from 0.01% to 10% applied at a constant frequency of 1.59 Hz. The AS tests were performed at 10 °C that is the minimum test temperature of the FS test. The FS tests were carried out at six test temperatures between 10 °C and 60 °C with an increasing rate of 10 °C at variable frequencies in the range between 0.01 Hz and 10 Hz. Both, AS and FS, tests were carried out using the 8-mm parallel plate geometry and a gap of 2 mm. Thanks to the MSCR test, the elastic response and the high temperature performances of the four bituminous mastics were determined. The confined 1 mm thick sample between 25-mm parallel plates were loaded at a constant creep stress for 1 s followed by a zero-stress recovery phase of 9 s, which represents one load-recovery cycle. All specimens underwent several load-recovery cycles at two stress levels, namely 0.1 kPa (20 cycles) and 3.2 kPa (10 cycles).

In order to compare the mixtures, the same experimental program was developed for each mixture and encompassed the following laboratory tests:

- Volumetric analysis through air voids content (EN 12697-8);
- Indirect Tensile Strength (ITS) at 25°C (EN 12697-23);
- Indirect Tensile Stiffness Modulus (ITSM) at 10°C, 20°C and 30°C (EN 12697-26);
- Particle loss (PL) of porous asphalt (EN 12697-17);
- Vertical permeability (EN 12697-19);

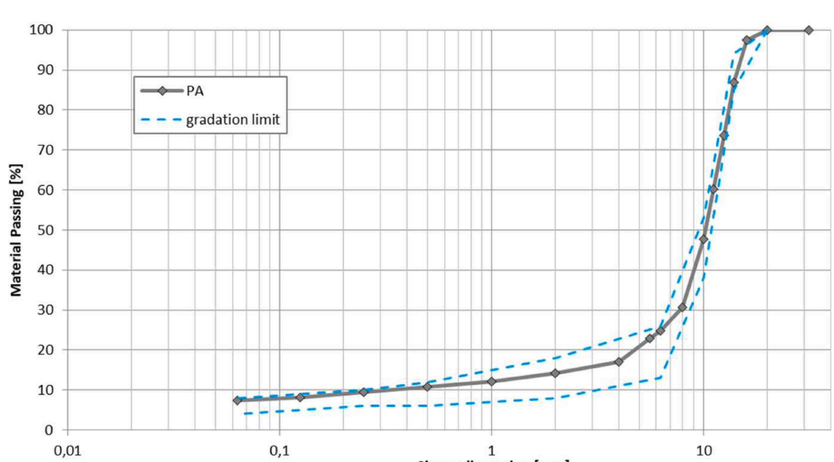

Fig. 2. Aggregates gradation.

- Skid resistance (EN 13036-4).

Each PA mix underwent volumetric, mechanical and functional analysis after being cured for a minimum of 24 h after compaction. Static and dynamic mechanical characterizations of all PA mixes were performed by means of ITS and ITSM tests after a samples' conditioning at the test temperature for at least 4 h. The ITS test in dry condition allows the evaluation of the cohesive properties of asphalt concretes and it was carried out by applying a compression load with a constant speed rate of 51 mm/min until its failure. The stiffness modulus was established in the indirect tensile configuration (IT-CY) by using a servo-pneumatic testing machine. A pulse loading was applied with a 124 ms rise-time to generate a horizontal deformation of $5 \pm 2\,\mu\varepsilon$. The particle loss, vertical permeability and skid resistance tests were employed to characterize the durability and functionality of open-graded asphalt mixes.

The water susceptibility of both, bituminous mastics and PA mixes, were evaluated. The four PA concretes underwent to Indirect Tensile Strength Ratio (ITSR) according to the EN 12697-12 standard, which quantifies reduction in ITS after conditioning in the water. The specimens of each mixture were conditioned in a water bath at 40 °C for 72 h. The same samples conditioning was applied to the bituminous mastics prior replicating the FS and MSCR tests.

3. Results and discussion

3.1. Rheological analysis

For each mastic, the complex shear modulus (G*) and phase angle (δ) master curves were evaluated and they are reported in Fig. 3. The master curves' construction employed a manual shift factor, α_T, as expressed in Eq. (1):

$$\alpha_T = \frac{f_r}{f} \tag{1}$$

Where f is the applied frequency during the FS test, and f_r is the reduced frequency at the reference temperature. Since the reference temperature was considered equal to 30 °C, the α_T at that temperature was equal to 1. The G*-f_r curves revealed a similar rheological behavior of all mastics overlapping each other over the entire range of frequencies and/or temperatures. The δ master curves exhibited the non-linear S-type curve with a peak at intermediate frequencies followed by a drop toward lower frequencies, which denoted the presence of SBS polymer in the bituminous matrix, and, hence, in the bituminous mastics (Asgharzadeh et al., 2015; Lagos-Varas et al., 2020). As well as in the G* master curves, no significant differences were found in the stress-strain response of all tested bituminous mastics.

The elastic behavior and the high-temperature responses of the four mastics were evaluated through the MSCR test by means of percent recovery (%R) and non-recoverable creep compliance (J_{nr}) parameters, respectively. Both parameters were evaluated considering the latest 10 runs at the lowest shear creep load (i.e. 0.1 kPa) and all 10 runs performed at 3.2 kPa according to the ASTM D7405 standard. The average %R and J_{nr} values over two test replicates are illustrated in Fig. 4.

Greater%R values indicate a better elasticity of the bituminous material; while, lower J_{nr} values mean enhanced rutting resistance as highlighted in literature (Liu et al., 2021). Albeit, the recorded values did not exhibit differences in terms of their magnitude, PmB-O experienced improved performances. Indeed, the mastic produced with oyster bio-filler showed the highest%R value and the lowest non-recoverable creep flexibility regardless the applied shear creep load. From elasticity and rutting resistance viewpoints, the bio-filler coming from clam shells acted similarly to the control filler (L). In general, a higher data variability was experienced from the samples containing bio-fillers rather than those with limestone. This may be ascribed to the higher variability of the wastes and a non-standardized process to produce the bio-fillers. The stiffening effect of filler either from shell wastes or virgin rocks were detected, since the based PmB had%R values equal to 76.4% and 63.0% and the J_{nr} data was 0.1810 kPa^{-1} and 0.3040 kPa^{-1} at 0.10 kPa and 3.2 kPa, respectively. The presence of elastic particles as shell/limestone powder inevitably increased the elastic response of the final bituminous mastic and the creep recovery rate as reported by Guo et al. (2021). Nonetheless, the MSCR results highlighted a stress-dependent behavior of all bituminous mastics as the%R and Jnr values change while increasing the shear creep load.

3.2. Volumetric analysis

According to the European standard EN 12697-8, the air voids content (V_a) for porous asphalt mixtures was calculated as the ratio of the maximum density of the mixture, using as guideline the EN 12697-5, and the bulk density of the sample by its dimension, according with the EN 12697-6 standard. The average values of the bulk and maximum densities and V_a of the three experimental mixtures and the control one are reported in the following Table 2.

The three mixes did not show significant differences in terms of porosity even when compared with the control one. The results of the air voids content are the average value obtained from six different samples. The designed open graded gradation allows the achievement of high porosity in the final materials, fitting the requirements suggested by the European standard EN 13108-7 (12% $< V_a <$ 32%). Between the

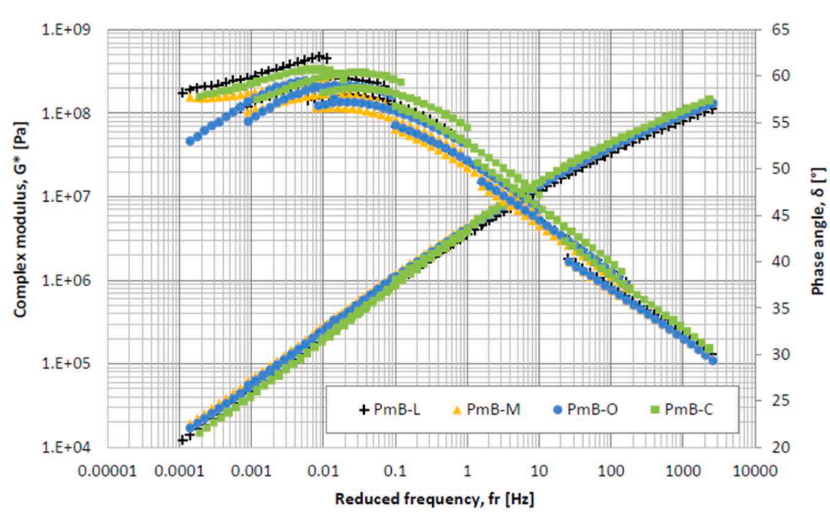

Fig. 3. G* and δ master curves of all considered bituminous mastics.

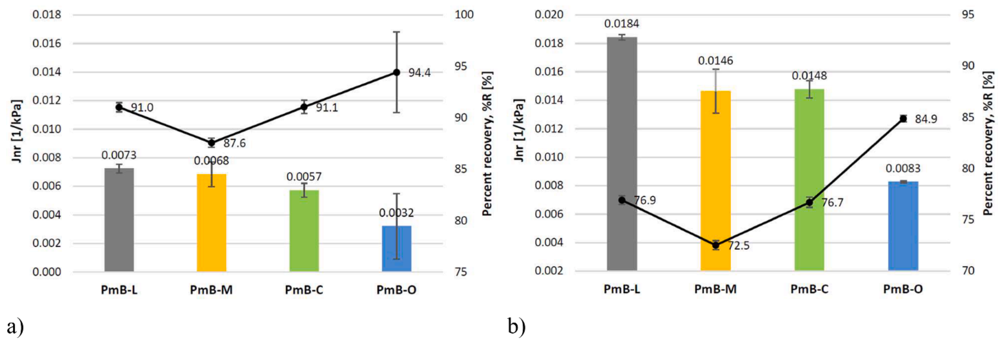

Fig. 4. MSCR results in terms of%R and J_{nr} and the related standard deviation at: a) 0.1 kPa; b) 3.2 kPa.

Table 2
Volumetric properties of the three mixtures.

Physical values	Unit	PA-L	PA-M	PA-O	PA-C
Apparent aggregate density	g/ cm^3	2.740	2.740	2.740	2.740
Maximum density	g/ cm^3	2.453	2.407	2.404	2.424
avg. Av content	%	21.56 (± 1.16)	20.21 (±0.67)	22.05 (± 1.8)	24.73 (± 1.33)

experimental mixtures, the highest porosity has been recorded for the PA-C.

3.3. Static and dynamic mechanical characterizations

The aim of ITS test is to determine the tensile resistance of asphalt mixtures. The maximum tensile stress is calculated on the peak load applied on the specimen that is loaded diametrically until it is broken. This test allows the determination of the cohesion properties of the asphalt concrete. The average ITS values at 25 °C for three specimens for each experimental mixture and the control PA mix are reported in Table 3.

By looking at the results in Table, it is evident the lowest mechanical performance of PA-C if compared to the other two mixtures containing the bio-fillers and with the control mix. This result might be strictly related to the higher presence of air voids of PA-C. As for PA-M and PA-O the value of the ITS demonstrated almost the same behavior as PA-L, meeting the Italian specification requirements of ITS > 0.40 MPa.

Through the ITSM test is possible to obtain an overview on the stiffness of the asphalt mixtures, according to the European standard EN 12697-26. The stiffness moduli were investigated at three test temperatures: 10 °C, 20 °C and 30 °C. In Fig. 5 the average value of stiffness detected during the test are reported.

Looking at the results at three different temperatures, the addition of the oyster and mussel bio-fillers did not heavily affect the ITSM values if compared with those of limestone mix. When looking at the results at 20 °C, the PA-M and PA-O values were in line with those founded in literature for a traditional porous asphalt, ranging between 4000 MPa and 5000 MPa (Andrés-Valeri et al., 2018; De Pascale et al., 2023).To further understand the temperature-related behavior of the PA mixtures, the thermal susceptibility was analysed. The thermal susceptibility can be evaluated with the temperature curves described by the following Eq. (2):

$$logS = -\alpha \cdot T + \beta \tag{2}$$

where S represents the ITSM results at the testing temperature, α and β are experimental parameters that refer to the properties of materials. Precisely the parameter α represents the temperature susceptibility and higher values implies a higher susceptibility to temperature changes of the materials. Fig.5 shows the ITSM values versus the test temperature and the temperature curves.

The ITSM-temperature curves clearly showed a similar response of the three innovative PA mixtures even if the PA-C exhibited a lower stiffness compared to the other two mixtures with bio-based fillers at every temperature. When compared with the control asphalt mix, it is evident that the three porous mixtures produced with the bio-fillers were less susceptible to the temperature changes. As a result, the mixture PA-L has a higher α parameter corresponding to a higher thermal susceptibility, which reflected the greater variability of ITSM data over the three test temperatures. In general, at intermediate and low temperatures, less differences of stiffness values were found among the four analysed asphalt concrete. Especially at 20 °C, the ITSM results confirmed the tensile response of the mixtures. In fact, the PA-C showed the lowest ITS and ITSM values; conversely, the remaining three PA mixtures do not differ from each other.

Table 3
Average ITS results of PA-L, PA-M, PA-O and PA-C.

Mechanical values	Unit	PA-L	PA-M	PA-O	PA-C
Max load	daN	679 (±56.83)	590 (±19.86)	492 (±51.55)	314 (±62.18)
Displacement	mm	2 (±0.19)	1.7 (±0.36)	1.6 (±0.40)	3.1 (±1.61)
ITS	MPa	0.59 (±0.06)	0.63 (±0.02)	0.53 (±0.06)	0.36 (±0.06)

3.4. Particle loss

According to the European standard EN 12697-17, the PL values of PA mixtures was assessed by measuring the mass loss of Marshall specimens after being introduced in the Los Angeles machine. The objective of the test is to evaluate the three mixtures in terms of abrasion resistance and the average results obtained from five samples of each mixture are reported in the following Table 4.

In terms of abrasion resistance, the PA-M, PA-O and PA-C behaved similarly and had lower percentage of particle loss when compared to the control mix. Thus, the addition of the three bio-fillers did not have a weakening effect of the mixtures. All mixtures met the maximum PL requirement stated by the Italian specification (i.e., PL < 25%).

3.5. Vertical permeability

The vertical permeability test analyses the laboratory vertical drainage capacity of open-graded asphalt mixtures. Through this test it is achievable the evaluation of the direct parameter that represents the drainage performance of PA mixes, by measuring the vertical flow of water through a standardized sideways confined specimen. The test was performed in compliance with the EN 12697-19 standard. Three

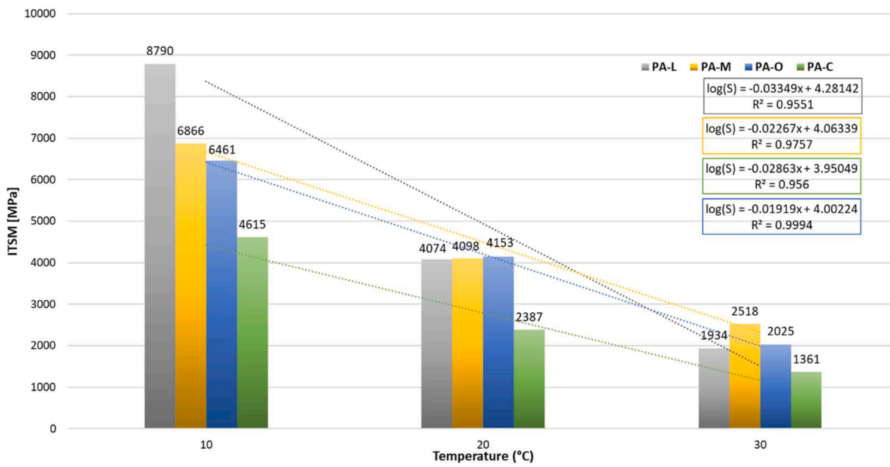

Fig. 5. Stiffness modulus behavior of each PA mixture.

Table 4
Average PL results for PA-L, PA-M, PA-O and PA-C.

Mechanical values	Unit	PA-L	PA-M	PA-O	PA-C
Particle loss	[%]	17 (± 3.79)	7 (± 1.59)	8 (± 3.52)	6 (± 1.49)

specimens were tested for each mixture and the average values of the vertical permeability and the air voids content are reported below in Table 5.

Despite the slightly lower air voids content than the other PA mixtures, PA-M had the higher vertical permeability. This suggests that the air voids in this mixture are more interconnected compared to the other two mixes, allowing a better permeability of the final asphalt concrete. On the other hand, PA-C and PA-O results were in line with those obtained for the control mixture, showing adequate permeability properties. Despite the experienced differences, all the three innovative mixtures followed the range of 0.5×10^{-3} m/s< Kv < 3.5×10^{-3} m/s suggested by the European standard EN 13108-7 for porous mixtures.

3.6. Skid resistance results

Being the innovative PA mixes employed as surface layer in an urban pavement, one of the most important properties to test is the slip/skid resistance. The skid resistance is a functional property of the material, which was measured using a slider attached at the end of a pendulum tool, following the procedure suggested by the EN 13036-4 standard. The surface characteristic was defined by the dimensionless parameter, PTV. The top surface of the cylindrical specimens were tested. The PTV results are reported in the Table 6.

All in all, the mixtures showed a relevant skid resistance, since value of the PTV around 80 units are connected to high friction properties (Kotek and Kováč, 2015). Even if the values obtained for the three innovative mixtures were not completely in line with the control PA-L, all of them fulfilled the requirements of the Italian specifications (i.e. PTV > 55).

Table 6
Average PTV values for DV, D1 and D2.

Mixtures	PTV
PA-L	89 (±2.75)
PA-M	78 (±0.53)
PA-O	74 (±3.22)
PA-C	79 (±2.37)

3.7. Water susceptibility

The water damage resistance of the PA mixes was evaluated by following the EN 12697-12. Hence, the ITS test was performed on specimens preliminarily conditioned in a water bath at 40 °C for 72 h and then conditioned in a climate chamber at 25 °C for 4 h. The same wet conditioning was applied to the bituminous mastic specimens prior carrying out the FS and MSCR tests. The G* and δ master curves of dry and wet samples are illustrated in Fig. 6; while the%R and J_{nr} results of water conditioned bituminous mastics and their percent variation from dry samples data are listed in Table 7.

All bio-based bituminous mastics experienced an overall increased stiffness in terms of G*, especially at low frequencies and/or high temperatures. Only PmB-L showed less water susceptibility. On the other hand, the δ-f_r curves were lower if compared to those of dry samples. This trend could be related to a coupled oxidative- hydrothermal aging of the bituminous mastics since specimens were exposed to relatively high temperature (40 °C) (Varveri et al., 2021). Albeit similar responses were found among all mastics and especially among those produced with shell wastes, the type of filler influenced the stress-strain behavior of the resulting bituminous mastics. Oyster bio-filler seemed to be more affected by the water conditioning as the G* and δ values were slightly higher and lower, respectively, compared to the others at low frequencies/high temperatures. The MSCR results revealed an overall reduction of the total recorded strains of all bituminous materials (i.e. PmB and mastics) as both parameter, %R and J_{nr}, reported lower values as showed in Table 8. In general, the PmB-O showed the best elastic responses and rutting resistance compared to the other fillers regardless the applied stress. In terms of elastic recovery, all bituminous mastics exhibited similar %R values at both shear creep stresses. Only the

Table 5
Mean vertical permeability of PA-L, PA-M, PA-O and PA-C.

Mechanical values	Unit	PA-L	PA-M	PA-O	PA-C
Air voids content	V_a [%]	21.56 (± 1.16)	20.21 (±0.67)	22.05 (± 1.8)	24.73 (± 1.33)
Avg. Vertical Permeability	K_v [m/s]	2.5×10^{-3} (±0.00006)	3.37×10^{-3} (± 0.0002)	2.21×10^{-3} (±0.0003)	2.26×10^{-3} (±0.0003)

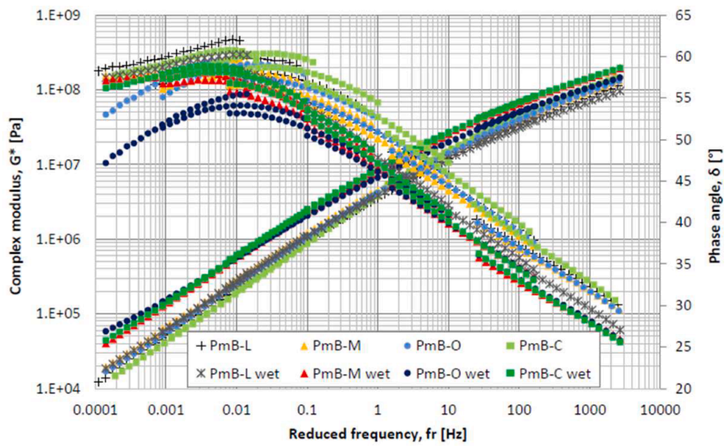

Fig. 6. G* and δ of dry and wet bituminous mastics.

Table 7
%R and Jnr values of the bituminous mastics and base PmB after wet conditioning.

Mastics	0.10 kPa		3.2 kPa		0.10 kPa		3.2 kPa	
	%R [%]	Δ [%]	%R [%]	Δ [%]	J_{nr} [1/kPa]	Δ [%]	J_{nr} [1/kPa]	Δ [%]
PmB	69.0	−10.8	62.4	−1.0	0.1095	−65.3	0.1358	−123.9
PmB-L	85.3	−6.7	73.5	−4.7	0.0070	−3.5	0.0138	−33.5
PmB-M	77.2	−13.4	72.4	−0.3	0.0045	−51.3	0.0089	−65.3
PmB-O	85.7	−5.4	75.4	−4.6	0.0004	−196.9	0.0040	−67.0
PmB-C	86.4	−10.1	73.3	−12.6	0.0019	−680.8	0.0088	−106.1

Table 8
Average results of ITS_{dry}, ITS_{wet} and ITSR.

Mechanical values	Unit	PA-L	PA-M	PA-O	PA-C
ITS_{dry}	MPa	0.59 (±0.06)	0.63 (±0.02)	0.53 (±0.06)	0.36 (±0.06)
ITS_{wet}	MPa	0.79 (±0.07)	0.57 (±0.08)	0.32 (± 0.01)	0.30 (±0.02)
ITSR	%	135	91	61	91

PmB-M had a significant lower value at 0.10 kPa. With regards to the J_{nr} values, the PmB-O was followed by the PmB-C, PmB-M and PmB-L in a descending order. However, considering the percent reduction of %R and J_{nr} values from dry to wet conditions, it can be highlighted an important reduction of PmB-O followed by PmB-C elasticity and rutting resistance at both creep loads. This trend conforms the higher ΔR&B and Rigden Voids values experienced by oyster and clam fillers that tend to be more prone to the simultaneously oxidative and hydrothermal aging mechanisms. Among bio-fillers, the intrinsic high porosity of oyster fillers may have a negative effect on mastic properties due to the more pronounced physical and chemical bitumen-filler interactions (Varveri et al., 2021).

At the asphalt mixture level, the average results of the ITSR test are shown in Table 8.

It can be observed that the ITS values of the wet samples of the experimental mixtures were lower than the ones of dry samples. A relevant discrepancy can be detected between the control mixture and the three innovative mixtures, which might be connected to the binder-aggregates adhesion. As different studies suggested, the use of seashells as filler in HMA might involve some changes in the tensile strength of the mixture (Alharthai et al., 2021; Çevrim and Iskender, 2022). Nonetheless, PA-M and PA-C obtained results in line with the requirements of the Italian technical specification, suggesting a value higher than 75%. On the other hand, PA-O showed a reduction of water-damage resistance, also verified in the rheological tests. However, this ITS reduction was unexpectedly very low compared to the other PA mixes. Further investigations are needed to better explain this phenomenon.

4. Conclusions

The present study aims to evaluate the possible use of three biowaste fillers coming from bivalve shells as alternative filler in the production of porous asphalt concrete. The considered biowaste fillers came from oyster shells, mussel shells and clam shells. The rheological characterization of the mastics and the physical, mechanical and functional properties of the PA mixtures were fully investigated at laboratory scale. According to the presented data, the following conclusions can be delineated:

- The bio-fillers behaved similarly to the control limestone filler from rheological point of view. No significant differences were found in the stress-strain response of the bituminous mastics. However, the filler obtained from oyster shells exhibited higher rutting resistance compared to the other bio-fillers and control filler.
- The volumetric analyses of the PA mixes confirmed the high porosity of the produced asphalt concrete. The PA-C showed the highest air voids content, while the PA-M had the lower V_a value. Thanks to the high porosity of the PA mixtures, their vertical permeability met the European standard. By looking at the mixture PA-M the lower percentage of voids did not affect the vertical permeability, thus suggesting a higher amount of interconnected voids. Furthermore, with the use of bio-fillers, the workability of the mixture remained constant.
- The static and dynamic mechanical investigations showed good mechanical performances of the innovative PA mixes, which were similar to that of the PA-L mixture. From the ITSM values could be observed a lower thermal susceptibility of the samples produced with the bio-fillers than the control PA. The use of filler from clam shells seems to negatively affect the mechanical properties of the PA. This phenomenon can be ascribed to the higher air voids content of the mix, that might reduce the structural properties of the PA.

- In terms of durability properties, an improved particle loss resistance and a high skid resistance were observed in all innovative PA mixture. Both, cohesion and friction properties of the open-graded asphalt concrete represent critical aspects to assess their feasibility as road construction materials.
- The water-damage resistance is a key factor for PA mixtures due to their high porosity. Both rheological and mechanical tests highlighted the influence of filler type on the water susceptibility of the bituminous materials. Among all fillers, the one obtained from oysters was found to be more prone to oxidative and hydrothermal aging, which turned into higher water susceptibility.

These preliminary results verified the feasibility of using bio-fillers from bivalve shell wastes as alternative filler in PA mixtures. Even if the rheo-mechanical characterizations highlighted the influence of filler type at both mastic and mixture scales, no relevant differences were detected in the use of the different fillers except for the water-damage resistance. This negative behavior may be mitigated by combining the recycled fillers. Their combination may represent also better choice for improving the recyclability of these wastes as the process will be less time consuming and more cost-effective. Nonetheless, a standard recycling chain and recyclability process is necessary to reduce the variability of the resulting alternative bio-fillers, which would ensure best performances, especially at the mastic level.

CRediT authorship contribution statement

B. De Pascale: Writing – original draft, Investigation, Formal analysis, Data curation. **G. Tarsi:** Writing – original draft, Investigation, Formal analysis, Data curation. **P. Tataranni:** Writing – review & editing, Supervision, Conceptualization. **C. Sangiorgi:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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