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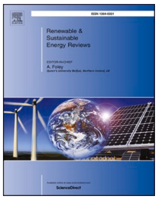

Review and analysis of advances in functionalized, smart, and multifunctional asphalt mixtures

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ABSTRACT

Road pavements are designed to withstand road traffic and weathering actions while ensuring comfortable and safe riding conditions as well as low costs and damage to the environment. When a road pavement has additional abilities or reacts to an external stimulus, it is considered to be smart and multifunctional. Examples of such abilities that have been investigated in asphalt mixtures are photocatalytic, superhydrophobic, self-cleaning, de-icing/anti-icing, self-healing, thermochromic, and latent heat thermal energy storage abilities. These abilities are developed using different materials such as nano/microparticles (including semiconductor materials and microcapsules), fibers, phase change materials (PCMs), and dyes, often using dissimilar techniques such as spray coating, volume incorporation, spreading, and asphalt binder modification. Owing to their large surface areas, road pavements are true recipients for large amounts of nano/micromaterials, and consequently, act as important "tools" to stimulate an emerging sector related to the scale of production of materials in the form of nanoparticles. Moreover, smart and multifunctional road pavements can be included in the domain of clean technology (e.g., photocatalytic pavements that promote the environmental depollution of NO_x-type gases emitted as vehicle exhaust gases). In this context, they can contribute to materializing the transition to a novel socio-economic model known as "Green Recovery" that is environmentally friendly, sustainable, and inclusive. This model is a very important path toward economic and employment recovery, a vision to which many countries are strongly committed. Therefore, this work reviews new capabilities imparted to asphalt mixtures and provides recommendations.

Abbreviations: Powder Dimension, (α); Volume Fraction of the Dispersed Powder, (Ø); Atomic Force Microscopy, (AFM); Bismuth Vanadate, ($BiVO_4$); Breath Figure, (BF); Contact Angle, (CA); Calcium Magnesium Acetate, (CMA); Calcium Chloride, ($CaCl_2$); Carbon Fiber, (CF); Carbon Nanofiber, (CNF); Dimethylphenol, (DMP); Differential Scanning Calorimeter, (DSC); Ethylene Methyl Acrylate, (EMA); Effective Medium Theory, (EMT); Fourier Transform Infrared spectroscopy, (FTIR); Potassium Formate, (HCOOK); Heating, (IH); Layer by Layer, (LBL); Layered Double Hydroxide, (LDH); Latent Heat Thermal Energy Storage, (LHTS); Methylene Blue, (MB); Methylene Orange, (MO); Microwave Heating, (MH); N-(1-Naphthyl)ethylenediamine Dihydrochloride, (NEDA); Nitrogen oxides, (NO_x); Nitric Oxide, (NO); Nitrogen Dioxide, (NO_2); Sodium Formate, (NaF); Sodium Acetate, (NaAc); Sodium Chloride, (NaCl); Oxygen, (O_2); Pressure Aging Vessel, (PAV); Performance Grade, (PG); Phase Change Materials, (PCM); Polytetrafluorethylene, (PTFE); Roughness Ratio, (*r*); Rhodamine B, (RhB); Original Asphalt Binder Reflectance, (R_m); Thermochromic Asphalt Binder Reflectance, (R_{mix}); Thermochromic Powder Reflectance, (R_p); Rolling Thin Film Oven Test, (RTFOT); Styrene-Butadiene-Styrene, (SBS); ratio between the interfacial and projected area, (S_{dr}); Steel Fiber, (SF); Steel Wool, (SW); Steel Slags, (SS); Sulfur dioxide, (SO_2); Scanning Electron Microscopy, (SEM); Triethylenetetramine, (TETA); Titanium Dioxide, (TiO_2); Urban Heat Island, (UHI); Ultraviolet, (UV); Vanadium dioxide, (VO_2); Volatile Organic Compound, (VOC); Zinc Oxide, (ZnO).

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1. Introduction

The idea of the design of smart and multifunctional cement concrete was first proposed in late 1980 by Japanese researchers [1]. After extensive research on the design, manufacturing, characterization, performance, and mechanisms, various types of smart and multifunctional cement concretes have been successfully employed in real-scale scenarios [1]. In the case of asphalt mixtures, the concept is new, and in terms of practical experiences (test sections), very few applications exist [2–6].

Based on Han's definition [1], smart and multifunctional concrete is either an intelligent material with characteristics that differ from the original ones or can respond to external stimuli, such as temperature and stress. This concrete can be composed of cement, asphalt, or polymers. These abilities can be classified in terms of smartness or function as follows: smartness, optical, electrical, mechanical, and electromagnetic wave/radiation shielding/absorbing, energy-harvesting, and related to water. This concrete is designed through special processing, composition design, introduction of new functional materials, or microstructure modification of the original materials [1,7].

The design and implementation of asphalt pavements should meet the relevant requirements to withstand the actions of road traffic (different mechanical efforts) and weathering, in addition to ensuring comfortable driving conditions, economy, and safety, as well as reducing environmental damage (e.g., low noise levels). Smart and multifunctional capabilities have been applied to asphalt mixtures, becoming a significant subject in road engineering once the road pavements present a vast surface area and can show other benefits that will be addressed in this study. The literature has already shown important results on the functionalization of asphalt pavements and the development of smart and multifunctional asphalt mixtures, mostly for the top layer [8].

Previous literature reviews generally covered issues related to road infrastructure features, such as paintings, and flexible and rigid pavements, from the concept of nanotechnology to the results of mechanical and multifunctional performance [9–12]. These studies concluded that nanomaterials can provide novel capabilities by improving the mechanical properties, and nanoscale tests are essential for the design of these materials.

This paper addresses the major results and discussion of functionalized, smart, and multifunctional asphalt mixtures imparted by different materials. The latest literature reviews have approached nanotechnology in transportation engineering (namely pavements, bridges, and vehicles) from a different approach from this work, which discusses the multifunctionality of smart asphalt mixtures. In addition, literature reviews only refer specifically to some capabilities, such as photocatalytic [13], self-healing [14], and thermochromic [15] capabilities. However, advances in smart asphalt mixtures, where all capabilities or even reviews on some other specific capabilities are considered, have not yet been reported in the literature.

This literature review aims to discuss the main capabilities imparted to asphalt mixtures, namely photocatalytic, superhydrophobic, self-cleaning, de-icing/anti-ice, self-healing, thermochromic, and latent heat thermal energy storage. Their contextualization, functionalization methods, materials application, results, conclusions, and limitations are presented and critically discussed.

2. Photocatalytic capability

In recent years, the photocatalytic capabilities of asphalt mixtures have been one of the most investigated topics, as they may be directly associated with benefits related to road safety (e.g., photodegradation of various organic compounds adsorbed on road surfaces), as well as the environment and health of populations via the removal of toxic gases resulting from gaseous emissions from thousands of automobiles in the transport sector.

Roads can become ideal places to reduce atmospheric pollution owing to the large paved areas and the vicinity between the roads and pollutant gases (mainly from vehicle exhausts), especially in urban areas [16]. Fig. 1 shows the operation of the photocatalytic asphalt mixtures using TiO_2. Semiconductors, such as TiO_2 and ZnO, are commonly used to functionalize asphalt mixtures for photocatalytic purposes [3,17–22]. TiO_2 is the most commonly used semiconductor material for photocatalysis owing to its high ability to photodegrade pollutants, chemical stability, and availability in the earth's crust (0.44 % of its elemental chemical composition is titanium), among other characteristics [23–25].

Despite the various pollutants, photocatalytic asphalt mixtures can degrade NO_x, SO_2, and volatile organic compounds. The photocatalytic process is simple to understand (Eqs. (1)–(6)). With the excitation of electrons from the valence to the conduction band in semiconductors via photons with appropriate energy, charge carriers, namely electrons (e^-) and holes (h^+), are formed (Eq. (1)). They can react with O_2 and OH^- species, respectively, producing free radicals (Eqs. (2)–(4)) that can degrade pollutants, such as NO_x in nitric acid (HNO_3) (Eqs. (5) and (6)) [17,26–28].

$$TiO_2 \xrightarrow{hv} h^+ + e^- \tag{1}$$

$$h^+ + OH^- \rightarrow OH^* \tag{2}$$

$$e^- + O_2 \rightarrow O_2^- \tag{3}$$

$$H^+ + O_2^- \rightarrow HO_2^* \tag{4}$$

$$NO + HO_2^* \rightarrow NO_2 + OH^* \tag{5}$$

$$NO_2 + OH^* \rightarrow HNO_3 \tag{6}$$

Regarding the functionalization methods of photocatalytic asphalt pavements, four main approaches exist that differ in the application process of the nano/micromaterials: i) spray coating [18,27,29–32], ii) volume (or bulk) incorporation [18,32], iii) asphalt binder modification [30], and iv) spreading [32,33]. The modification of the asphalt binder was previously performed for the production of asphalt mixtures. The particles were inserted into the asphalt binder and mixed. Volume incorporation is performed by adding particles (with fillers and/or aggregates) during asphalt mixture manufacturing. The spreading and spray coating processes were performed over the surface of the compacted asphalt mixture. The spraying method is performed using a compressed air paint gun, whereas the spreading technique is performed by the deposition of a particular photocatalytic solution over the surface, similar to surface dressing or using a paintbrush.

From an application viewpoint, spray coating is a simple technique. Thus, any worker, even with low qualifications, is qualified to perform this coating process. In addition, for a given coated area, spray coating requires the use of the least amount of material. Therefore, from the perspective of the combined relations - material cost/simplicity of application/achieved results, it is a technique with advantages [18,27,29–32]. The spreading technique uses more particles than spray coating. They are deposited using paintbrushes or surface dressings. Because both techniques are applied over the surface (most of the particles are irradiated by sunlight), they are very efficient as regards their photocatalytic activity. Immobilization (particle fixation) remains the major challenge in surface treatments, such as spray coating and spreading.

The asphalt binder modification and volume incorporation possibly assure the most efficient immobilization process; nevertheless, more particles are needed. However, some traffic wear is necessary to expose the semiconductor particles previously encapsulated by the asphalt binder. Its modification by semiconductor materials retards aging because semiconductors absorb and reflect the ultraviolet (UV) light associated with the long-term aging process [30,34–36].

Regarding the spraying method, the literature refers to the use of

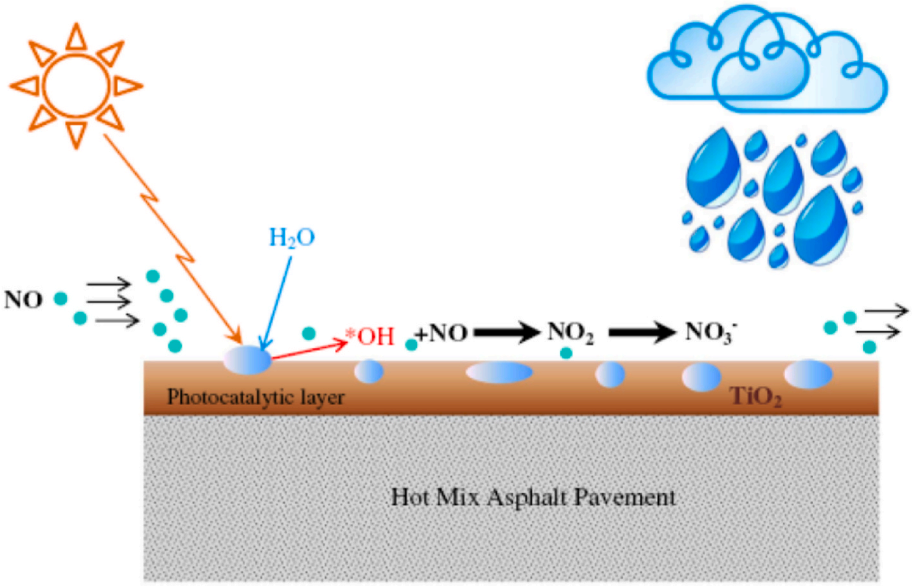

Fig. 1. Photocatalytic asphalt mixture [29].

different solvents and binders to enhance the particles' immobilization, such as an aqueous solution [18,27,29,30], emulsions [3], cement, resins [28,33], polymers [37], and rubber [38]. The dispersion of TiO_2 nanoparticles is a significant concern in the literature. The particles may agglomerate, thus decreasing the photocatalytic efficiency. To avoid the agglomeration phenomenon, TiO_2 solutions can be subjected to ultrasonic treatment [31,32] or prepared with a zeta potential different from the isoelectric point [18]. These preparations reduce particle agglomeration owing to van der Waals forces (attraction forces) that compete with Coulomb forces (repulsive electrostatic forces) [18].

TiO_2 semiconductors trigger photocatalytic reactions with UV irradiation. Nevertheless, for outdoor applications, sunlight mainly comprises the visible and infrared regions of the electromagnetic spectrum, thus offering a small fraction of 3–5 % of UV light [39]. To decrease the semiconductor energy activation (band gap), and therefore, promote its absorption shift to visible light wavelengths (approximately 47 % of the sunlight spectrum) and increase the photocatalytic efficiency, doped materials have been used. In asphalt roads, dissimilar materials have been used to perform the doping of TiO_2, namely La [31], Ce [32,40], Cu and Fe [40], N [41], C [5], and Ag [38]. The best content of these materials was 0.5 % La (mol%) [31] and 0.2 % Ce (mass ratio) [32], both of which have the highest photocatalytic efficiency. Chen et al. reported a 2:1 ratio of TiO_2 to urea (molar proportions) [41]. Neither Ag [38] nor C [5] content was indicated in the research papers.

As regards the photocatalysis assessment in the laboratory, the literature refers to tests of gas degradation, for example, NO_2 and NO (when they are analyzed together, NO_x), SO_2, and VOCs, following JIS TR Z 0018 and ISO 22197 [19,30,32], and degradation of dissimilar organic dyes, such as methylene blue (MB) [18,32], methylene orange (MO) [5], and rhodamine B (RhB) [17,42], using spectrophotometry.

The assessment of the functionalized asphalt mixtures without sample removal from test sections is possible through techniques such as analysis of white pixels of the surface by digital image processing [3], using NO_x measurement equipment placed on movable air-conditioned trailers [29], or by the indirect method of NEDA [38,41]. Another technique, developed by Osborn et al. involves the addition of an amount of water to the photocatalytic asphalt pavement and its collection to evaluate the presence and concentration of nitrates [19,29].

The photocatalytic characteristics of asphalt pavements can be affected by wind (pollutant flow rate), air pollution concentration (pollutant concentration), the intensity of solar irradiation (power density), relative environmental temperature, and humidity. The literature shows a brief experience with these factors. Asadi et al. found a NO_x reduction efficiency when the traffic count and wind speed were increased [43]. Excessive relative humidity causes competition between water and pollutant molecules, inhibiting the reaction, and consequently, decreasing the photocatalytic efficiency [4,29,43]. In addition, the higher the pollutant flow rate, the lower the photocatalytic efficiency. This behavior results from the insufficient interaction time between the pollutant molecules and the photocatalytic surface [29,31].

Furthermore, a high gas concentration decreases the photocatalytic efficiency [31,38]. Regarding the irradiation characteristics, a shorter wavelength is more effective than a longer wavelength. Higher solar irradiation intensities increase photocatalytic efficiency [4,38]. Moreover, a high environmental temperature led to a decrease in photocatalytic efficiency. This phenomenon can be explained by the kinetic energy of the molecules that grows, speeding up the gasification, and consequently, reducing pollutant contact with the photocatalyst [38]. In addition, dust particles block light irradiation [44].

Photocatalytic asphalt mixtures have already been evaluated from a mechanical viewpoint by a few researchers. For example, by bulk incorporation, TiO_2 nanoparticles lead to an increase in water sensitivity. Fatigue cracking and permanent deformation may also be influenced by the introduction of TiO_2. Although the use of 6 % TiO_2 improved the permanent deformation resistance, it reduced the fatigue cracking resistance. Three percent TiO_2 slightly increased the permanent deformation resistance and preserved the fatigue properties [42].

Functionalization techniques with a sprayed aqueous solution containing nano-TiO_2 and/or micro-ZnO and nano-TiO_2 by volume incorporation led to a change in the SR between −7% and 3 %. All functionalization techniques did not influence the microtexture amplitude parameters, except for the skewness of AC 14, incorporating 6 % TiO_2 by volume [45].

Zhang et al. [44] reported that TiO_2 did not influence the stiffness moduli of asphalt mortars (in this specific case, composed only of asphalt binder, limestone mineral powder, and TiO_2). The low-temperature anti-cracking performance and water sensitivity were not affected by the volume incorporation of TiO_2 in the asphalt mixtures. Regarding the permanent deformation criteria of dynamic stability, the authors reported a value of 4 % as the maximum percentage of TiO_2. For photocatalytic efficiency, the best TiO_2 content was 3.1 %. Furthermore, the contact area between pollutants and the asphalt mixture surface increases with an increase in voids, thus enhancing photocatalysis.

Photocatalytic asphalt mixtures have already been tested in a real context. When applied using the spraying method, the fixation of the emulsion containing TiO_2 was mainly influenced by the climatic conditions (rain) because its efficiency was reduced by approximately 80 % in 100 days [3]. Thus, it can be concluded that the immobilization process needs to be improved. Osborn et al. suggested a durability time between 10 and 16 months for photocatalytic asphalt pavements with sprayed TiO_2 [19]. After an abrasion equivalent to 8–15 years of traffic, their results indicated the samples had 10.7 % photodegradation efficiency for the TiO_2 coating bonded with epoxy [28] and 15 % for the pore-filling method by spreading [33]. Chen et al. [41] reported a 13 months durability by spraying TiO_2 doped with nitrogenous compounds and a silane coupling reagent [41].

In addition to the air-cleaning property of semiconductor materials, this functionalization provides self-cleaning capability related to the degradation of organic compounds, such as oils and greases. In asphalt pavements, self-cleaning effects can mitigate the friction decrease caused by surface contamination using organic compounds degraded by semiconductors [18].

Photocatalytic asphalt pavements are ideal solutions to reduce atmospheric pollution owing to the existing large paved areas and the vicinity of the vehicles' gases. However, field experience is quite limited, and methods to immobilize semiconductors need to be enhanced. The effectiveness of immobilization should be assessed, and novel techniques should be developed to improve it. Further research is required in other aspects, such as the functionalization of different types of asphalt mixtures, the influence of functionalization on the surface morphology and its mechanical performance, the effect of the spraying rate, the effect of UV and visible light intensities, and the influence of air relative humidity and pollutant flow rate. Additionally, comparative cost studies are essential to promote the implementation of this sustainable technique.

3. Wettability characteristics

Water is the most abundant and vital liquid existing on earth. Owing to intermolecular interactions, wetting is the ability of a liquid to maintain contact with a solid surface. Thus, controlling the surface wettability with water is crucial for many applications [17,46–49].

The surface of any material can be classified by its wettability as superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic capability. The classification is based on the contact angle (CA) measurement between a water droplet and the surface (Fig. 2). The superhydrophobic capability is ensured when the CA is higher than 150° [50]. Conversely, superhydrophilic capability is achieved if the CA is near 0° [51,52]. Some authors have stated that the CA should be lower than 5° or 10° to develop a superhydrophilic (or super-wettable) surface [48,52–54].

A greater intensity of surface energy exists on a rough surface than on a smooth surface. Consequently, the design of superhydrophobic materials is achieved by creating a rough surface [55]. The benefits brought to the materials by the endowment of this capability are diverse, such as promoting antibacterial, anti-corrosive, anti-freeze, contaminant-free, self-cleaning, and water-resistant functions [46,56–60].

The force balance between the cohesive and adhesive forces determines the wettability. Wettability can be studied by measuring the CA of a solid surface with a certain liquid [49,50,52]. Young's well-known equation describes the equilibrium at the three-phase contact of solid, liquid, and vapor [61]. Young's equation assumes the surface is chemically homogeneous and ideally smooth from a topographic point of view. However, this condition does not occur in real surfaces, which are rough; that is, the surface topography comprises many peaks and valleys. Thus, on a real surface, the contact angle (CA) is the angle between the tangent to the liquid–vapor interface and the solid's local (real) surface. The relationship between roughness and wettability was defined in 1936 by Wenzel [62], who stated that adding surface roughness improves the wettability caused by surface chemistry.

The roughness ratio r is defined as the ratio between the real and projected solid surface areas, based on Eq. (7) [63].

$$r = 1 + S_{dr} \tag{7}$$

where S_{dr} is a roughness parameter known as the area factor, which is defined as the ratio between the interfacial and projected area, given by the following expression (Eq. (8)).

$$S_{dr} = \frac{(Textured\ surface\ area) - (Cross\ sectional\ area)}{Cross\ sectional\ area} \tag{8}$$

Based on Eq. (7), if the surface is considered ideally smooth, then $r = 1$, whereas $r > 1$ for a rough surface where the area factor S_{dr} gives the additional surface area contributed by the texture.

In the case of a measured unit area on a rough surface, more surface area exists; therefore, for the same measured unit area, a greater intensity of surface energy exists on a rough surface than on a smooth surface. Hence, the roughness ratio r can be regarded as a factor that "magnifies" the affinity of a solid surface to a certain liquid, that is, the wettability conditions. For example, if a particular surface is chemically hydrophobic, it becomes even more hydrophobic when roughness is added, leading to an increase in the CA.

In the case of superhydrophobic materials, the self-cleaning effect is based on the ability of water droplets to carry dirt particles, similar to the lotus flower effect, which corresponds to a biomimetic approach for material applications. Lee and Fearing [64] showed scanning electron microscopy (SEM) micrographs of functionalized microfibers, which is evidence of their self-cleaning capability (see Fig. 3) [64]. Superhydrophilic surfaces are self-cleaned. The water droplets spread over the surface, making washing easier during rainy periods [65].

Researchers from road engineering aim to provide superhydrophobic capability to asphalt mixtures because its benefits are mainly the increase in water-repelling, water sensitivity resistance, and ice formation avoidance. In addition, it is possible to clean dusty surfaces. All these aspects are mostly related to the mitigation of the decrease in friction caused by the presence of water, ice, or even dust over the surface of the pavement. For porous asphalt mixtures, it is possible to attenuate the

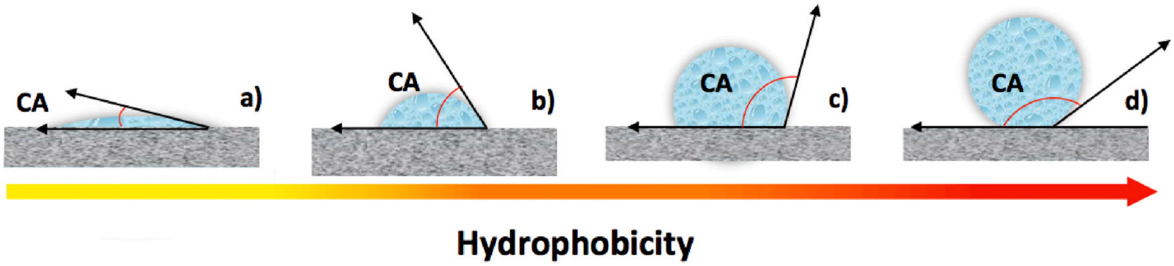

Fig. 2. Surface classification based on the wettability condition: a) superhydrophilic (CA < 5 or 10°); b) hydrophilic (CA < 90°); c) hydrophobic (90° < CA); and d) superhydrophobic (CA > 150°).

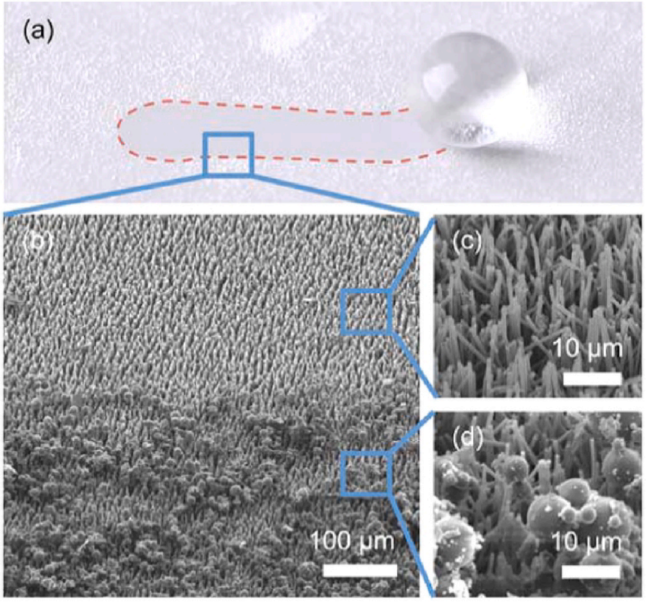

Fig. 3. a) Self-cleaning effect showed by a 9 μL water droplet rolling over a microfiber-covered with ceramic microspheres simulating dirt, SEM surface micrograph of b) both (self-cleaned and dirty) areas with a magnification of 100 μm, c) the self-cleaned area with a magnification of 10 μm, and d) the dirty area with the microspheres with a magnification of 10 μm. Adapted from Ref. [64].

phenomenon of pore-clogging (filling of voids by dirt) owing to the self-cleaning property, thus facilitating the flow of water. However, this hypothesis requires further evaluation.

In asphalt mixtures, superhydrophobic capability was developed using some micro/nanomaterials. However, little scientific experience still exists in this specific application case. Nascimento et al. [47] showed that it is possible to obtain a superhydrophobic asphalt mixture by coating the surface with a colloidal dispersion composed of a nanoparticulate copolymer fluoroacrylate modified with CaO nanoparticles (5 mg/L). The major result of this work showed a water CA of approximately 163° for the superhydrophobic asphalt mixture, whereas, in the case of the conventional mixture, the water CA was 92° [47]. Moreover, the asphalt mixture with the incorporated nanoparticles showed an increase of 338 % in the roughness and a reduction in adhesion work of 95 % when compared to the conventional mixture (see Fig. 4).

Arabzadeh et al. [66,67] developed a superhydrophobic asphalt mixture using polytetrafluorethylene (PTFE) in an acetone solution at different concentrations. Initially, the authors applied an epoxy resin dissolved in xylene to samples of the asphalt mixture. PTFE dispersions were applied layer by layer. The highest water CA recorded was 166° for the sample with 40 % of the mass fraction and a spray time duration of 12 s, whereas the lowest was 125° for the lower mass fraction (10 %) and spray time duration of 3 s. When this specific sample is excluded, all the others presented a water CA greater than or equal to 150°, thus behaving as superhydrophobic surfaces. The friction was measured using a microtribometer. The results showed that for all samples with the shortest spray time duration (3 s), the friction values were lower than the control, irrespective of the PTFE concentration (10 %, 20 %, 30 %, and 40 %). For longer spray durations, the samples with 10 % PTFE showed reduced friction. The other samples showed friction values of at least 9 % higher than that of the conventional asphalt mixture [66,67].

Using a superhydrophobic coating (the authors did not describe the materials), the CA between the water and the surface of the functionalized asphalt mixtures reached 157° [68]. The same authors performed skid resistance using a British pendulum tester under three different conditions: dry, wet, and iced. The untreated samples decreased the British pendulum number from 70 (dry) to 60 and 48 after wet and frozen conditions, respectively. Nevertheless, the treated samples almost maintained the results, namely 81 for the dry situation and 77 for the wet and iced situations, respectively [68].

Rocha Segundo et al. promoted the superhydrophobic capability of different asphalt mixtures (AC 14 and AC 6) with a combination of TiO_2 and ZnO semiconductor materials, which were applied by spraying an aqueous solution of these materials. A water CA of up to 155° was reached. They studied the effect of several factors on the superhydrophobic capability and concluded that the type of mixture, testing time, type of material used in the treatment (with TiO_2 and/or ZnO), and abrasion (at different levels) had a significant influence on water CA [17].

Despite the expected importance of road safety, only a few studies concerning asphalt mixtures have reported on the superhydrophobic capability of road pavements. This functionalization can provide fast water-repelling, avoid ice formation, be less sensitive to moisture damage, and clean dusty surfaces. In the case of porous drainage asphalt mixtures, pore-clogging (filling of voids by dirt) can be mitigated because of the self-cleaning property. Additionally, immobilization of the particles remains a challenge. This capability must be applied to a real-scale scenario to test its effectiveness.

4. De-icing and self ice-melting capabilities

In very cold countries and during the winter, it is usual to observe a rapid formation of ice on the pavement surface, contributing to the reduction of friction, and therefore, resulting in road accidents, traffic congestion, and economic losses [69]. To prevent this problem, road administrations usually use de-icing solutions or chlorine salt to melt the snow/ice over the pavement surface, which requires high financial resources [70,71]. The application of anti-ice or self-ice-melting additives into asphalt mixtures can present advantages such as the prevention of traffic jams when compared to conventional methods, which are time-consuming processes and require intensive work. Usually, there are two ways to obtain an asphalt pavement with this capability: i) using anti-icing additives as an asphalt binder modifier or filler, and ii) using a conductive material as aggregates or fibers.

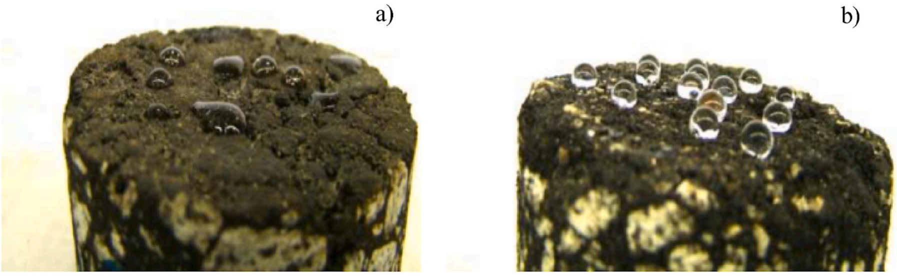

Fig. 4. Asphalt mixture wettability: a): untreated sample; and b): treated sample (superhydrophobic surface) [47].

4.1. Self-ice-melting pavements using anti-icing additives

The incorporation of anti-icing additives into asphalt pavements creates an anti-icing liquid layer between the ice/snow and the surface, which contributes to slow or avoid ice formation, facilitating the melting process of snow and ice, and consequently, maintaining the original friction of asphalt mixtures. Consequently, some additives have been applied to asphalt mixtures as asphalt binder modifiers or fillers, such as potassium formate (HCOOK) with a styrene-butadiene-styrene (SBS) matrix [72], Mg–Al Cl^- layered double hydroxide (LDH) [70], commercial fillers, such as IceBane (composed of chloride salt–$CaCl_2$ and NaCl) [71] and Mafilon (composed of NaCl, SiO_2, MgO, and CaO) [73]. The most commonly used materials were chloride-based anti-freeze [71, 74,75]. Other options were also investigated: i) liquids: glycol-based fluids and potassium acetate-based fluids and ii) solids: urea, calcium magnesium acetate (CMA), sodium formate (NaF), and sodium acetate (NaAc) [76].

The tests most commonly used to evaluate this capability are conductivity tests, ice layer rupture tests (shear strength and pullout), and another that relies on the observation of the melting process after the accumulation of snow, taking into account the thickness of the ice/snow, temperature, and melting time [71,73,74]. The anti-icing additives used as fillers do not require changes in the asphalt mixture design. However, they can negatively affect mechanical properties, such as permanent deformation, thermal cracking, and water sensitivity resistance. To prevent the damage caused by the introduction of anti-icing additives and maintain the mechanical characteristics, 0.3 % polyester fibers by the weight of the aggregates can be used. Moreover, with 6 % of anti-icing additives (as filler by the mass of the aggregate), the melting of snow over the asphalt pavements was facilitated, and the strength of the ice layer was reduced by half [74]. This material has already been tested on the road, holding this capability one year after the application [77].

Regarding the commercial anti-freeze filler IceBane, Liu et al. reported that it is desirable to use a coarser size of anti-freeze filler (the 0.075 mm sieve size passing rate of 21 % was the most efficient). They concluded that the anti-freeze filler with large particles dissolved in water more quickly than smaller salt particles [71].

Ionic salts are used as anti-icing additives to reduce ice formation on asphalt surfaces. The limitation of using these salts is related to their high corrosive power in bridges, buildings, and airports. Regulations regarding this type of material exist for airfield asphalt pavements, limiting their use [76]. In addition, these salts negatively influence the mechanical characteristics of the asphalt mixture and are harmful to the environment when used in high amounts. Therefore, it is essential to evaluate the environmental impact of these materials and include anti-icing additives in the design of asphalt mixtures to guarantee adequate mechanical performance.

4.2. De-icing pavements using conductive materials

The Joule effect is a physical phenomenon that justifies the incorporation of conductive materials into asphalt mixtures to remove snow and/or prevent ice formation over the pavement surface. This effect can be described by the occurrence of an electric current passing through the composite material that can generate heat, thus reducing the snow and ice accumulation over the asphalt mixture surface [78]. Three conductive materials are used in asphalt mixtures: i) powders such as graphite, aluminum chips, and carbon black; ii) fibers, including carbon fiber (CF), steel fiber (SF), steel wool (SW), and carbon nanofiber (CNF); and iii) conductive coarse and fine aggregates such as steel slags (SS) [79]. When irradiated by microwave radiation, road pavements composed of these materials can melt the ice on their surface during the winter more quickly than traditional road pavements (i.e., pavements without conductive materials) [80]. To assess the de-icing capability, some properties, such as electrical resistivity and thermal conductivity, and the behavior of the asphalt mixture subjected to microwave heating (MH) were evaluated.

The asphalt binder resistivity is approximately 10^{11} and 10^{13} Ωm, whereas the asphalt mixture resistivity is between 10^7 and 10^9 Ωm, owing to the presence of aggregates and air, which are classified as insulating materials. When materials such as graphite, steel fiber, and CF are added, the resistivity of the asphalt mixture can be reduced to values between 10 and 10^3 Ωm, thus significantly improving the electrical conductivity, as graphite and CF have an electrical resistivity of approximately 10^{-6} and 10^{-5} Ωm, respectively [81]. In general, the conductivity of the asphalt mixture for the electrical heater does not exceed 100 Ωm [79].

The incorporation of SS into asphalt mixtures not only improves road safety during winter but also increases the recycling potential of this material, mitigating the use of natural raw material and its depletion. Compared to CF, graphite, and steel fibers of wide sources, SS presents other advantages. For instance, this material is eco-friendly and inexpensive. Nevertheless, it also has limitations; for example, it should be pretreated to avoid use during the expansion phase. Moreover, as this material has a high density, it can incur extra costs for transport. Gao et al. suggested an SS content between 40 % and 60 % and aggregate sizes of 9.5, 2.36, and 0.6 mm for the promotion of MH, thermal conductivity, and surface temperature [80].

In the design of asphalt mixtures, it is crucial to consider the effects of the shape, size, composition, and conductivity of the raw materials, as well as the final conductive and mechanical characteristics of asphalt mixtures. The average melting speed of snow for asphalt mixtures with SF and SS using MH is 53.9 and 48.5 g/min, respectively [82]. Although both techniques are feasible to provide this capability, the use of fibers is probably more efficient; however, SS is more sustainable.

The use of salt has a negative effect on the performance of asphalt mixtures with SF or graphite. After performing few freeze-thaw cycles, the saltwater led to an increase in air voids and reduced water sensitivity resistance, compared to distilled water, probably owing to the loss of aggregate-binder adhesion [81]. It is essential to consider the oxidation of these materials during the design and performance of asphalt mixtures. Anti-icing additives can be used in combination with CF to obtain good mechanical properties and prevent the formation of snow/ice. The use of recycled materials, such as SS, is strongly recommended owing to its eco-friendly and low-cost benefits.

5. Self-healing capability

The typical mechanical stresses for conventional asphalt mixtures are fatigue (and temperature) cracking and rutting [79]. Self-healing capability aims to assist materials to heal after damage. It is defined as “the ability to return to an initial, proper operating state or condition prior to exposure to a dynamic environment by making the necessary adjustments to restore to normalcy and/or the ability to resist the formation of irregularities and/or defects [14,83]. This capability is also based on biomimetics from the biological systems of wound healing in the skin of living organisms [84–86].

The asphalt binder was a self-healing material. After rest periods, asphalt mixtures can recover their strength and stiffness by closing the microcracks that open after traffic loading [87]. The cracks healed instantly after the load was removed. Two phenomena occur during this process: viscoelastic recovery and healing in the cracked area. The difference is that the former results from the rearrangement of the molecules, and the consequence is the wetting and inter-diffusion between the crack faces. The following stages explain the self-healing mechanism: i) both faces of a nano-crack are wetted, ii) immediate strength gain by interfacial cohesion between the crack faces, and iii) long-term strength gain owing to the diffusion and randomization of molecules from one face to the other [88].

Improving the self-healing ability of asphalt mixtures can provide a higher life cycle for pavements. The free energy of the surface is the most important factor causing the first cracks to shrink and then progressively disappear in the asphalt binder with an increase in temperature [89]. Two techniques enhance self-healing in asphalt mixtures: i) heating the asphalt material improved by good electrically conductive materials, and ii) adding nanomaterials or healing agents to their composition [87].

5.1. *Self-healing capability by heating*

With the incorporation of materials such as graphite, carbon black filler, carbon and steel fibers, SW and slags, and some nanomaterials (carbon nanotubes and nanofibers), the asphalt mixtures improve their electrical conductivity. By induction heating (IH), the cracks are repaired, and the raveling effect (loss of aggregates) is prevented, self-repair, preservation, and renewal of asphalt pavements.

Consequently, microwaves have been used to heat the asphalt mixtures; although they are fast and easy to apply, the high cost and difficulty in controlling heat deepness penetration are the major drawbacks of this technique [88]. In addition, MH increases the temperature of the asphalt binder but not that of the aggregates.

Consequently, the surface temperature of the asphalt mixtures was inferior to the asphalt binder temperature when both were subjected to this procedure. Therefore, metallic fibers or particles are used to improve the effectiveness of microwaves [90,91]. IH, based on the electromagnetic induction phenomenon, is another possibility for increasing the temperature of pavements. It is fast, expensive, and has a complex heating mechanism [88]. The IH does not heat the asphalt binder or aggregates. Metallic particles are required to increase the temperature of the asphalt mixture after heating [90]. MH heals the cracks better than IH owing to the increase in the asphalt binder temperature [90].

There is an optimal time to heal the asphalt mixture. Heating should not be too late or too early [92]. On the one hand, when heating is early, it is useless because the asphalt mixture heals the crack by itself. On the other hand, when it is too late, the healing process is drastically decreased because the asphalt binder is aged, and it is not effective for large cracks. In addition, mechanical damage, such as rutting or raveling, could occur before [90].

This self-healing property can be measured in binders, mastics, and asphalt mixtures by the electrical conductivity, temperature rate after IH, and rate between healed strength/modulus and initial strength/modulus. This property is influenced by factors such as temperature, number of heating cycles, healing time, and IH confining pressure. The rest of the periods are essential for healing [88]. The temperature has an exponential relationship with the self-healing mechanical property, whereas the healing time has a linear relationship with the self-healing index. The confining pressure can accelerate the crack healing. Fan et al. concluded that the confining pressure effect on self-healing capability is relevant for temperatures lower than 60 °C, and a deeper crack has a greater self-healing potential than a surface crack [93].

The asphalt mastic (here, crushed sand less than 2 mm, asphalt binder, and SW) can be healed severally using IH. The stiffness of the asphalt mixture with SW recovered faster with the application of IH than when submitted only to the rest period. The fatigue life of the modified asphalt mixture was significantly prolonged owing to heating only (135,408 cycles more – H_3). Fig. 5 shows the fatigue recovery of the porous asphalt mixture containing SW before and after healing [92]. H_1 and H_3 were caused by the rest period and IH, respectively, whereas H_2 was the increase in fatigue life owing to IH and rest periods.

A major limitation of the use of this type of material is oxidation (corrosion). In contrast, CFs can be used without this problem.

5.2. *Self-healing capability by the addition of nanomaterials or healing agents*

In this approach, three techniques can be applied in asphalt mixtures to provide self-healing capability, namely incorporation of i) microcapsules with a high percentage of maltene oils with a shell, ii) ionomers, and iii) nanomaterials. The first comprises the microencapsulation of a high percentage of maltene oils by a shell (usually polymeric). In the asphalt binder (Fig. 6a), when a crack reaches the microcapsules, the shells break, releasing the healing agent (Fig. 6b), and restoring the ratio of asphaltene/maltenes (Fig. 6c) [94, 95]. This technique has a good recovery ratio and compatibility; nevertheless, it works only once and should be applied only to the top layers.

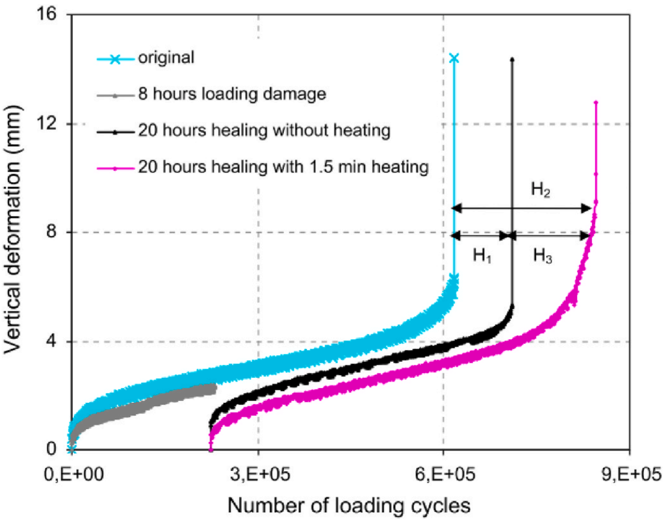

Fig. 5. Fatigue life of porous asphalt mixture with 8 % SW [92].

Chung et al. tested microcapsules of urea/formaldehyde resin (forming the shell) and solutions of triethylenetetramine with only dimethylphenol (DMP) or with SBS (comprising the core). The microencapsulated asphalt binders showed an increase in the parameter ratio strength during rest periods and the original strength. SBS/DMP microcapsules showed a faster self-healing effect than DMP alone [96].

From tests on mixtures with sunflower oil (core) capsules with cement and epoxy (shell), Garcia et al. concluded that the capsules gradually break during the load cycles, releasing the oil and rejuvenating the asphalt mixture (Fig. 7). One limitation of this technique is the non-uniform dispersion of the capsules [97].

The high percentage of maltene oil microencapsulation requires good compatibility between the agents and the asphalt binder, high stability, and good thermal properties during mixing at high temperatures (150–180 °C). In addition, it needs to be activated at the service temperature of asphalt pavement (from −30 to 70 °C) [98].

On the one hand, microencapsulation can repair the first cracks of the top layer only once. Ionomers or nanoparticles, on the other hand, can be activated multiple times because the ductile polymer can elastically rebound to its original position and the nanoparticle movement, respectively.

The second self-healing technique comprises the application of ionomers, a thermoplastic copolymer containing ionic groups (less than 30 % mol) in their backbone. Ductile polymers can elastically rebind a crack to its original position. They can be recovered multiple times and provide high thermal stability and good compatibility; however, they blend and are limited to first-stage cracks [88]. The healing process is attributed to the attraction of ionic bonds.

Regarding ionomer use, physical ionic cluster crosslinking can present the network structure of polymer-modified asphalt [99]. Shi [100] addressed the rheological properties of an asphalt binder modified with an ionomer (ethylene and methacrylic acid systems) and reported the best ionomer content of 5 % [100]. Chen et al. [101] incorporated ethylene methyl acrylate (EMAA), zinc ions, sodium ions, and

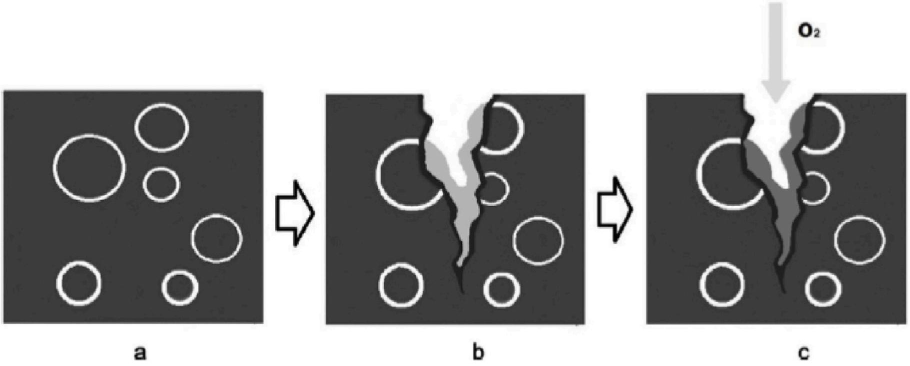

Fig. 6. Microencapsulation technique: a) asphalt binder with microencapsulation, b) microcapsules are broken by the crack, and c) release of the healing agents [96].

Fig. 7. Detail of the sunflower oil coming out [97].

lithium-ion ionomer polymers as asphalt binder modifiers with a content of 3 %. Analyzed by the T-peel test, the EMAA asphalt binder presented higher self-healing ability with a lower peel force when compared to the unmodified samples. This was shown by the lower values of the destructive forces of the EMAA asphalt samples because the rupture mainly occurred in the interface tape-asphalt (weak) instead of the asphalt-asphalt (strong).

Finally, the incorporation of nanoparticles. The nanoparticles relocate toward the crack tip, stimulated by the high surface energy, stopping its propagation, and consequently, healing the composite material [98]. Different nanomaterials, such as rubber, clay, SiO_2, and TiO_2, were used as asphalt binder modifiers for this purpose. In addition to their self-healing capability, these materials can improve the adhesion between the asphalt binder and aggregates owing to their high specific surface area [102] and improve the water sensitivity and rutting resistance of asphalt mixtures [103].

When nanomaterials were used for self-healing effects, Amin and Esmail [104] modified asphalt binders with different contents of nano-SiO_2 (from 0 to 5 % increasing at a rate of 0.5 %). SEM showed that the asphalt mortar flowed into the microcracks. By analyzing the resilient modulus of the asphalt mixtures composed of nano-SiO_2, they concluded that an increase in the nanomaterial content from 0 to 3 % enhanced the healing index from 71 to 89 %. Contents higher than 3 % absorbed a large volume of binder because of the high specific area of the nanomaterial, increasing the viscosity of the binder, restricting its mobility, and consequently interfering with the self-healing process.

Only a few studies have addressed the use of ionomers and nanomaterials to promote self-healing effects. Fig. 8 shows the self-healing mechanism of these materials. In the case of the ionomers, the self-healing effect is achieved by ionic group rearrangement (owing to the attraction of ionic bonds). In the case of the nanomaterials, cracks are repaired because these materials tend to move to the crack tip owing to the high surface energy.

Self-healing technology has already been applied to highways in the Netherlands, where 400 m of self-healing porous asphalt concrete containing SW fibers to avoid the raveling effect was laid [6,87,105]. Research on this highway is underway. Tabakovic and Schlangen [87] stated that if the asphalt binder with self-healing agents was twice the price of the conventional asphalt binder, the Netherlands, for example, would save €90 million per year to extend the lifespan by 50 % by investing in this capability.

Moreover, if the pavement lifetime is longer owing to the application of the self-healing capability to asphalt mixtures, rehabilitation and paving of new roads will be performed less often, requiring less raw material consumption, leading to less CO_2 emissions and traffic disruption.

6. Thermochromic capability

Thermochromism is a phenomenon of reversible color change in response to temperature changes. Thermochromic materials are classified as conjugated oligomers, metallic oxides, and leuco dyes [106,107]. In inorganic compounds, color changes can result from phase transitions and variations in the coordination geometry [108], whereas inorganic compounds can result from reversible chemical reactions and molecular rearrangements [109].

The application of thermochromic materials in civil engineering must consider the transition temperature. Vanadium dioxide (VO_2) and vanadate compounds have been intensively studied; however, their transition temperatures are too high for this type of application, 68 °C for VO_2 [108], and 255 °C for $BiVO_4$ [106].

Because of their black color, asphalt binders strongly absorb energy from sunlight. During summer, the surface temperature of asphalt pavements may increase to almost 70 °C, impacting their durability owing to the acceleration of distress mechanisms such as rutting. In contrast, during winter, low temperatures promote the thermal cracking of asphalt pavements and ice formation over their surfaces [110–112]. Therefore, it is crucial to control the temperature of the asphalt mixture by cooling the surface during summer and warming it during winter. To achieve this goal, a novel thermochromic capability has been applied to asphalt mixtures using materials such as leuco dyes, for use as asphalt binder modifiers.

The reflectivity of asphalt mixtures changes with the introduction of thermochromic materials owing to the color variation with temperature. At high temperatures, this composite material can reflect more solar

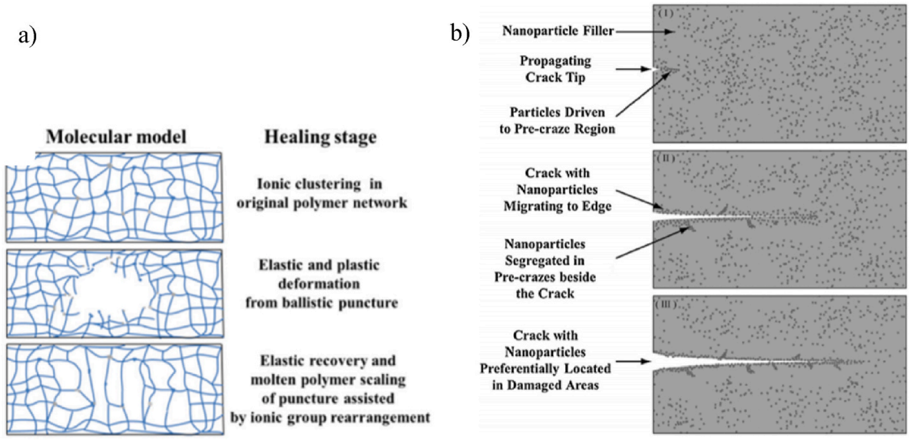

Fig. 8. Mechanism of the healing effect using: a) ionomers and b) nanomaterials [99].

energy, and at low temperatures, reflect less solar energy [110]. Moreover, during winter nights, the treatment helps to control the surface temperature of the functionalized asphalt mixtures, thus mitigating the low-temperature cracking effects [110]. The primary goal of the introduction of thermochromic materials is to promote the control of temperature variation and amplitude because the climate is one of the essential agents that reduce the mechanical performance of asphalt pavements.

The properties that can be considered to evaluate this capability are the color change with different temperatures combined with color coordinates, physical (penetration, softening point, photoluminescence, and reflectance), rheological properties, and aging behavior if the asphalt binder is modified [109,110,113–115].

A few studies have been conducted on the application of thermochromic capability in asphalt mixtures. Hu and Yu evaluated the use of 10 % black, blue, and red thermochromic powders (leuco dyes with a transition temperature of approximately 31 °C) as an asphalt binder modifier to decrease the surface temperature of the asphalt binder by changing its color. At high temperatures, the maximum reduction in the asphalt binder surface temperature was 6.6, 2.7, and 4.9 °C for the black, blue, and red asphalt binders, respectively. Moreover, at low temperatures, the thermochromic powders increased the maximum surface temperature by approximately 1 °C [110].

The asphalt binder modification using thermochromic powders (Fig. 9) improves its high-temperature stability, increases the complex modulus, viscosity, and softening point, and decreases the phase angle and penetration when compared to conventional asphalt binders.

These materials can also extend the performance grade of the asphalt binders. The modified asphalt binder with thermochromic powder showed better aging resistance after RTFOT, PAV, and UV aging. The best anti-aging properties were achieved using a red thermochromic powder content of 6 % [113].

In addition to surface temperature, Hu et al. studied the physical and rheological characteristics of modified asphalt binders with thermochromic powders (black, blue, and red) composed of organic mixtures of leuco dye (electron donor), a developer (electron acceptor), and a solvent, all encapsulated by trioctanoin. The increase in the reflectance spectra is associated with a reduction in the solar absorption on the surface. The highest reflectance in the visible wavelengths of the electromagnetic spectrum was obtained for the blue powder, followed by the red and finally black powders. In addition, the thermochromic asphalt binder was more reflective than the conventional asphalt binder. The highest reflectance was achieved for the black (when deactivated) thermochromic asphalt binder, followed by the blue and red thermochromic asphalt binders. The authors recommended that the use of these thermochromic powders should be less than 5%–6% (by the mass of the asphalt binder) to assure the physical and rheological properties [109].

Thermochromic powder improved the low-temperature cracking behavior and aging resistance. When the anti-aging properties of asphalt binders were considered only, the ideal content to achieve the best performance was 4 %, as Zhang et al. [97] concluded. The results showed a higher spectral reflectance for higher powder content [114].

Based on the reflectance spectra of thermochromic asphalt binders at different temperatures, it is possible to simplify the design of these road pavement materials. Maxwell (Eq. (9)), effective medium theory (Eq. (10)), and Mori-Tanaka (Eq. (11)) models were successfully used to predict the effectiveness of the reflectance spectral capacity of thermochromic asphalt binders [115].

$$R_{mix} = \left(1 + \frac{3(\alpha - 1)\varphi}{(\alpha + 2) - (\alpha - 1)\varphi}\right) R_m \alpha = \frac{R_p}{R_m} \tag{9}$$

$$(1 - \varphi)\frac{R_m - R_{mix}}{R_m + 2R_{mix}} + \varphi\frac{R_p - R_{mix}}{R_p + 2R_{mix}} = 0 \tag{10}$$

$$\frac{R_{mix} - R_m}{R_p - R_m} = \frac{\varphi}{1 + (1 - \varphi)\left(R_p - R_m\right)/3R_m} \tag{11}$$

In the equations above, α, R_m, R_{mix} $R_{p,}$ and Ø represent the powder dimension (μm), original asphalt binder reflectance (%), thermochromic asphalt binder reflectance (%), thermochromic powder reflectance, and

Fig. 9. Thermochromic powders (blue, black, and red): a) deactivated below 31 °C and b) activated above 31 °C (right) [113].

volume fraction of the dispersed powder, respectively.

The urban heat island (UHI) can also be mitigated by controlling the thermochromic asphalt pavement color under high-temperature conditions. It can be concluded that thermochromic materials can positively affect the mechanical performance of mixtures by controlling their surface temperature and improving the aging resistance. For this new capability, the literature review shows little experience. Consequently, many opportunities to explore this capability exist, including mechanical performance and cost analysis.

7. Latent heat thermal energy storage (LHTS) capability

Phase change materials (PCMs), under the principle of LHTS, absorb large amounts of energy when there is excess and release it when there is a deficit. PCM reduces the peak heating and cooling loads when applied to materials in different areas [116–118]. PCMs are applied in civil engineering, mostly on floors, roofs, wallboards, and concrete, to improve building energy efficiency (reducing the energy per area needed for heating/cooling).

In the case of building applications, PCM increases the thermal comfort owing to smooth temperature fluctuations at the inner spaces, reducing the energy needed by the heating/cooling equipment, that is, heaters and air conditioners. Thus, there are benefits to the environment because energy consumption from power stations will decrease, resulting in fewer emissions.

When PCMs are incorporated into asphalt mixtures, the primary purpose is to prevent rutting [119] and avoid thermal cracks or rapid temperature changes owing to the reduction in the magnitude of temperature fluctuations [120]. In addition to the mechanical component addressed in the research, another goal is to avoid the UHI by controlling the interaction between the asphalt pavement surface and the environment, which is a socioenvironmental goal [121].

For the design of LHTS materials, including LHTS asphalt mixtures, it is essential to have at least three components: i) appropriate PCM with the desired temperature range of melting point, ii) a suitable heat exchange surface, and iii) an appropriate container compatible with the PCM [122].

Differential scanning calorimetry is the technique most commonly adopted to obtain the melting temperature through the phase change enthalpy of the materials [123]. The observation of temperature during heating to calculate the heat and cooling rates is also relevant to assess this capability.

Different types of PCMs with different relations between the melting enthalpy and melting temperature exist, as shown in Fig. 10a and b [123,124]. Its phase transition can be classified as solid –liquid phase transition, solid-solid phase transition, solid-gas phase transition, and liquid-gas phase transition [121]. The most commonly used PCMs are fatty acids and esters, such as paraffin, salt hydrates, and ionic liquids [125].

The recommendation for rutting mitigation is the use of PCM with a maximum phase change temperature between 3 and 5 °C below the softening point of the asphalt binder. With this limit, an acceptable trade-off exists between the amount of PCM and the energy absorbed. The material must not store much energy because the reverse process will occur and affect the air temperature, enhancing the UHI [119].

Silica powder, floating beads, and activated carbon with PCM used as raw materials via the sol-gel process can improve the high-temperature stability of asphalt mixtures [126]. Activated carbon with PCM has a larger latent heat storage capacity (phase change enthalpy 19 J/g) and a proper phase change transition temperature (−3 °C). When 0.3 % of unsaturated organic acid and polypropylene is used as PCM in the mass of the asphalt mixture, this material decreases the rising and cooling rate of temperature and delays the occurrence time of extreme temperatures [125]. He et al. compared the performance of polyethylene glycol 2.000 as a PCM and SiO_2 as a matrix in asphalt binders. They concluded that the modified asphalt binder had a large phase change enthalpy (38.2–117.5 J/g), good chemical compatibility, and thermal stability [120].

The PCM (phase change temperature between 40 and 50 °C and latent heat of 150 J/g) was used to lower the temperature and prevent rutting by MeiZhu et al. [119]. These PCMs were used because the dynamic stability of asphalt mixtures considerably decreased in the range of 48–52 °C. Thus, it was possible to reduce the rate of temperature increase [119].

Granular-shaped solid-liquid PCM composed of unsaturated organic acid and polypropylene with a melting point of 22.1 °C and latent heat of 46.97 °C were used as aggregates in a proportion of 0.3 % of the asphalt mixture weight (added in bulk incorporation during the mix). The material decreased the temperature rise and cooling rate and delayed the occurrence of high temperatures [125].

Manning et al. tested 1.25 % and 2.5 % paraffin waxes as PCM (by mass of the mixture) with phase changes at 6 °C to delay freezing, decrease the cooling rate, and reduce the freezing time [127]. Their results showed that this material can reduce cooling and heating rates. However, they did not conclude on the effect of extremely low temperatures, and the phase change when the time was above 5 h is a limitation. In addition, no reduction in the extremely high temperature with the use of PCM occurred.

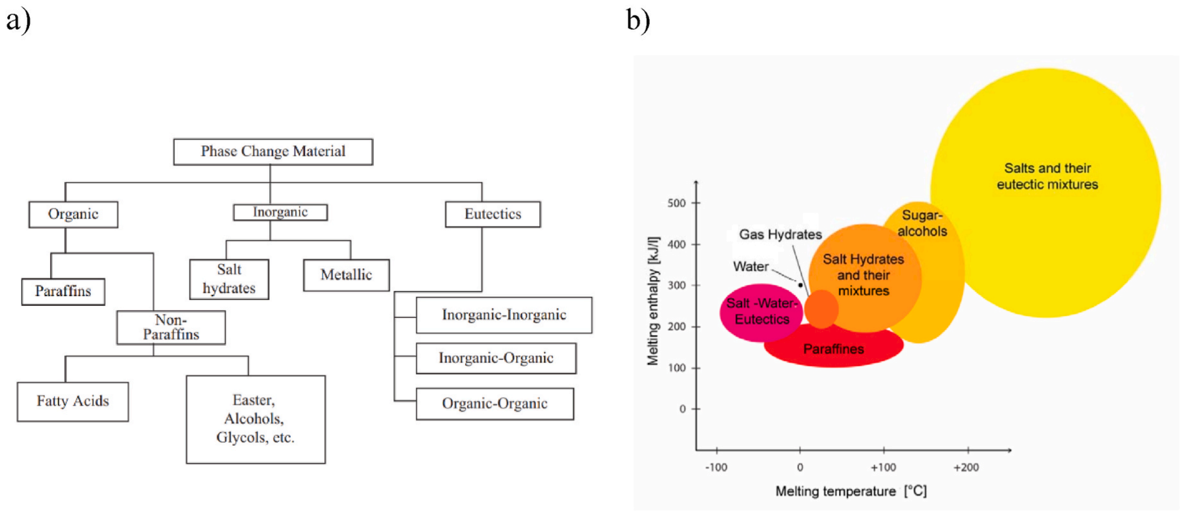

Fig. 10. a) Different types of PCM [123] and b) Melting enthalpy versus melting temperature [124].

Ma et al. tested PCMs composed of unsaturated acid, Υ-linolenic acid, β-linolenic acid using SiO_2 as a matrix with a phase changing temperature between 8 and 25 °C in a content of 20 % (in the mass of the asphalt binder) during the mixture. The results showed that the incorporation of the PCM in the mixture reduced the heating and cooling rates and improved the low-temperature crack and rutting resistance [128]. After analyzing the mechanical behavior, Ma et al. recommended 0.3 % of two types of PCMs composed of hydrocarbon PCM with porous SiO_2 or unsaturated organic acid with polypropylene in the weight of asphalt mixture to adjust the phase change temperature to meet the technical requirements of roads [129].

To avoid the UHI, a solid-liquid phase transition PCM composed of unstable acids and SiO_2, resulting in latent heat of 95 kJ/kg and a phase change temperature of 17 °C, was tested with a content of 50 % of asphalt binder by weight. The results show an increase in the specific heat of the asphalt mixture, which required more energy to change the temperature. Consequently, it is possible to have cooler roads, thus mitigating the UHI [121].

To develop the LHTS capability, heating and cooling tests were performed; however, conventional rutting, fatigue, and water sensitivity tests are also essential to design LHTS asphalt mixtures. PCM encapsulation could have advantages such as a larger heat transfer area, a decrease in the PCM reactivity owing to the external environment, and control of changes in the volume (expansion or retraction) of the storage materials when the phase change occurs [130]. The capsule shell prevents interactions between the PCM and the smart material [130], thus avoiding future mechanical problems. Researchers can also study the use of PCMs to avoid UHIs.

8. Summary

New capabilities are under investigation to enhance the performance of the surface and improve the structural properties of asphalt pavements. Table 1 summarizes the previously detailed capabilities, namely their influences, benefits, the most used materials, and the main functionalization methods. The capabilities directly related to the socio-environmental impacts are the photocatalytic, thermochromic, and latent heat thermal energy storage (LHTS) capabilities, whereas those that directly impact mechanical behavior are superhydrophobic, LHTS, self-healing, and thermochromic capabilities. Last, the ones related to safety are superhydrophobic, self-cleaning, and de-icing capabilities.

Some of these capabilities are interrelated. From the review, it is clear that the optimization of some techniques could promote more than a single capability. The self-cleaning capability can be treated as superhydrophobic or photocatalytic. On the one hand, on a superhydrophobic surface, the rolling water drops remove the dirt particles. On the other hand, on a photocatalytic surface, oils and greases are removed by chemical reactions (heterogeneous photocatalysis).

A strategy to extend the thermochromic capability with time involves the inclusion of specific semiconductor materials in thermochromic coatings. Owing to their photocatalytic and self-cleaning capabilities, these materials can degrade oils and greases, thus eliminating contaminants that block the path of light [131]. Moreover, with the application of highly electrically conductive materials or nanomaterials, such as carbon nanotubes and nanofibers, it is possible to provide both self-healing and de-icing capabilities.

Thermochromic and LHTS capabilities can also be used to mitigate UHI. A photocatalytic coating applied over a pavement surface can prevent this problem, as the treatment usually provides a white color (low absorptivity), thus the original surface black color (high absorptivity) is covered. Semiconductor nanomaterials can also provide self-healing capability when applied by asphalt binder modification, as nanoparticles relocate toward the crack tip, stopping its propagation, and consequently, healing the composite material.

9. Critical analysis and conclusions

The major goal of this work is to perform a literature review on the smart and multifunctional capabilities of asphalt mixtures. The photocatalytic, superhydrophobic, self-cleaning, de-icing/anti-ice, self-healing, thermochromic, and LHTS capabilities were analyzed in detail. In this section, the major conclusions are followed by a critical analysis, addressing the life cycle of smart asphalt pavement layers, from raw materials to the end of life, including costs.

- The essential characteristics of asphalt pavements must be assured: resistant to traffic loading, and climatic actions, and rolling conditions such as comfort and safety, low impact on the environment and low cost. Therefore, in addition to tests conducted to evaluate the novel capabilities, it is fundamental to perform standard tests to guarantee adequate mechanical and functional performance, based on the technical requirements of asphalt mixtures.
- The development of novel capabilities in asphalt mixtures is achieved by the application of different materials, such as nano/microparticles (including semiconductor materials and microcapsules), fibers, PCM, and dyes. In addition, a novel potential for the application of recycled materials, such as steel slag (SS), from the steel industry.

Table 1

Influences, benefits, materials and major applications of the multifunctional capabilities.

Capability	Direct Influence	Indirect Influence	Benefits	Materials	Main application
Photocatalytic	Environmental	Social	Air and surface cleaning	Semiconductors, mostly TiO_2	Spray coating, bulk incorporation, asphalt binder modification, and spreading
Superhydrophobic	Safety and mechanical	Social and economic	Non-wetting pavements and better resistance	PTFE, nanoparticulate copolymer fluoroacrylate with CaO, TiO_2, and TiO_2 ZnO	Spray coating
Self-cleaning	Safety and Environmental	Social and economic	Surface cleaning and higher friction	Semiconductors/superhydrophobic treatments	Spray coating, bulk incorporation, asphalt binder modification, and spreading
De-icing	Safety	Social and economic	Anti-snow/ice pavement	Salts and high electrical conductor materials	Asphalt binder modification bulk Incorporation
Self-healing	Mechanical	Economic, environmental, and social	Crack healing: lifetime increase	High electrical conductor materials, microcapsules, nanomaterials, ionomers	Bulk incorporation asphalt binder modification
Thermochromic	Mechanical, safety, and social	Economic	Mitigate UHI or temperature control sensor	Leuco dyes	Asphalt binder modification
LHTS	Social, environmental or mechanical	Financial	Mitigate UHI or control of very high/low temperatures	Phase change materials	Bulk incorporation

- Regarding the design process of smart and multifunctional asphalt mixtures, different tests can be used to assess and characterize novel capabilities. The advanced material characterization tests recommended are X-ray computed tomography (CT), SEM, Fourier transform infrared spectroscopy, DSC, and atomic force microscopy. Complementarily, the development of abrasion techniques, performed on small samples, is an excellent opportunity to investigate the durability of novel capabilities (mainly the capabilities applied by coating treatments) and test the degree of immobilization of nanomaterials on functionalized surfaces.
- Regarding the functionalization methods of all the capabilities, they are simple and controlled by the paving industry, i.e., bulk incorporation, spray coating, spreading, and asphalt binder modification.
- Most studies have focused on the functionalization of a single new function. However, the combination of different functionalization methods and/or capabilities can result in the development of a better final product, a multifunctional asphalt mixture.
- The transfer technology of some capabilities from the laboratory to real-scale roads is already a concern. However, the construction of real-scale functionalized asphalt pavements is still a challenge for the paving industry. This study showed some opportunities of use (including nano/micromaterials), which do not require expensive technological improvements to functionalize the asphalt pavement. In fact, it is reasonable to state that, very soon, one of the potential destinations for the large-scale application of nanomaterials is the road sector, as it can act as a great lever to promote the dynamism and economic growth of industries related to the production of nanomaterials and nanotechnology use. Thus, it can be inferred that the transfer technology of the capabilities not yet tested on a real scale will be successful. With the large-scale use of nano/micromaterials, cost reduction is expected because the production of these materials is limited.
- Studies addressing the life cycle of smart and multifunctional asphalt mixtures are few but important. Cost analysis is still lacking in the literature for all the capabilities. Only a short economic analysis of a few techniques exists, for example, photocatalytic coatings. This evaluation is strongly recommended to guarantee economic feasibility. Furthermore, some topics need to be evaluated for those capabilities related to environmental benefits, such as environmental indicators, pollution reduction level, risk of cancer, biochemical analysis of the byproducts, and incorporation in cost analysis.
- When the general design process is a concern, further studies should focus on a smart asphalt mixture, which must consider the requirements of traffic and weathering (mechanical and functional characteristics). It is recommended to design multifunctional asphalt mixtures made up of recycled materials and use techniques that cause less environmental damage and low noise. Accordingly, asphalt mixtures are eco-friendly and provide several social, environmental, and financial benefits.

Because of the large surface area of paved roads, the process to provide them with multifunctional capability can deliver a very positive contribution to the users because, in addition to having a good mechanical structure and good surface properties that result from the application of novel capabilities, they have environmental benefits, for example, the ability to photodegrade organic compounds adsorbed on the road surface or even toxic gases (NO_x and SO_x) that are released from the exhausts of road vehicles.

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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.

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