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A New Life for Cross-Linked Plastic Waste as Aggregates and Binder Modifier for Asphalt Mixtures

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Featured Application: This work deals with recycling materials for pavement application purposes. It shows a new potential use for a specific plastic waste material with a limited demand (cross-linked polyethylene waste), which can be applied as an aggregate substitute and/or binder modifier for asphalt mixtures, thus adding value to the whole paving solution.

Abstract: Every year, millions of tons of plastic waste, with potential to be reused, are wasted in landfills. Based on a literature review and in a local market analysis, cross-linked polyethylene (PEX) waste arose as the material with the greatest potential to be tested for incorporation in asphalt mixtures due to the difficulty in its recycling and the lack of solutions for its reuse. Thus, in the present work, mixtures produced with and without PEX were tested in order to compare their performance, aiming at understanding if this waste could successfully be used as an alternative material for this type of application. Thus, water sensitivity, rutting resistance, stiffness modulus and fatigue cracking resistance tests were carried out on asphalt mixtures with up to 5% PEX. Based on the results obtained, it can be concluded that the incorporation of PEX in asphalt mixtures is a viable solution for paving works, especially when high service temperatures are expected. It also decreases the density of the mixture, which can be attractive to lighten structures. Thus, this technology contributes to give new life to cross-linked polyethylene plastic waste.

Keywords: plastic waste; cross-linked polyethylene; binder modification; aggregate substitution; mix design; asphalt mixture performance

1. Introduction

The contemporary Society is stimulated by consumption, resulting in increasing demands for the use of scarce natural resources and in the production of large amounts of waste. This unsustainable scenario is also observed in the road infrastructure sector, where significant amounts of construction and demolition waste are sent to landfills every year. Therefore, the development of solutions that promote road pavement durability and reduce the amount of waste shall be promoted. Furthermore, several other wastes are difficult to recycle and may even need some treatment before being disposed. Taking that into account, it would be interesting to use wastes to improve the performance of road pavements.

Among the wastes used in road pavements, reclaimed asphalt pavement (RAP) materials are those that have been most successfully incorporated [1,2], even though some sort of rejuvenation additive may be needed [3,4]. Nevertheless, there are other wastes with high potential to be used in this type of application. Plastic wastes are one of the most promising solutions [5], while millions of tons of are sent to landfills every year [6]. Most of these plastics have a simple process of recycling, but the thermosetting plastics cannot be reprocessed, so finding the proper use for the disposal of this plastic waste is an emerging need [7].

Polymers can be incorporated into asphalt mixtures by a wet process, as bitumen modifier, or by a dry process, as partial substitute of the aggregates [8–10]. The wet process is the most widely used [11], since this method requires a smaller amount of polymer, which in its virgin state significantly increases the price of the binder. There are several examples of the use of virgin polymers in bitumen modification. Among the most commonly used are styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), ethylene-vinyl acetate (EVA), polyethylene (PE) and polypropylene (PP) [12–14].

According to some authors, it is possible to use plastic wastes in substitution of virgin polymers to achieve that goal, which leads to ecological and possibly economic benefits [15,16]. There are some plastic wastes with potential to be used in bitumen modification, but polyethylene has the advantage of being the most used polymer and thus resulting in the plastic waste available in higher quantities [6,17].

Some authors concluded that the use of recycled polyethylene by the wet method promoted improvements in the resistance to permanent deformation, decreasing the thermal susceptibility [18], increasing the stiffness [19] and promoting the best fatigue performance, when compared to unmodified asphalt mixtures [20].

The dry method was also studied by some researchers, which added recycled and virgin polymers directly to the aggregates [11]. This technique may reduce pavement deformation, increasing fatigue resistance and providing a better adhesion between the bitumen and the aggregates [10,17,21].

As mentioned above, some other plastic wastes are more difficult to recycle due to their nature, namely the thermosets, which are not possible to melt again after being produced. Cross-linked polyethylene (PEX) is a material used in the production of pipes and cables. Every year, in Europe, 400,000 tons of plastics from cable recycling are sent to landfills, and 20% of those are PEX [22]. Thus, based on a literature review and a market survey, it was concluded that it would be interesting to include this waste material in the production of asphalt mixtures with superior performance, while giving a new life to this polyethylene-based polymer that is difficult to recycle.

Therefore, the possibility of using this thermoset plastic waste in asphalt mixtures as a partial substitute of the aggregates would promote the use of higher amounts of this waste material, increasing its value, while saving landfill space and reducing the extraction of mineral aggregates. Thus, this work intended to replace part of the mineral aggregates with recycled PEX and improve the performance of the asphalt mixtures, which was obtained by using 5% of PEX, by volume of mixture.

2. Materials and Methods

2.1. Materials Used in This Study

Three different constituent materials were used in this work in order to study new asphalt mixtures incorporating a plastic waste. As usual, mineral aggregates and asphalt binders were used as indispensable components of asphalt mixtures, and a specific plastic waste was the third material used, applied both as an aggregate substitute and/or asphalt binder modifier.

Crushed granite aggregates were supplied by a local quarry in the Northwest of Portugal, being divided into three fractions with the following dimensions: 6/14 gravel, 4/6 gravel and 0/4 dust. A small quantity of limestone filler was also used, as it is usual practice for the production of asphalt mixtures with those aggregates. These aggregates were selected to produce AC surf 14 mixtures for pavement surface layers.

Two commercially available binders typically applied in Portugal were used in this study, both supplied by Cepsa Corporation, Madrid, Spain. A 50/70 pen grade bitumen (according to EN 12591) was used as the base binder for comparison purposes, before and after incorporation of plastic waste in the mixtures. A polymer modified binder PMB 45/80-60 (according to EN 14023) was also used for an additional comparison, taking into account that the use of plastic waste may change the base 50/70 bitumen into a PMB.

The plastic waste applied in this study was a cross-linked polyethylene (PEX), mainly recovered from pipe, tubing and electrical cables, and it was supplied by Gintegral S.A., Póvoa de Varzim, Portugal. This material is composed of particles with a lamellar flake shape and an equivalent diameter ($Ø_{eq}$) ranging between 0.5 and 10.0 mm. In order to reduce their size and lamellar shape, PEX flaxes were ground to obtain smaller particles with a nominal diameter between $0.5 < Ø_{eq}$ (mm) < 4.0.

2.2. Characterization of the Plastic Waste Material Used

First, the PEX waste was characterized in order to assess its main properties, which may directly influence the design of asphalt mixtures or their future performance in the pavement.

Taking into account that PEX will be used as aggregate substitute, it is essential to evaluate its grading curve (according to EN 933-1 standard) and particle density (EN 1097-6 standard). In fact, the results of these tests will be taken into consideration when designing the asphalt mixture, namely to adjust its grading curve.

Almost all PEX material is made from high-density polyethylene, containing cross-linked bonds in the polymer structure that change the thermoplastic to a thermoset nature. The cross-linking process can be more or less effective, but it is never complete. In fact, a higher degree of cross-linking could result in brittleness of the material, while a lower degree of cross-linking could result in products with poorer physical properties, especially at elevated temperatures. In this study, the PEX waste will be mixed with bitumen and aggregates at very high temperatures. It is not expected that the cross-linked part of PEX will be changed during the mixing phase, thus working as an aggregate substitute, while the remaining part will certainly interact with the base bitumen, modifying its properties. Thus, it is very important to assess the GEL content, or degree of cross-linking, of PEX waste, which can be carried out according to the ASTM D2765 standard. In order to quantify the amount of PEX waste that cannot melt, a sample with a known mass is immersed in xylene and boiled for 24 h and then the remaining sample is dried and weighed.

Finally, DSC tests were performed in order to evaluate the melting temperature of the PEX portion that is not cross-linked, which should be lower than the asphalt mixing temperature to ease the bitumen modification. The DSC tests were carried out in a DSC Diamond Pyris, Waltham, MA, U.S.A. About 10 mg of sample was sealed in an aluminium capsule, and then the following protocol was applied: two heating and one cooling cycle ranging from −40 °C to 160 °C at a rate of 10 °C/min. The two heating cycles should provide the same thermal history for the entire sample in order to assure that this range of temperatures used for asphalt production does not change the polymer properties.

2.3. Definition of the Asphalt Mixtures to Be Studied and Their Aggregate Grading Curves

The mineral aggregates and the filler were also characterized regarding their grading curves, according to the EN 933-1 standard. By knowing the gradation of all aggregates, including the PEX waste, it is possible to calculate the amount of each material to be used in order to fit the standard grading limits of the asphalt mixture to be produced in this work, i.e., an AC 14 surf mixture (Portuguese annex of standard EN 13108-1).

The main objective of this work is to incorporate a significant amount of PEX in an asphalt mixture for a road pavement surface layer and compare its performance with a conventional mixture without PEX. Thus, two comparable asphalt mixtures were defined in this work to carry out the study: (i) a conventional mixture with only mineral aggregates; (ii) a new mixture incorporating PEX, with 5% of PEX by volume of the aggregates used in the mixture. Taking into account that polymer modifiers are typically included only as a small percentage of the bitumen, the amount of PEX used in this work is remarkably high, in order to highlight the outcomes of this solution.

The calculated amounts of each aggregate fraction and PEX waste used in both asphalt mixtures, with or without PEX, in order to fit their gradation within the limits of an AC 14 surf mixture are presented in the Table 1.

Table 1. Percentage of each fraction of aggregates used in this work for asphalt mixture production.

Asphalt Mixture	Aggregate Fractions Used in the Mixtures (% in Volume)				
	6/14 Gravel	4/6 Gravel	0/4 Dust	Filler	PEX Waste
Conventional mixture (only with mineral aggregates)	46.0	13.0	39.3	1.7	-
Mixture incorporating PEX (with mineral aggregates and PEX)	45.0	10.9	37.4	1.7	5.0

The aggregate grading curves of the different mineral aggregates, filler and PEX waste are presented in Figure 1a. Then, by using the amount of each aggregate fraction and PEX waste previously presented, the aggregate grading curves of the conventional mixture (without PEX) and the mixture incorporating PEX are presented in Figure 1b, perfectly adjusted to the standard limits of the AC 14 surf mixture.

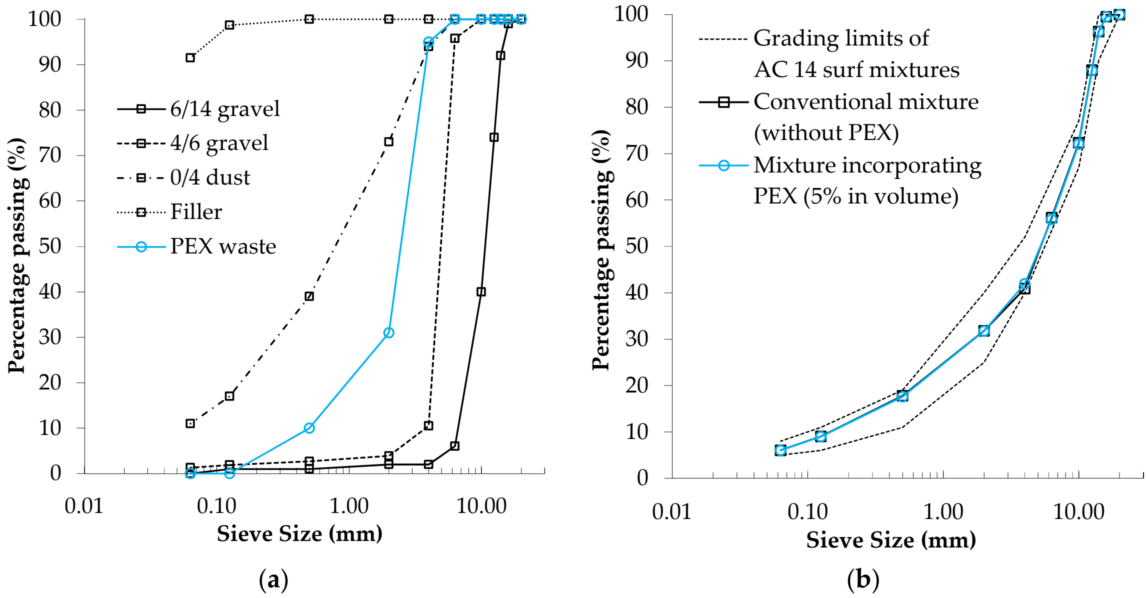


Figure 1. Aggregate grading curves of: (**a**) Mineral aggregates, filler and cross-linked polyethylene (PEX) waste and; (**b**) Asphalt mixtures (with and without PEX) fitted within the limits of an asphalt concrete mixture AC 14 surf.

PEX waste presents a 0.5/4 dimension, which will partially substitute the coarser part of 0/4 mineral dust. It should be noted that these dimensions could be changed in future studies, namely by further reducing the PEX size in order to increase the interaction with bitumen, but the industry costs associated with this operation shall be taken into consideration.

It can also be observed that the particle size distribution obtained for both asphalt mixtures, with or without PEX, is almost equivalent. Thus, the performance of both mixtures can be compared without direct influence of their gradation, which should only be influenced by PEX waste.

2.4. Evaluation of Asphalt Binder Characteristics after Interaction with the Plastic Waste

The use of PEX waste in an asphalt mixture, incorporated by the dry process as an aggregate substitute, will also cause the modification of the base bitumen used in the mixture because PEX is not totally cross-linked. Thus, the direct influence of the melting part of PEX waste in the properties of the base bitumen 50/70 was evaluated in this work because the polymer may be able to modify the binder during the short period of asphalt mixture production [13] when PEX and bitumen can interact at very high temperatures.

In order to simulate the interaction between the bitumen and the PEX waste during the asphalt mixture production, a PEX modified binder was produced by mixing the PEX with bitumen for 2 min at 180 °C (reproducing the time and temperature used for asphalt mixture production), in an IKA blender at 250 rpm (Figure 2a). The amounts of PEX waste and 50/70 bitumen used to produce the PEX modified binder were proportional to those used for asphalt mixture production. The amount of PEX used in the asphalt mixture is 5% by volume of aggregates, which corresponds to approximately 1.8% by weight due to the low density of PEX in comparison with that of the mineral aggregates. For an asphalt mixture with a bitumen content of 5% (typical value for AC 14 surf mixtures), the amount of PEX waste will be 1.71% by weight of the entire mixture, corresponding to 34.2% by weight of 50/70 bitumen. Thus, in order to produce 1000 g of PEX modified binder, 745 g of bitumen and 255 g of PEX were used. At the end of the mixing process, the binder was filtered with a metal mesh (sieve size of 0.5 mm) in order to separate the cross-linked part of PEX waste (Figure 2b) from the binder that was modified with the melted part of PEX, which will be further characterized to evaluate the actual modification process.

(**a**) (**b**)

Figure 2. Evaluation of PEX interaction with bitumen: (**a**) Binder preparation for 2 min at 180 °C and; (**b**) The binder was filtered to separate the cross-linked part of PEX undissolved in bitumen.

At the end of this process, the filtered binder was characterized according to the EN 12591 standard. The basic characterization included penetration at 25 °C (EN 1426) and softening point or ring and ball (R&B) temperature (EN 1427) tests. Dynamic viscosity tests were also carried out in a Brookfield viscometer (EN 13302 standard) in order to evaluate the behaviour at mixing and compaction temperatures. The base bitumen (50/70) and a commercially available PMB (PMB 45/80-60) were also characterized using the same test protocol for comparison purposes and also because they will be used for the production of asphalt mixtures.

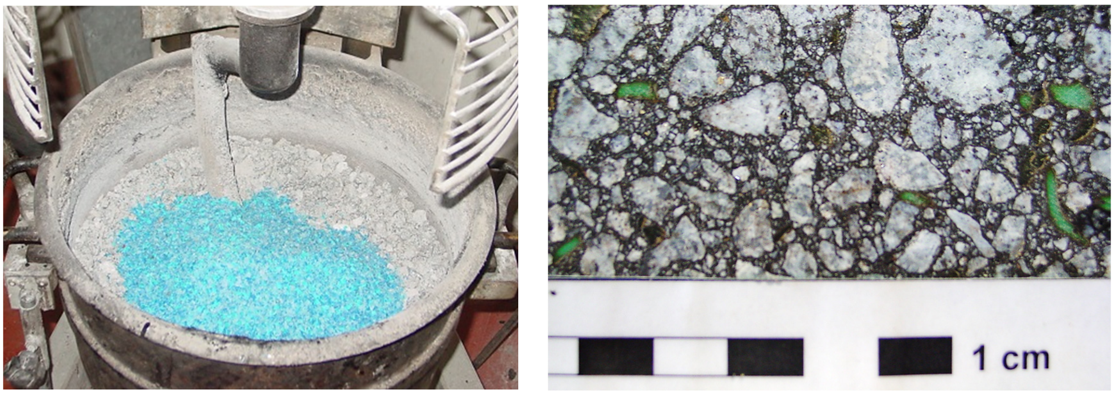
2.5. Design of the Asphalt Mixtures Incorporating PEX

The design of the conventional AC 14 surf mixtures without PEX has been previously presented [23,24], and the optimum binder content was found to be 5.0%. The same value was used in this work to produce the asphalt mixtures with mineral aggregates. However, the design of the asphalt mixtures incorporating PEX was performed for the first time in this work.

Taking into account the higher absorption of bitumen by the PEX waste in comparison with mineral aggregates, and the partial interaction of those two materials, it is expected that a higher binder content would be required to produce the new asphalt mixtures with PEX. Thus, the design of these mixtures was carried out according to the Portuguese annex of the NP EN 13108-1 standard, but only using three binder contents equal or higher than those of the conventional mixture (i.e., 5.0, 5.5 and 6.0%). The optimum binder content to be determined is the average value of the binder contents that results in the maximum Marshall stability (EN 12697-34 standard), an air void content of 4.0% for AC 14 surf mixtures (EN 12697-8) and the maximum bulk density (EN 12697-6, procedure B).

A complementary validation study was also performed to confirm the Marshall Mix design results by evaluating the water sensitivity (EN 12697-12 standard) of the mixtures with PEX for those three binder contents. The main result of this test is the ITSR, which is the ratio between the average indirect tensile strength test (EN 12697-23) results from a group of three specimens immersed in water (ITSw) and another group of three similar specimens tested under dry conditions (ITSd). The design and validation study of the asphalt mixtures with PEX allowed determination of the binder contents to use in the production of these mixtures for additional performance evaluation.

After defining the composition of all mixtures, two mixtures without PEX (with 50/70 and PMB 45/80-60 binders) and three mixtures with PEX (Figure 3a) were produced in order to obtain all test samples (Figure 3b) necessary to carry out several performance-related tests.



(**a**) (**b**)

Figure 3. Asphalt mixtures with PEX developed in this work: (**a**) Production stage applying the dry method of incorporation; (**b**) Tests samples with PEX particles clearly visible.

2.6. Performance Evaluation of Studied Asphalt Mixtures

The performance related tests included the determination of the water sensitivity, rutting resistance, stiffness modulus and fatigue resistance of the studied asphalt mixtures.

The design of a bituminous road pavement involves the definition of a structure that ensures the capacity of withstanding the loads applied by vehicles and by weather conditions. The mechanical properties of the bituminous mixtures to be used in the road structure should be evaluated, such as the stiffness modulus, phase angle, and pavement resistance to failure mechanisms such as cracking due to fatigue and permanent deformation.

Among the resistance to the weather conditions, the evaluation of asphalt mixture water sensitivity is very important, since this property is directly related to the performance of the road pavement. This property was determined by the EN 12697-12 standard. The indirect tensile strength test was carried out according to the EN 12697-23 standard, after a volumetric characterization of the specimens to determine the air void content, which significantly influences the results.

The rutting resistance of the mixtures was assessed by means of the wheel tracking test (WTT), according to the EN 12697-22 standard, using the procedure B (in air), with a standard wheel load of approximately 700 N. The test was carried at a temperature of 50 °C, being representative of our country's hotter summer days.

The stiffness modulus test was carried out on prismatic specimens, using the four-point bending configuration (4PB-PR), according to the EN 12697-26 standard. The test was carried out at 10, 20, 30 and 40 °C for a range of frequencies (0.1, 0.2, 0.5, 1, 2, 5, 8 and 10 Hz). Based on the principle of superposition time temperature, used to relate the equivalence between frequency and temperature, it was possible to construct master curves, in this case using 20 °C as temperature of reference. The results are represented by the stiffness modulus and the phase angle, which are the most relevant properties of viscoelastic materials such as asphalt mixtures.

The fatigue resistance of the studied mixtures was also determined using the four-point bending beam test procedure, according to the EN 12697-24 standard. The tests were carried out at 20 °C, in strain control mode, and using a frequency of 10 Hz. The fatigue laws of the studied mixtures can be represented by Equation (1):

$$N = \mathrm{a} \times (1/\varepsilon_t)^{\mathrm{b}}, \quad (1)$$

which relates the level of extension applied in the test (ε_t) with the number load cycles (N) that cause test specimen failure (reduction of stiffness to half of its initial value), and where a, b are coefficients determined experimentally.

3. Results and Discussion

3.1. Properties of the Plastic Waste Material

In this work, the PEX waste is the new material applied, originally, in asphalt mixtures. The results of its experimental characterization are presented below, according to the methodology presented in Section 2.2.

The particle density of PEX waste at 25 °C was evaluated as being 938.6 kg/m^3. This value is slightly lower than that of bitumen (nearly 1030 kg/m^3), but is clearly lower than that of mineral aggregates (nearly 2650 kg/m^3) that PEX is partially substituting. The knowledge of this value was crucial to calculate important volume and weight proportions between the different materials used in the asphalt mixtures. Furthermore, the grading curve of the ground PEX waste particles, previously presented in Figure 1a, was also essential to adjust the grading curve of the new asphalt mixtures with PEX within the standard limits of an AC 14 surf mixture.

The ability of PEX particles (Figure 4a) to partially melt under application of heat (180 °C) and pressure, specifically because they are not totally cross-linked, can be observed in Figure 4b. However, the cross-linked part of PEX is not changed by the presence of solvents, heat or pressure.

(a) (b)

Figure 4. PEX waste particles: (**a**) Before being heated; (**b**) After applying heat and pressure at 180 °C.

The GEL content (or degree of cross-linking) of the PEX waste used in this work was determined to be 54%. This percentage of PEX will certainly not melt, working only as aggregate substitute, but the other part of PEX waste (nearly half of it) can melt and modify the asphalt binder during the production of asphalt mixtures, thus improving the mixture performance.

The calorimetry results (DSC) of PEX waste, presented in Figure 5, can be used to evaluate the melting temperature of this material. The melting temperature of PEX particles obtained in the DSC was nearly 130 °C, for both heating cycles, which is within the typical melting temperature range of polyethylene materials. This value is clearly lower than the temperature used for asphalt mixture production (180 °C). Thus, the PEX waste, introduced in the asphalt mixture by the dry process, as aggregate substitute, could easily interact with the asphalt binder at those temperatures.

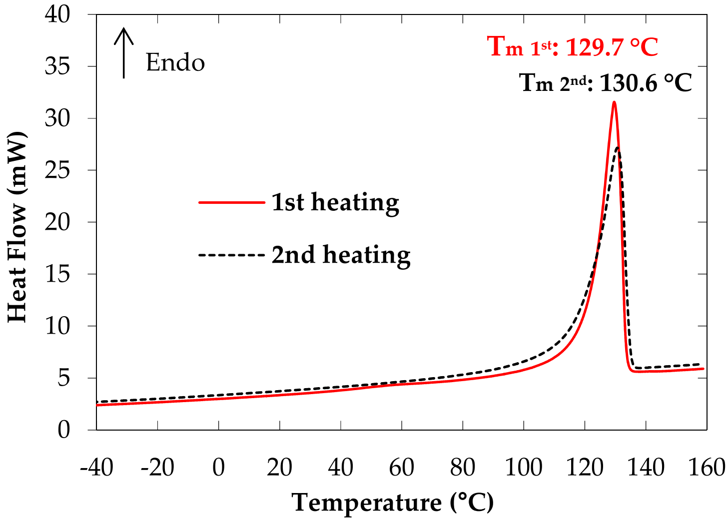


Figure 5. Differential scanning calorimetry (DSC) results of PEX waste.

Therefore, the binder properties should be assessed, before and after interaction with PEX, in order to quantify the binder modification attributed to this waste material.

3.2. Properties of the Asphalt Binders Used in This Study

Three binders were characterized in this part of the work: two commercially available binders selected for this study (base bitumen 50/70 and modified binder PMB 45/80-60) and the PEX modified binder obtained according to the process presented in Section 2.4. The basic properties (penetration and softening point or R&B temperature) of those binders are presented in Figure 6.

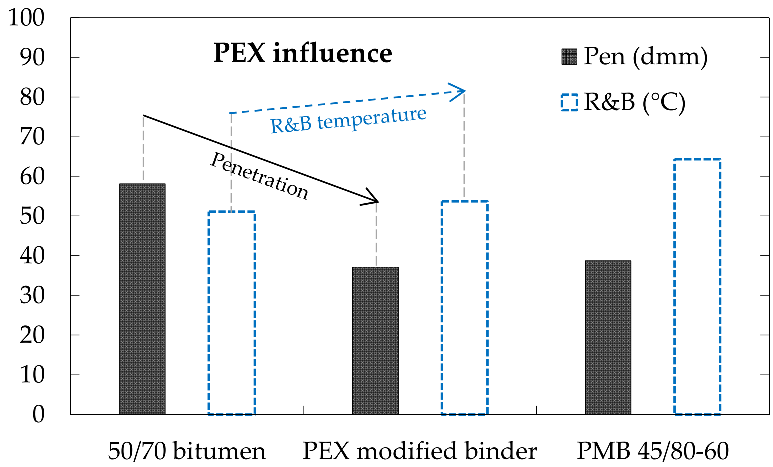


Figure 6. Basic properties of the asphalt binders used in this study, including the PEX modified binder.

Although PEX particles are only able to melt partially and they have been interacting with bitumen for only 2 min, it becomes clear that PEX waste certainly modified the 50/70 bitumen properties. In fact, the use of PEX reduced the penetration value and increased the softening point result in comparison with the base bitumen 50/70, which should also increase the stiffness modulus and permanent deformation resistance of the new mixtures incorporating PEX.

The effect of PEX is more evident in the penetration test than in the softening point test, which is usual when modifying binders with polyethylene-based polymers [18]. Actually, the penetration of PEX modified binder is lower than that of PMB 45/80-60, while its softening temperature is far from being similar to the commercially available PMB.

The viscosity of the studied binders could give valuable information about the performance at very high temperatures, being helpful to define the mixing temperatures to be used for production of asphalt mixtures. Figure 7 shows the evolution of the dynamic viscosity of the studied binders at different temperatures.

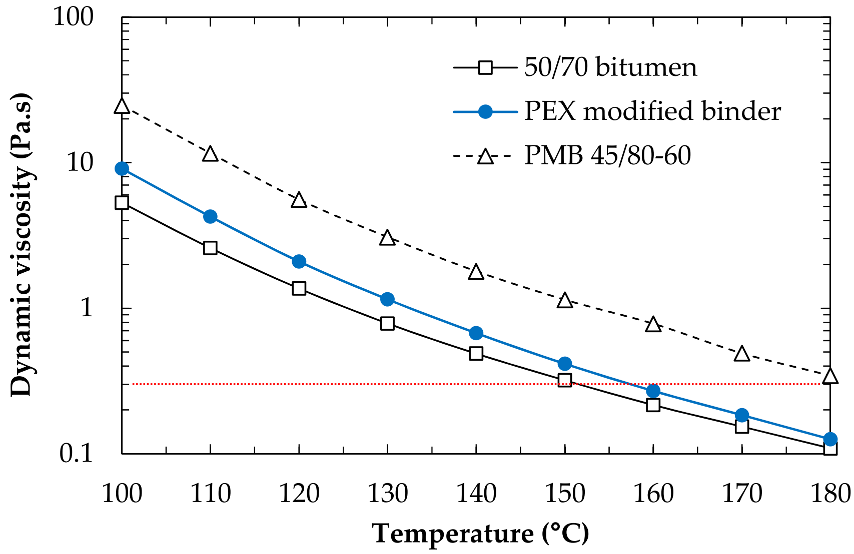


Figure 7. Dynamic viscosity results of the asphalt binders used in this study, including the PEX modified binder.

It can be observed that the interaction between PEX waste and 50/70 bitumen resulted in a modified binder with increased viscosity, even though it is clearly lower than that of PMB 45/80-60. Thus, the modification of 50/70 bitumen by PEX waste changes its behavior in the whole range of temperatures of asphalt mixtures in service or during paving works.

Moreover, by evaluating the mixing equiviscosity (fine and dotted line at 0.3 Pa·s) temperatures of all binders used in this study, it was concluded that the asphalt mixtures with 50/70 binder, PEX modified binder and PMB 45/80-60 should be produced, respectively, at the temperatures of 150 °C, 160 °C and 180 °C. However, in order to increase the interaction between the PEX and the asphalt binders, and also by aiming at using the same production conditions for all mixtures, a single mixing temperature of 180 °C was selected to produce all mixtures, independently of the used binder.

3.3. Marshall Mix Design of Asphalt Mixtures Incorporating PEX Waste

As explained previously, the mixtures without PEX have already been designed and presented an optimum binder content of 5.0%. Therefore, two mixtures with 5% PEX waste were used in this part of the work, namely a mixture produced with 50/70 bitumen and another mixture produced with PMB 45/80-60. The Marshal Mix design results obtained are presented in Table 2.

Table 2. Marshall Mix design results obtained for the mixtures incorporating PEX waste, either using 50/70 bitumen or polymer modified binder PMB 45/80-60.

Properties	Specifications	Design of Mixtures with PEX and 50/70 Bitumen			Design of Mixtures with PEX and PMB 45/80-60		
Binder content (%)	≥4.0	5.0	5.5	6.0	5.0	5.5	6.0
Bulk density (kg/m^3)	–	2284	2283	2308	2219	2257	2268
Air void content (%)	[3–5]	4.3	2.8	1.4	5.8	4.4	3.7
VMA (%)	≥14	15.4	15.0	14.8	16.6	16.2	16.9
Marshall stability (kN)	≥7.5	14.3	14.3	14.1	19.4	19.8	18.4
Deformation (mm)	[2–4]	2.9	3.2	3.5	3.7	3.9	4.3

These Marshall Test results showed that the optimum binder content should be between 5.0 and 5.5% for both mixtures with PEX, with the binder 50/70 and PMB 45/80-60. In fact, the results indicate that the optimum binder content of the mixture produced with the 50/70 pen bitumen may be closer to 5.0%, while the optimum binder content of the PMB 45/80-60 mixture should be 5.5%, taking into account the values of the air void content and permanent deformation obtained.

In order to better understand the effect of the binder content on the performance of these mixtures, water sensitivity tests were carried out on specimens produced with the same binder contents used in the Marshall Tests, i.e., 5.0%, 5.5% and 6.0%. The results of this additional water sensitivity study are presented in Figure 8.

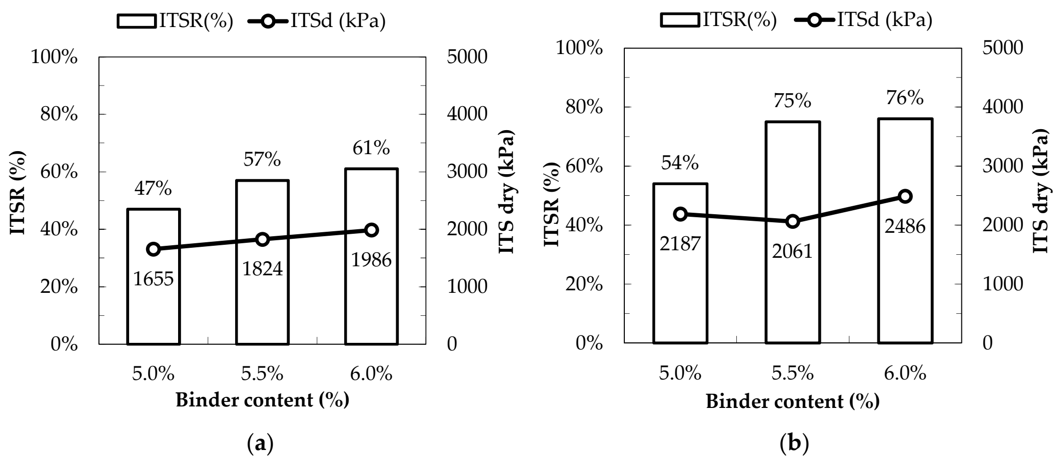


Figure 8. Influence of binder content in the water sensitivity test results for: (**a**) Asphalt mixture with PEX and 50/70 bitumen; (**b**) Asphalt mixture with PEX and PMB 45/80-60 binder.

The results presented in Figure 8 show that 5.0% binder content may not be enough to assure an adequate performance of the mixture. The ITSR test results have increased more significantly between the binder contents of 5.0 and 5.5% than between 5.5 and 6.0%. Therefore, based on both Marshall and water sensitivity tests results, the optimum binder content should be 5.5% for both mixtures with PEX. However, since the 50/70 binder is softer than the PMB 45/80-60, the former may result in a mixture more susceptible to permanent deformation. Thus, an additional mixture with the lower binder content (5.0%) was also produced and its performance evaluated, as presented in the ollowing section.

3.4. Performance of Studied Asphalt Mixtures

The performance of the five mixtures was evaluated as previously specified in Section 2.6, and the results will be presented and discussed next, taking into account the mixture composition presented in Table 3.

Table 3. Composition of the studied mixtures.

Mixture	Aggregate Volumetric Composition		Asphalt Binder	
	Mineral Aggregate	PEX Waste	Type	Content
M1	100%	0%	50/70 bitumen	5.0%
M2	100%	0%	PMB 45/80-60	5.0%
M3	95%	5%	50/70 bitumen	5.0%
M4	95%	5%	50/70 bitumen	5.5%
M5	95%	5%	PMB 45/80-60	5.5%

3.4.1. Volumetric Characteristics and Water Sensitivity of Studied Asphalt Mixtures

Before assessing the water sensitivity of the mixtures, the test specimens were volumetrically characterized. Thus, the maximum density of the mixtures was determined according to the procedure described in EN 12697-5, and the bulk density of all specimens was determined according to EN 12697-6, Procedure B. After that, the air void content of each specimen was calculated (EN 12697-8), and the average values of the five asphalt mixtures were assessed (Table 4).

Table 4. Volumetric characteristics of the studied mixtures.

Properties	Specifications	Mixture				
		M1	M2	M3	M4	M5
Binder content (%)	≥4.0	5.0	5.0	5.0	5.5	5.5
Air voids content (%)	[3–5]	2.8	4.8	5.0	2.9	5.3
Bulk density (kg/m^3)	–	2374	2369	2254	2285	2242

From the results obtained it was found that the volumetric characteristics of asphalt mixtures with PEX are different from those of mixtures with conventional aggregates. This is essentially related to the maximum density of the mixtures, which is much lower in the former due to the low density of PEX. This can be considered as one of the advantages of these mixtures, reducing its transportation costs and offering other advantages when applied on bridges or other structures intended to be lighter.

The results of the indirect tensile strength and water sensitivity tests obtained for the five mixtures are shown in Figure 9.

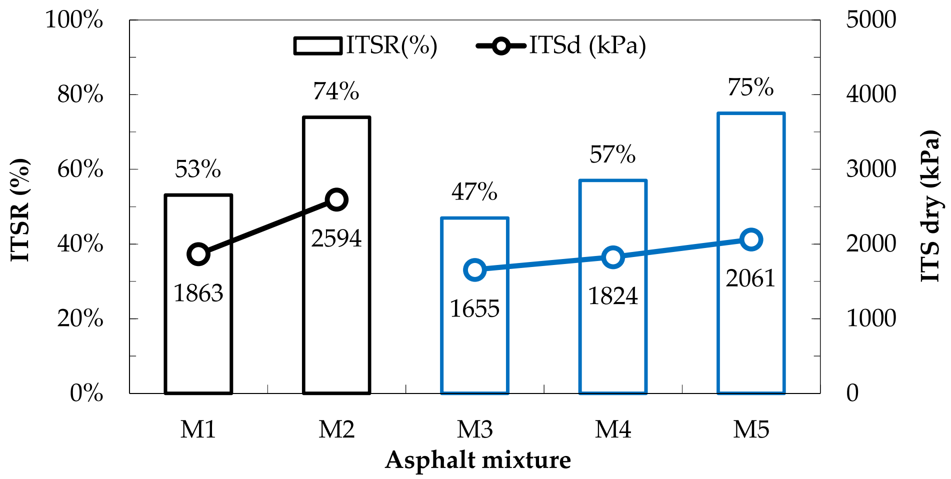


Figure 9. Water sensitivity test results of the studied mixtures.

Comparing the performance of the mixtures with the same binder type (50/70) and binder content (5.0%), but with and without PEX as aggregate, i.e., M1 and M3, the introduction of PEX slightly reduces the water sensitivity performance. However, when the binder content is increased by 0.5% (M4 or M5) in the mixtures with PEX, the situation is reversed, being the mixtures with the best performance in terms of water sensitivity.

3.4.2. Permanent Deformation Resistance of Studied Asphalt Mixtures

The rut resistance test evaluates the susceptibility of asphalt materials to permanent deformation. It consists of measuring the depth of a rut formed after a number of load applications of a wheel over an asphalt slab at high temperature conditions. Figure 10 represents the rut depth measured, for each mixture, up to the 10,000th cycle, and the wheel-tracking slope ($WTS_{AIR)}$ calculated as the average rate at which the rut depth increases with repeated applications of a wheel load (mm/10^3 cycles), between the 5000th and the 10,000th cycles.

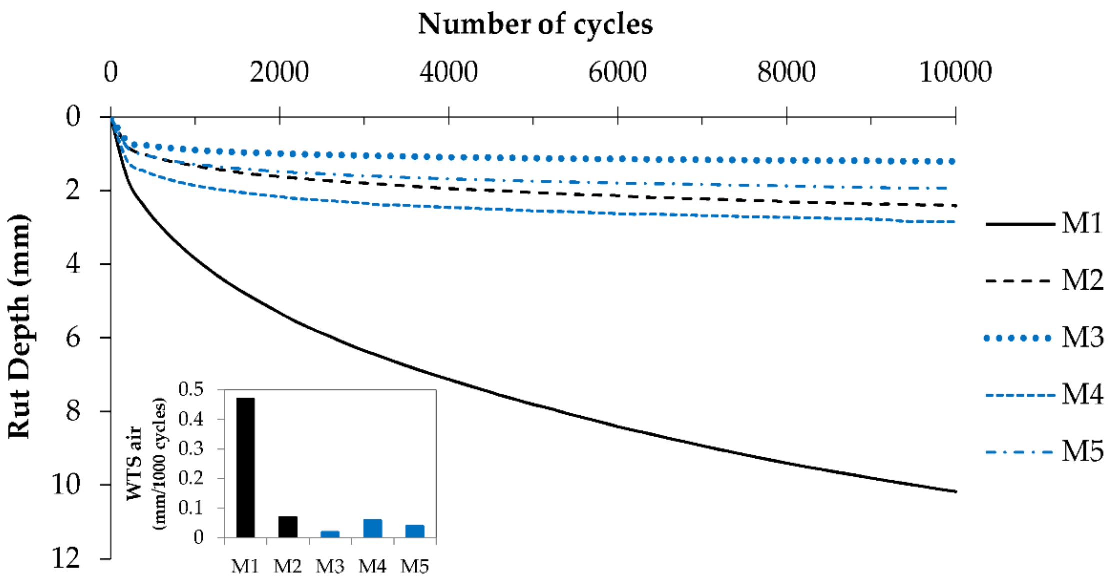


Figure 10. Evolution of the rut depth of the studied mixtures in the wheel tracking test (WTT) (the inset presents the resulting wheel tracking slope in air (WTS_{AIR}) values).

By analysing the results obtained for the rut resistance, it can be concluded that the mixtures with PEX deformed much less than the mixtures with mineral aggregates. Looking at the performance results of M1 and M3 (same binder and binder content but with and without PEX as aggregate) the reduction in terms of deformation is very significant, which is also visible in the reduction of the WTS_{AIR} value. When increasing its binder content by 0.5% (M4), the deformation increases, as expected when compared with M3, but the performance is still very good, being close to the performance to the PMB mixture without PEX (M2). Between the mixtures with PMB binder, the use of PEX also decreased the deformation, but in this case, its effect is not that significant.

Regarding the WTS_{AIR}, the conclusions are similar. Thus, the asphalt mixtures with PEX have much better permanent deformation performance than the conventional mixture (M1).

3.4.3. Stiffness Modulus of Studied Asphalt Mixtures

Based on the test results of stiffness modulus and phase angle, carried out for a range of frequencies (0.1 to 10 Hz) at different temperatures, it is possible to predict the same parameters over a larger range of frequencies, from a reference temperature (20 °C), using the time-temperature superposition principle. The resulting curves (master curves) are presented in Figure 11 and cover a frequency range far beyond the experimentally accessible values. They were obtained by translation of each isotherm curve (0, 10, 30, 40 °C) based on the reference curve of 20 °C. In order to evaluate the applicability of this method, the horizontal translation factor should be overlapped by viscoelastic functions. The Arrhenius function was used for the construction of these master curves, and this process was performed using IRIS 9.0 software.

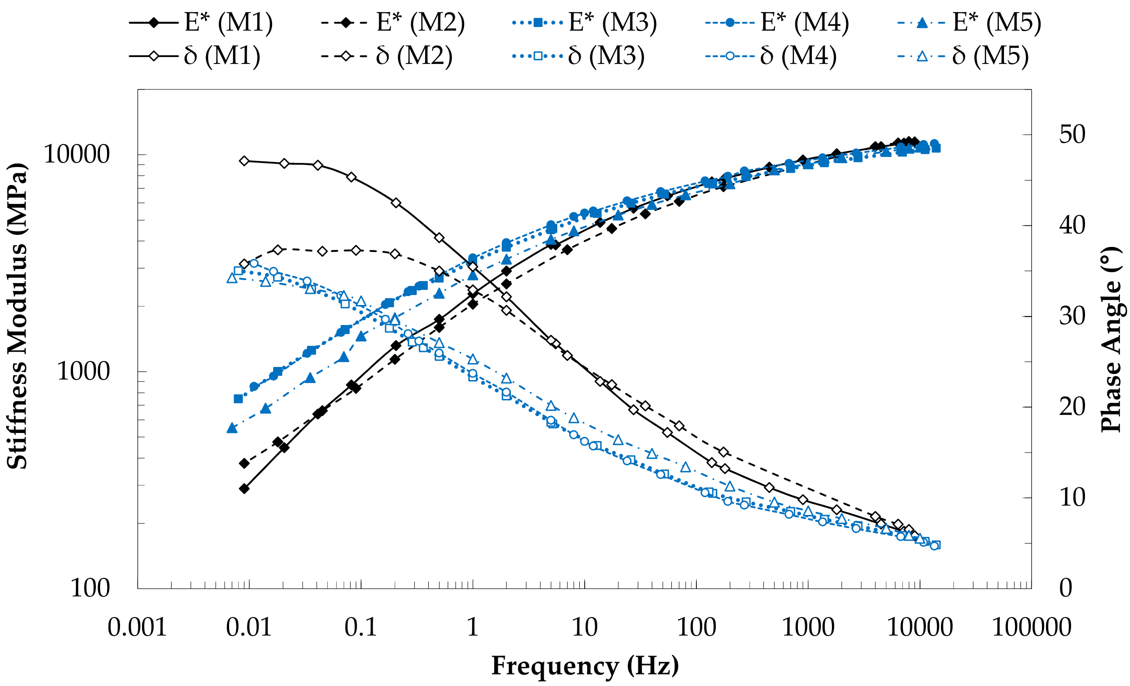


Figure 11. Master curves of the stiffness modulus and phase angle of the studied mixtures for a reference temperature of 20 °C.

The conventional mixture M1 has lower values for the stiffness modulus at lower frequencies (or high temperatures), which is in agreement with the permanent deformation results, followed by M2 (PMB mixture without PEX). The influence of the addition of PEX on stiffness modulus can be observed by comparing the results of M1 and M3 (50/70 pen bitumen, with and without PEX, respectively), these results showed that the addition of PEX increases the stiffness modulus, in a more noticeable way at low frequencies (or high operating temperatures). The same is observed for the mixtures with the PMB 45/80-60 binder (M2 and M5), and there is even an increase of 0.5% in the binder content. Looking at the results obtained for mixture M4, one could expect to obtain stiffness modulus values lower than those of mixture M3, due to its higher binder content. However, that behaviour was not observed, possibly due to the existence of a higher amount of bitumen available to interact with the PEX portion that was able to melt during the mixing operation, increasing its stiffness.

In terms of phase angle, only the conventional mixture (M1) showed values above 45° (tan δ higher than 1), i.e., M1 is the mixture that provides a more viscous behaviour, followed by mixture M2, while mixtures with PEX have a more elastic behaviour.

Generally, it becomes evident that PEX increased the stiffness moduli and reduced the phase angle values in comparison with the mixtures without this waste material.

3.4.4. Fatigue Cracking Resistance of Studied Asphalt Mixtures

In order to assess the fatigue cracking performance of the studied mixtures, 4 point bending beam tests were carried out at 20 °C. The results of those tests are presented in Figure 12.

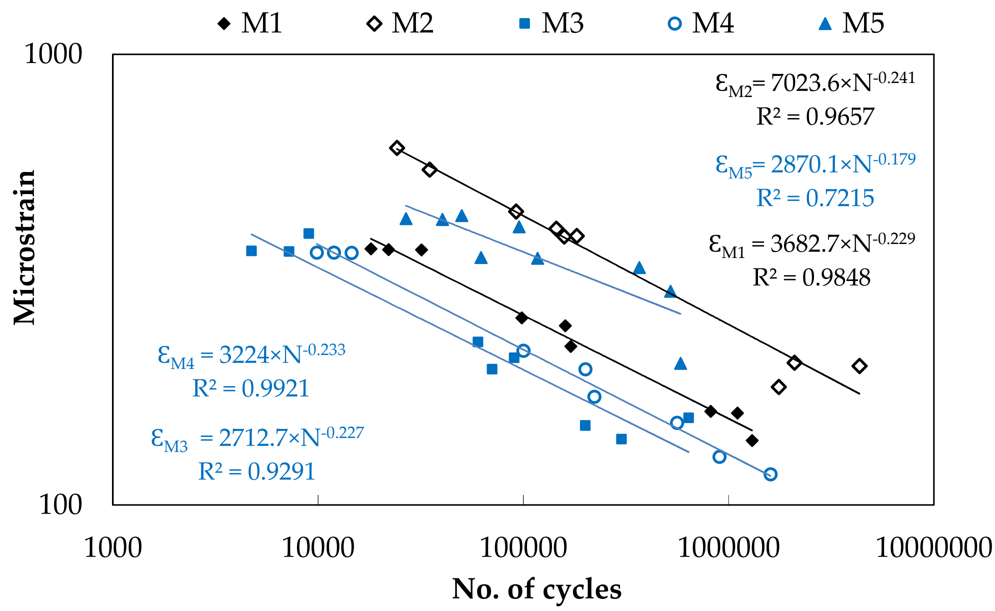


Figure 12. Fatigue cracking laws of the studied mixtures.

In Figure 12, it can be observed that the fatigue performance of the mixtures with PEX is not higher than that of the mixtures without PEX and a similar binder content. However, an increase of 0.5% in the binder content of the 50/70 pen bitumen is enough to improve the fatigue performance of the mixture (M3). This behaviour can be explained by the nature of the polymer that is contained in the PEX (plastomer), which does not perform in the same way as the elastomer used in the PMB 45/80-60 mixtures (M2 and M5). In fact, the mixture with the best fatigue performance was M2, which contains only the natural aggregates and the elastomer modified binder.

From the fatigue life equations (fatigue cracking laws) of the studied mixtures, two main fatigue performance parameters, ε_6 and N100, were calculated (as specified in EN 12697-24 standard) and are presented in Table 5.

Table 5. Fatigue parameters, N100 and ε_6, of the studied mixtures.

Fatigue Parameter	Mixture				
	M1	M2	M3	M4	M5
ε_6	156	252	117	129	242
N100 ($\times 10^6$)	6.9	45.9	2.1	3.0	140.0

The ε_6 results, representing the strain level at which the mixture would fail after 1 million cycles, showed that for the same binder type and content (comparing M1 and M3), the addition of PEX slightly reduced the fatigue resistance. The increased binder content used in mixture M4 was not enough to assure a fatigue performance equivalent to that of mixture M1, although the ε_6 value was not significantly lower.

As previously observed in Figure 12, the mixture with the best ε_6 value is M2, due to the increased flexibility given by the elastomeric additive used in the binder modification. However, if the binder content is increased by 0.5% a considerable amount of PEX could be introduced in the mixture, as aggregates, without compromising the performance of the mixture (M5), demonstrating that the use of PEX could be an interesting solution in ecological and technical terms.

Regarding the N100 values, which are the number of cycles corresponding to a test carried out at 100 microstrain, the mixtures produced with the PMB 45/80-60 binder are those that present the highest performance, which confirms the results presented in Figure 12. For those mixtures, the addition of

PEX, associated with a small increase in the binder content, resulted in the best performing mixture (M5), while in the mixtures produced with the conventional 50/70 pen bitumen, the addition of PEX did not have the same effect, even when a higher binder content was used.

4. Conclusions

According to the study presented in this manuscript, regarding the use of PEX as a partial substitute of aggregates and a binder modifier in asphalt mixtures, a series of conclusions can be drawn, as follows:

Cross-linked polyethylene (PEX) waste can be partially melted into hot bitumen, modifying the final properties of the resulting binder.

When incorporated into asphalt mixtures as an aggregate partial substitute, PEX reduces the density of the mixtures by about 5%, which may be an advantage in specific circumstances, namely, during transport and in the application over structural elements, like bridges.

Regarding the water sensitivity test results, the introduction of PEX was not able to improve the performance of the mixture, unless an increased binder content (0.5% higher) was used. Similar results were observed in the fatigue cracking resistance tests because polyethylene based polymers are not able to improve the flexibility of asphalt mixtures in the same way as the elastomeric polymers that were used in the PMB 45/80-60 mixtures.

Permanent deformation results of the mixtures with PEX were clearly better than those of the mixtures without PEX, even when higher binder contents were used. This is a result of the lower susceptibility to temperature variation of those mixtures, which can also be observed from their higher stiffness modulus and lower phase angle values. These properties are related to each other and can be seen as the main performance related improvements of incorporating PEX in asphalt mixtures.

The inclusion of PEX in asphalt mixtures is a viable solution that can assure adequate performance of a road pavement, especially when high service temperatures are expected. This technology also contributes to give new life to cross-linked polyethylene plastic waste. Nevertheless, further research should be carried out regarding low temperature and in situ performance, in order to validate this technology with a broader range of application, loading and climatic conditions.

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References

1. Abreu, L.P.F.; Oliveira, J.R.M.; Silva, H.M.R.D.; Fonseca, P.V. Recycled asphalt mixtures produced with high percentage of different waste materials. *Constr. Build. Mater.* **2015**, *84*, 230–238. [CrossRef]
2. Silva, H.M.R.D.; Oliveira, J.R.M.; Jesus, C.M.G. Are totally recycled hot mix asphalts a sustainable alternative for road paving? *Resour. Conserv. Recycl.* **2012**, *60*, 38–48. [CrossRef]
3. Kowalski, K.; Król, J.; Bańkowski, W.; Radziszewski, P.; Sarnowski, M. Thermal and fatigue evaluation of asphalt mixtures containing rap treated with a bio-agent. *Appl. Sci.* **2017**, *7*, 216. [CrossRef]
4. Xiao, Y.; Li, C.; Wan, M.; Zhou, X.; Wang, Y.; Wu, S. Study of the diffusion of rejuvenators and its effect on aged bitumen binder. *Appl. Sci.* **2017**, *7*, 397. [CrossRef]
5. Zhu, J.; Birgisson, B.; Kringos, N. Polymer modification of bitumen: Advances and challenges. *Eur. Polym. J.* **2014**, *54*, 18–38. [CrossRef]
6. PlasticsEurope; EPRO. *Plastics—The Facts 2015. An Analysis of European Plastics Production, Demand and Waste Data PlasticEurope*; European Association of Plastics Recycling & Recovery Organisations: Wemmel, Belgium, 2015.

7. Shang, L.; Wang, S.; Zhang, Y.; Zhang, Y. Pyrolyzed wax from recycled cross-linked polyethylene as warm mix asphalt (wma) additive for sbs modified asphalt. *Constr. Build. Mater.* **2011**, *25*, 886–891. [CrossRef]
8. Robinson, H.L. Polymers in asphalt. *Smith. Rapra Technol.* **2004**, *15*, 73.
9. Bocci, M.; Colagrande, S.; Montepara, A. Pvc and pet plastics taken from solid urban waste in bituminous concrete. In *Waste Management Series*; Woolley, G.R., Goumans, J.M., Wainwright, P.J., Eds.; Elsevier: Amsterdam, The Netherlands, 2000; Volume 1, pp. 186–195.
10. Zoorob, S.E.; Suparma, L.B. Laboratory design and investigation of the properties of continuously graded asphaltic concrete containing recycled plastics aggregate replacement (plastiphalt). *Cem. Concr. Compos.* **2000**, *22*, 233–242. [CrossRef]
11. Kalantar, Z.N.; Karim, M.R.; Mahrez, A. A review of using waste and virgin polymer in pavement. *Constr. Build. Mater.* **2012**, *33*, 55–62. [CrossRef]
12. Becker, Y.; Mendez, M.P.; Rodriguez, Y. Polymer modified asphalt. *Vis. Tecnol.* **2001**, *9*, 39–50.
13. Airey, G.D. Rheological evaluation of ethylene vinyl acetate polymer modified bitumens. *Constr. Build. Mater.* **2002**, *16*, 473–487. [CrossRef]
14. Zhang, F.; Yu, J. The research for high-performance sbr compound modified asphalt. *Constr. Build. Mater.* **2010**, *24*, 410–418. [CrossRef]
15. Murphy, M.; O'Mahony, M.; Lycett, C.; Jamieson, I. Recycled polymers for use as bitumen modifiers. *J. Mater. Civ. Eng.* **2001**, *13*, 306–314. [CrossRef]
16. García-Morales, M.; Partal, P.; Navarro, F.J.; Martínez-Boza, F.; Gallegos, C.; González, N.; González, O.; Muñoz, M.E. Viscous properties and microstructure of recycled eva modified bitumen. *Fuel* **2004**, *83*, 31–38. [CrossRef]
17. Awwad, M.T.; Shbeeb, L. The use of polyethylene in hot asphalt mixtures. *Am. J. Appl. Sci.* **2007**, *4*, 390–396. [CrossRef]
18. Fuentes-Audén, C.; Sandoval, J.A.; Jerez, A.; Navarro, F.J.; Martínez-Boza, F.J.; Partal, P.; Gallegos, C. Evaluation of thermal and mechanical properties of recycled polyethylene modified bitumen. *Polym. Test.* **2008**, *27*, 1005–1012. [CrossRef]
19. Ahmadinia, E.; Zargar, M.; Karim, M.R.; Abdelaziz, M.; Shafigh, P. Using waste plastic bottles as additive for stone mastic asphalt. *Mater. Des.* **2011**, *32*, 4844–4849. [CrossRef]
20. Casey, D.; McNally, C.; Gibney, A.; Gilchrist, M.D. Development of a recycled polymer modified binder for use in stone mastic asphalt. *Resour. Conserv. Recycl.* **2008**, *52*, 1167–1174. [CrossRef]
21. Vasudevan, R.; Sekar, A.R.; Sundarakannan, B.; Velkennedy, R. A technique to dispose waste plastics in an ecofriendly way—Application in construction of flexible pavements. *Constr. Build. Mater.* **2012**, *28*, 311–320. [CrossRef]
22. Rasmussen, E.; Boss, A. Plastsep—A new technology for sorting and recycling of cable polymers. In *Proceedings of the 21st Nordic Insulation Symposium, NORD-IS 09*; Institutionen för Material–och Tillverkningsteknik, Högspänningsteknik: Göteborg, Sweden, 2009.
23. Silva, H.M.R.D.; Oliveira, J.R.M.; Peralta, J.; Zoorob, S.E. Optimization of warm mix asphalts using different blends of binders and synthetic paraffin wax contents. *Constr. Build. Mater.* **2010**, *24*, 1621–1631. [CrossRef]
24. Oliveira, J.R.M.; Silva, H.M.R.D.; Abreu, L.P.F.; Gonzalez-Leon, J.A. The role of a surfactant based additive on the production of recycled warm mix asphalts—Less is more. *Constr. Build. Mater.* **2012**, *35*, 693–700. [CrossRef]