Iron oxide nanoparticles for magnetically-triggered healing of bituminous materials

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Abstract

Healing of micro-cracks is crucial for recovering the mechanical properties and extending the service time of bituminous materials. However, crack closure is often challenged by the efficiency and repeatability of the healing process or its technical and economic feasibility for large-scale applications. Here, we propose an innovative method to close micro-cracks in bituminous materials by using magnetically-triggered iron oxide nanoparticles as heating agents. Heating is generated through the so-called hyperthermia effect upon exposure of the nanoparticles to an external oscillating magnetic field. When mixed in a low volume fraction of 1 % within bitumen, the nanoparticles generate enough heat to decrease the viscosity of the

surrounding material and thus promote crack closure. Oleic acid is used to coat the iron oxide nanoparticles and enable their homogeneous distribution in the bitumen. Because of high hysteresis losses, γ -Fe₂O₃ nanoparticles with a mean crystallite size of 50 nm exhibited specific absorption rates (SAR) as high as 285 W/g when subjected to a magnetic field of 30 mT at 285 kHz. In contrast to the relatively slow heating of electrically-conductive additives, we find that iron oxide nanoparticles pre-embedded in bitumen allows for crack closure in a few seconds when subjected to similar magnetic field conditions. This represents a new efficient way to heal damage in thermoplastic road pavements in the presence of mineral aggregates.

Keywords

Crack healing, Magnetic nanoparticles, Bitumen, Bituminous materials, Magnetic field, Dynamic polymers

1. Introduction

Bituminous materials are widely used for road pavements and buildings because of their ease to handle, economical attractiveness, performance and recyclability using conventional thermoplastic processes [1]. Most prominent examples for bituminous materials are asphalts, which are usually composed of mineral aggregates bound by bitumen in the presence of 0 - 20 vol % air voids and eventually additives such as polymers, rubber and cellulose fibers.

Bitumen is a thermoplastic material obtained from crude oil distillation that mainly consists of mixtures of high molecular weight organic hydrocarbons with functional groups that can range broadly in polarity [2]. Remarkably, this very well-established and industrially-relevant complex material exhibits some features of the most advanced dynamic polymers [3], such as the viscoelastic response, the presence of reversible bonds and the capability of self-healing under certain conditions. Polar functional groups in bitumen molecules favor physical and chemical interactions of such macromolecules with polar inorganic surfaces, which ultimately lead to high binding affinity to stones and mineral phases. However, when exposed to years of mechanical and thermal stresses as well as environmental effects (oxidation from the air, UV, moisture), debonding at the interface between bitumen and mineral aggregates can occur. As a result, cohesive and adhesive cracks are formed within the microstructure. These initial micro-scale cracks may grow and propagate into macro-cracks, eventually causing irreversible damage that result in large maintenance costs. Thus, different approaches to promote crack closure at an early stage have been proposed recently [4, 5]. Crack-healing can be defined as the capability of a material to recover the original mechanical properties by externally induced cohesive crack closure.

Depending on the material, crack-healing can be induced by a variety of mechanisms either autonomously or under external stimulus [6-9]. Because of its thermoplastic nature, a

straightforward approach to promote crack-healing in bituminous materials is to reduce the viscosity of bitumen by increasing the temperature or releasing bitumen-miscible diluting agents. Indeed, increasing the temperature of pavement material up to 50 - 100 °C (depending on the type and composition) is sufficient to initiate flow of bitumen. Lower viscosities facilitate healing through the flow of the material into micro- and macrocracks. Autonomous healing systems using pre-embedded encapsulated solving agents have been investigated previously [10, 11]. However, the irreversible nature of the capsule rupture for releasing the solving agent makes this a “one shot” approach that is not repeatable.

Intense research has been concentrated on promoting crack healing by reducing the viscosity of bitumen through externally-triggered heating. Different approaches have been proposed to initiate crack-healing by heating up bituminous materials using magnetic fields from tens of kilohertz (kHz) to several gigahertz (GHz) [12, 13]. In all cases, electrically-conductive additives are embedded in the material to generate heat through dissipative electrical currents. For example, Liu et al. [12] presented a healing method which relies on steel wool fibers added to asphalt concrete to promote local heating in the presence of an alternating magnetic field. Depending on the concentration of fibers, the bitumen can be heated in a few minutes and eventually flow into the cracks, leading to a partially or completely-healed material after solidification of the bitumen upon cooling.

Despite the positive effect of electrically-conductive additives in recovering the mechanical properties of asphalts by thermally-induced fluidization, such additives also have disadvantages that often reduce the material’s integrity. Since metal particles are usually used as electrically-conductive additive, corrosion on the surface of the pavement may be a critical issue. In case of conductive metal fibres, mixing of the asphalt becomes an additional problem. Poor mixing may produce clusters of a few millimetres in size which locally weaken the mechanical properties of the pavement [14]. In addition, the large size of clusters or of the

millimeter-scale particles needed for fast heating can cause overheating at the bitumen-metal interface and consequently damage of the bitumen microstructure.

In contrast, magnetic oxide nanoparticles may offer a powerful new alternative for closing micro-cracks in bituminous materials if one exploits their ability to generate heat in the presence of an oscillating magnetic field (hyperthermia). Due to their size typically below 100 nm, these nanoparticles should enable a fast and uniform temperature increase when well dispersed in a matrix exposed to an oscillating magnetic field. Furthermore, as opposed to electrically-conductive additives, magnetic oxide nanoparticles are not susceptible to corrosion.

The phenomenon of hyperthermia using magnetic nanoparticles has been extensively investigated as a means to treat cancer in biomedical applications [15-17] or to generate localized heat in a wide range of synthetic materials [18-20]. Different methods have been applied for example to embed magnetic nanoparticles in stimuli-responsive polymers for healing purposes [21, 22] or to trigger shape memory effects [23]. Heating can be tuned by selecting the size, shape and concentration of the nanoparticles. Overall, it was found that iron oxides in the form of magnetite (Fe_3O_4) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are the most common materials because of their relatively strong magnetic response, ease of synthesis, low toxicity and low price [15].

To avoid the loss in mechanical properties of bituminous materials from weathering and aging, we propose in this study a new magnetically-assisted crack healing method that relies on the local on-demand heating and softening of a bitumen matrix containing homogeneously dispersed oxide nanoparticles (Figure 1). Alike the magnetic hyperthermia processes widely investigated in biomedical applications, we exploit the ability of iron oxide nanoparticles to locally heating the surrounding medium when exposed to a high-frequency alternating magnetic field (AMF). Due to the high surface-to-volume ratio of the

nanoparticles, it is anticipated that local heating can be quickly dissipated into the surrounding matrix if the nanoparticles are homogeneously dispersed.

Figure 1. Schematics illustrating the proposed crack healing method for bituminous materials using magnetic nanoparticles embedded in bitumen.

2. Materials and methods

2.1. Materials

Three commercially available iron oxide nanoparticles were investigated (Table 1) using oleic acid (OA) ($\geq 99\%$, Sigma Aldrich) as surfactant and straight-run bitumen with a penetration grade 70/100 (Kuwait Petroleum) as matrix (1032 kg/m^3).

Table 1. Description of the investigated iron oxide nanoparticles as provided by the suppliers

Particle Type	Supplier	Particle size (nm)	Specific area (m^2/g)	Density (kg/m^3)
Fe_3O_4 (Magnetite)	IO-LI-TEC	20 – 30	40 – 60	5175 ¹²⁵
$\gamma\text{-Fe}_2\text{O}_3$ (Maghemite)	Alfa Aesar	20 – 40	30 – 60	5240 ¹²⁶
Fe_3O_4 (Magnetite)	NanoAmor	50 – 100	20 – 50	5175 ¹²⁹

2.2. Methods

2.2.1. Sample preparation

For the surface modification of the iron oxide particles, 0.52 g and 0.49 g of dry magnetite and maghemite nanoparticles, respectively, were dispersed in 10 ml of distilled water containing 1.65 g of oleic acid. The suspensions were sealed and sonicated in an

ultrasonic bath for 30 min (TCP-120, Telsonic AG, Switzerland) and then heated up to 60 °C for 24 h. 10 ml of acetone were used to precipitate the nanoparticles and to separate them from the excess oleic acid. In this procedure, a magnet was used to trap the nanoparticles while the supernatant was removed.. After repeating this step three times, 10 ml of toluene were then added to re-disperse the nanoparticles by using ultrasonic bath for 30 min. For the preparation of bitumen/nanoparticles nanocomposites, the toluene/nanoparticle suspensions were mixed with 10.21 g of bitumen in an evaporation flask and heated to 160 °C for 1 h to evaporate the toluene using a rotary evaporator with a constant rotation of 80 rpm. Afterwards, cylindrical samples with diameter of 22 mm and height of 3 mm were produced by filling up silicone molds and kept in the freezer at -10°C. This procedure was repeated for bitumen samples without nanoparticles for comparison purposes.

2.2.2. Material characterization

Powder X-ray diffraction patterns were obtained using a PANalytical X'Pert PRO MRD scan system equipped with a Johansson monochromator (Cu-K α_1 radiation, 1.5406 Å) and an X'Celerator linear detector. The diffraction patterns were recorded between 20° and 70° (2 θ) with an angular step interval of 0.0167°. The crystal sizes were calculated by the Scherrer equation [24]. The instrument's contribution to the peak broadening was estimated by measuring the standard reference sample CeO₂ (NIST SRM674b).

The morphology of the as-received nanoparticles was characterized by scanning electron microscopy (SEM, LEO 1530, Zeiss, Germany). To this end, a droplet of nanoparticles in water was placed onto a glass slide previously displayed on a carbon tape. Water was used to efficiently disperse the nanoparticles in a liquid state and prevent the formation of large agglomerates on the sample holder. This dispersed state should be representative of the morphology of the particles when surface is modified with oleic acid and suspended in toluene (as described later in the text). The nanoparticles were linked to the SEM holder by a silver tape and were finally sputtered with a 5 nm- thick platinum layer for imaging.

Magnetic measurements were performed using the AC measurement system (ACMS) of a Model 6000 Quantum Design Physical Property Measurement System (PPMS). At room temperature, magnetization curves of the three above stated materials were obtained in fields up to 500, 30, 22.6 and 15 mT in a sweeping mode. To prevent any influence of pre-existing

magnetization on the hysteresis parameters, the magnetic history was removed prior to each hysteresis measurement upon the application of an alternating field with a 2 mT/sec rate.

In order to assess the success of the surface modification procedure of the nanoparticles with oleic acid, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed at room temperature using a diamond crystal in a Nicolet iS5 instrument. The spectra were collected in the 4000–600 cm^{-1} wavenumber range with a resolution of 4 cm^{-1} . The data were collected with the OMNIC software and processed such that each final spectrum represents an average of 32 individual spectra.

To quantify the amount of oleic acid adsorbed on the surface of the nanoparticles, thermogravimetric analysis (TGA) was conducted on dried nanoparticles using a TGA/SDTA 851e equipment (Mettler Toledo, Switzerland) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ up to 600 $^{\circ}\text{C}$ in an argon atmosphere.

For the measurement of the particle size distribution, dynamic light scattering (DLS) experiments of nanoparticles suspended in toluene were carried out using a Zetasizer NanoZS instrument (Malvern instruments, UK) and a Malvern Zetasizer v7.03 software for data analysis.

The distribution of nanoparticles throughout the bitumen matrix was evaluated by imaging cross-sections of representative nanocomposite samples in the cryogenic scanning electron microscope Leo-1530 Gemini (Zeiss, Germany). Bitumen samples containing nanoparticles were cooled to -20 $^{\circ}\text{C}$ for 20 min, fractured using two tweezers and finally glued onto a Cryotable by using silver glue. After being loaded into the freeze fracture system EM BAF060 (Leica, Germany), samples were cooled down to -60 $^{\circ}\text{C}$. A first 3 nm layer of tungsten at 45 $^{\circ}$ was sputtered to create a shadow, followed by a second 3 nm layer at 90 $^{\circ}$ to generate a continuous coating onto the sample surface. The studied sample was then transferred via the vacuum cryo transfer system EM VCT100 (Leica, Germany) to the CryoSEM. Imaging was carried out at -60 $^{\circ}\text{C}$ with acceleration voltages of 5 and 15kV.

2.2.3. Experimental setup for magnetically induced heating

Heating measurements were carried out using an alternating magnetic field (Ambrell EasyHeat) at a fixed frequency of 285kHz and different amplitudes $\mu_0 H_{\text{max}}$ of 30, 22.6 and 15 mT. Samples were inserted into a copper coil with a diameter of 50 mm (3 turns) and then

heated during 30 s . The surface temperature of the sample was recorded as a function of time using an infrared camera (Testo t885-2 33Hz).

2.2.4. Experimental setup for bitumen crack closure

In order to demonstrate the beneficial role of using magnetic nanoparticles for rapidly heating and healing micro-cracks, we created artificial cracks on the surface of nanoparticle-bitumen specimens using a Vickers diamond micro-indenter. Before indentation with a 1 kilogram load, bitumen samples with different types of nanoparticles were immersed in liquid nitrogen for approximately 10 s. Since bitumen is brittle at low temperature, micro-cracks were generated at the edges of the square impress of the Vickers indenter. Constrained by a mold to prevent bitumen from flowing in other directions, the samples were then heated up using an alternating magnetic field of 30 mT at 285 kHz to observe the dynamics of crack closure. The temperature on the sample surface was recorded from its initial value of 0 °C to the temperature where micro-cracks were closed. The speed of crack closure was determined from snapshot images using a Z16 APO Macroscope (Leica, Germany).

4. Results and discussion

4.1. Particle characterization

The crystalline phases and mean crystallite sizes of the magnetic iron oxide nanoparticles were investigated by powder X-ray diffraction measurements (Figure 2). The values of the mean crystallite sizes were used as part of the nomenclature adopted here for the different types of nanoparticles, as indicated in Table 2. The diffraction patterns obtained for particles NP13 and NP219 indicate the presence of characteristic reflections of Fe_3O_4 (JCPDS-PDF 03-065-3107) [25, 26]. In addition to Fe_3O_4 , the pattern of particles NP50 exhibit also reflections associated with $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS-PDF 01-80-2377). No diffraction peaks arising from any other secondary phases or impurities were detected.

Table 2. Physical properties of the investigated iron oxide nanoparticles. The mean crystallite sizes were calculated by the Scherrer equation from XRD measurements.

NP Type	Iron oxide type	Supplier	Mean crystallite size (nm) ($\pm 20\%$)
NP13	Fe_3O_4	IO-LI-TEC	13
NP50	$\gamma\text{-Fe}_2\text{O}_3$	Alfa Aesar	50
NP219	Fe_3O_4	NanoAmor	219

Figure 2. Powder X-Ray Diffraction (XRD) patterns of the investigated iron oxide nanoparticles.

To compare the magnetic response of the three types of nanoparticles investigated, magnetization measurements were carried out at ambient temperature until saturation. As shown in Figure 3a-b, the nanoparticles differ significantly with regards to their magnetic properties, including saturated magnetization (M_s), remnant magnetization (M_r), coercive field and hysteresis area. The sample containing nanoparticles with a mean crystallite size of 50 nm (NP50) exhibits the largest hysteresis loop area among the investigated materials (Figure 3a-b). This is reflected in a high magnetic coercivity value of 16.5 mT as compared to the values of 5.8 mT and 14.0 mT for particles NP13 and NP219, respectively (Table 3). Likewise, the M_r/M_s ratio for NP50 reaches 0.28, followed by values of 0.08 and 0.13 for particles NP13 and NP219, respectively. As the energy dissipated through magnetic hyperthermia is directly related to the magnetization hysteresis area, the bitumen sample containing NP50 particles is expected to show the strongest local heating effect under an alternating magnetic field.

The observed magnetic properties can be interpreted on the basis of the different particle sizes of the evaluated powders (Figure 3c). The magnetic coercivity usually exhibits a

maximum at a given particle size above which the internal magnetic structure of the material shifts from single- to multiple-domain [27, 28]. The particle size for which we observed maximum coercivity (50 nm) is in good agreement with previously reported values associated with this change in the domain structure, which typically range from 30 to 80 nm for magnetite [27-30].

Figure 3. Magnetic behaviour of the investigated iron oxide nanoparticles. (a) Hysteresis curves over a magnetic field ranging widely from -500 mT to 500 mT at 300 K. (b) Detailed view of the hysteresis curves over a magnetic field ranging from -50 mT to 50 mT. (c) SEM images of the three types of nanoparticles as-received, indicating the different particle sizes and morphologies.

Table 3. Magnetic properties of the investigated iron oxide nanoparticles. The magnetic coercivity and the ratio between the remnant and the saturation magnetization (M_r/M_s) were estimated from the hysteresis curves.

NP Type	Coercivity H_c (mT)	Mr/Ms
NP13	5.8	0.08
NP50	16.5	0.28
NP219	14.0	0.13

4.2. Surface modification of the nanoparticles

We modified the surface of the iron oxide nanoparticles with oleic acid to achieve a stable dispersion in organic solvents and enable good homogenization in bitumen. The successful modification of the nanoparticles with oleic acid (OA) was confirmed by ATR-FTIR spectroscopy and TGA measurements (Figure 4a,b). The presence of OA on the nanoparticle surface was confirmed by the peaks at 2920 cm^{-1} and 2852 cm^{-1} , which correspond to the asymmetric and symmetric stretching vibrations of the CH_2 groups, respectively. The intense peak at 1707 cm^{-1} observed in the OA spectrum corresponds to the C=O stretching vibration and is absent for the OA-modified Fe_3O_4 spectrum [26, 31]. Instead, characteristic peaks at 1570 cm^{-1} and 1523 cm^{-1} associated with stretching vibrations of COO^- groups are clearly visible in the spectrum obtained for OA-modified Fe_3O_4 nanoparticles. This results from the coordination between COO^- and Fe ions forming a bidentate metal carboxylate [26]. For both Fe_3O_4 and OA-modified Fe_3O_4 nanoparticles, the peak corresponding to the stretching vibration of the Fe-O bond is observed at approximately 540 cm^{-1} .

Thermogravimetric analysis (TGA) of dried Fe_3O_4 nanoparticles previously coated with oleic acid reveals a significant mass loss between $190\text{ }^\circ\text{C}$ and $390\text{ }^\circ\text{C}$ as compared to the moderate mass change observed for uncoated dried nanoparticles (Figure 4b). This high mass loss amounts to 7 wt% and corresponds to the thermal decomposition of the OA molecules adsorbed on the surface of the Fe_3O_4 nanoparticles. The weight loss around $100\text{ }^\circ\text{C}$ observed

for both curves is due to the presence of residual water, which represents less than 1 % of the total powder mass.

Figure 4. Chemical and physical characterization of the iron oxide nanoparticles modified with oleic acid (OA). (a) ATR-FTIR analysis of OA-modified Fe₃O₄ nanoparticles, as compared to OA and Fe₃O₄ reference samples. (b) Thermogravimetric analysis (TGA) of pure Fe₃O₄ and OA-modified Fe₃O₄ nanoparticles.

4.3. Dispersion of magnetic nanoparticles in bitumen

Iron oxide nanoparticles tend to agglomerate in non-polar organic solvents if no surfactants are present on the particle surface. Coating of the iron oxide nanoparticles with oleic acid was found to prevent the formation of particle clusters and agglomerates larger than 1 μm in organic solvents like toluene. This is evidenced by the particle size distributions shown in Figure 5a. The distribution widths for particles NP219 and NP50 are broader than for NP13, in agreement with the slight polydispersity observed in the SEM images shown in Figure 3c.

Despite the successful dispersion of the iron oxide particles in toluene, their incorporation in bitumen results in the formation of micron-sized clusters of particles that are

homogeneously distributed throughout the bitumen matrix (Figure 5b). This effect was observed for all samples. The formation of particle clusters limits the particle surface area in contact with the bitumen and might also lead to particle interactions that affect directly the hyperthermia effect [32]. The high processing temperature of 160 °C and the high viscosity of bitumen throughout the mixing procedure likely favoured the formation of particle clusters. Nevertheless, the fact that these clusters are not larger than a few micrometres suggests that the formation of high local temperature gradients that may damage the bitumen microstructure is prevented. Such damage is more likely to occur with large aggregates such as steel wool fibres or millimetre-range particles. In addition to the larger size, steel wool fibres tend to cluster and form large lumps during mixing, which further contribute to the build-up of larger temperature gradients. Complementary rheological measurements have shown that the presence of 1 vol% of NP50 particles does not affect the mechanical response of the bitumen.

In order to study the influence of the magnetic field on the clustering of particles in bitumen, we analysed the surface of a cross-section of a magnetized sample. Under an alternating magnetic field (AMF) with amplitude of 30 mT during 20 s at 285 kHz, the nanoparticles become sufficiently mobile in the bitumen matrix to form well-defined cluster chains (Figure 5b). The cluster chains tend to align in the direction of the applied magnetic field and can span as much as 20 µm in length. Although the nanoparticles remain magnetized and clustered after removal of the AMF, the smallest size of the observed chained clusters does not exceed a few microns suggesting that possible overheating of the bituminous matrix is negligible.

Figure 5. The dispersion of oleic acid-coated nanoparticles in toluene and bitumen. (a) Typical particle size distribution of the investigated nanoparticles dispersed in toluene before mixing with bitumen. (b) CryoSEM micrograph showing the efficient dispersion of NP219 particles in bitumen before heating and the particle alignment observed in some spots of the sample after heating up to 160 °C.

4.4. Thermal response of bitumen nanocomposites under alternating magnetic field

After we successfully embedded the iron oxide nanoparticles in bitumen, the thermal response under an alternating magnetic field was evaluated. The ability of iron oxide nanoparticles to generate heat at the micro-scale in the presence of an external AMF was exploited for effectively increasing the temperature of bitumen nanocomposites at macroscopic length scales (Figure 6a-c). The temperature on the surface of such composites increased linearly with time at a rate that depends on the characteristics of the nanoparticles in the bitumen. Bitumen samples containing NP50 particles exhibited a rapid temperature increase that was four- to six- times faster than in compositions containing NP219 and NP13

powders. Such heating speed is markedly higher than with previously studied additives, such as steel wool fibres. While minutes are required to increase by 50 °C the temperature of asphalt loaded with 4 - 10 wt% mm-long wool fibres [33], bitumen containing 1 vol% of NP50 particles can heat up the surface by 50 °C in not more than 8 s under an AMF with an amplitude of 30 mT. Although this comparison is based on very different systems and AMF conditions, it provides an order of magnitude indicative of the timescales involved in each one of the self-healing approaches. It is important to mention that the AMF conditions leading to optimum heating differ markedly depending on the size and nature of the additives used for induction heating. The nanoparticles used in this work are most effectively triggered at high frequencies, whereas metallic additives previously reported in the literature respond best at low frequencies. Thus, a meaningful comparison requires the analysis of results obtained at the optimum frequency for each one of the systems.

Another advantage of nano-scale particles as compared to larger additives lies in the homogeneous temperature increase in the material. As depicted in Figure 6d, the temperature on the surface of bitumen nanocomposites subjected to an AMF increases uniformly with heating time over large areas of the sample. In order to quantify such uniform heating, we investigated the surface temperature of a bitumen sample containing 1 vol% of NP50 after 7, 9, 12 and 16 s with an AMF. For each heating time, a nearly constant temperature was observed over the exposed surface of the sample. Indeed, our results show that the temperature varied less than 3% within at least 90% of the total surface area of the sample. Considering the small thickness of the specimen, we expect the temperature to be uniform throughout the entire sample during heating. Indeed, tests in larger specimens indicate that the penetration depth of the magnetic field should reach up to about 6 centimeters ,which is in the range of the thickness of the ordinary surface course of pavements.

Figure 6. Temperature changes recorded during the application of an AMF with frequency f of 298 kHz at the surface of bitumen samples containing 1 vol% of (a) NP13 (b) NP50 and (c) NP219 particles. (d) Measured temperature distribution on the exposed surface of a bitumen sample containing 1 vol% of NP50 after being subjected for 7, 9, 12 and 16 s to an AMF with $\mu_0 H_{\max}$ of 30 mT at 298 kHz.

The heat generated through the hyperthermia effect was quantified from the temperature data shown in Figure 6a-c by calculating the power loss per gram of nanoparticles dispersed in a medium using the relation:

$$SAR_{\text{heat}} = \frac{C_p}{x} \cdot \frac{dT}{dt} \quad (1)$$

where SAR_{heat} is the specific absorption rate in W/g, C_p is the heat capacity of the medium in $J \cdot g^{-1} \cdot ^\circ C^{-1}$, x is the mass fraction of magnetic nanoparticles in the medium and $\frac{dT}{dt}$ is the

experimentally observed heating rate in $^{\circ}\text{C}\cdot\text{s}^{-1}$. Although this calculation neglects heat losses through the surface of the samples and assumes a homogeneous temperature distribution within the material, we use it here as a first approximation to enable a comparative analysis between the different investigated nanoparticles.

SAR_{heat} values determined from the heating rate measurements (Figure 6a-c) using the three types of nanoparticles are shown in Figure 7a as a function of the applied H_{max} fields. For all samples, we observed a linear increase in SAR_{heat} with the amplitude of the AMF. The most pronounced effect of the magnetic field on SAR_{heat} was obtained for the NP50 particles, followed by the NP219 and NP13 powders. The fact that the SAR_{heat} values can be changed by a factor of 7 depending on the choice of the nanoparticles opens the possibility of tuning the desired heating rate for a specific application using an external AMF source of pre-defined field strength.

In order to correlate the heating behaviour of macroscopic bitumen samples with the microscopic energy dissipation mechanism at the nanoparticle level, we investigated the magnetic hysteresis losses of the nanoparticles under conditions corresponding to those of the macroscopic heating measurements. The hysteresis loop areas from the magnetization curves increased with the applied magnetic field strength for all the investigated nanoparticles (Figure 7b). To determine the heat generated from the nanoparticles under the AMF, we measured the area of one hysteresis loop, A_{magn} , defined as:

$$A_{\text{magn}} = \int_{-H_{\text{max}}}^{H_{\text{max}}} \mu_0 M(H) dH \quad (2)$$

where M is the magnetization of the material in emu/g and $\mu_0 H$ is the magnetic field in mT [34, 35].

The NP50 particles exhibit the largest hysteresis loops within the range of applied field strengths (Figure 7b), which are at least 3-fold below the field amplitude required for

saturation of the magnetization. The magnitude of the hysteresis loop area is governed by the different mechanisms of magnetization reversal [35], which depend on the intrinsic properties of the nanoparticles and on possible magnetic interactions between the particles [16, 35]. The higher losses observed for NP50 may be related to its particle size, which lies within a range where a change from single- to multi-domain structure is expected. This should enable easier switching of the magnetic moments.

The hysteresis loop area can be used to predict the macroscopic heating response of the bitumen-nanoparticles composites. The mass-specific power loss expected from the magnetic hysteresis loop area, SAR_{magn} , is given by the following equation:

$$SAR_{\text{magn}} = A_{\text{magn}} \times f \times 10^{-3} \quad (3)$$

where SAR_{magn} is the specific absorption rate determined through the magnetic hysteresis loop area measurements in W/g, A_{magn} is the hysteresis loop area in mJ/g and f is the frequency in Hz.

As observed for the SAR_{heat} values, the power losses predicted from the magnetic hysteresis loops, SAR_{magn} , increase linearly with the applied magnetic field strength (Figure 7c). Remarkably, good agreement is found between the two independent estimates of the magnetically-driven power losses when SAR_{heat} and SAR_{magn} values are directly compared (Figure 7d). This suggests that the heating mechanism in the bitumen-nanoparticles composites is predominantly governed by magnetic hysteresis losses. For samples containing the NP50 particles, we find that the SAR_{heat} values are consistently lower than those for the SAR_{magn} estimations. This might be related to the temperature dependence of the magnetic measurements which become significant for larger hysteresis area, as is the case for NP50 particles [36]. Moreover, the fact that the heating measurements were not carried out under strict adiabatic conditions might have led to calorimetric losses that could also explain the observed mismatch between the SAR values. The use of an AC field for the heating

measurements and a DC field to obtain the hysteresis is not expected to be the origin for the mismatch since previous studies show similar hysteresis area for AC and DC loops for ferro- and ferrimagnetic additives [37]. Given that the assumptions of negligible thermal loss at the surface and homogeneous temperature distribution might not have been completely fulfilled for the system with NP50 particles, it is striking to find that our simple calculations can be a good approximation of the macroscopic heating response of the bitumen-nanoparticle composites. Overall, the power loss achieved with the NP50 particles is comparable to that reported in the literature for maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles between 10 nm and 50 nm under similar field conditions. Such values typically range from 100 to 400 W/g [for magnetite or maghemite nanoparticles](#) [27, 38-40].

Figure 7. Magnetic dependence of power losses generated by the nanoparticles in bitumen. (a) Field dependence of power losses calculated from temperature measurements (SAR_{heat}) at $f = 285$ kHz. (b) Magnetization hysteresis curves measured at 300 K for the investigated iron oxide nanoparticles over magnetic fields ranging from -30 to 30 mT, -22.6 to 22.6 mT and -15

to 15 mT. (c) Field dependence of power losses calculated from magnetic hysteresis curves (SAR_{magn}) at $f = 285$ kHz. (d) Relationship between power losses calculated from temperature measurements (SAR_{heat}) and power losses estimated from magnetization hysteresis curves (SAR_{magn}) for three different maximum field amplitudes (30 mT, 22.6 mT and 15 mT).

4.5. Crack healing assessment through Vickers indentation

In order to demonstrate the crack-healing potential of bituminous materials using magnetic nanoparticles through hyperthermia, we designed an experimental system that allows us to create well-defined artificial cracks and to follow their morphological changes during magnetically-induced heating (Figure 8a). Our results show that artificial micro-cracks generated at -20°C by Vickers indentation can be closed within less than 10 s when bitumen nanocomposites with highly-dissipative NP50 particles are exposed to an AMF (Figure 8b).

The temperature increase during the healing process leads to significant changes in the crack morphology, as illustrated in Figure 8c for the system containing NP50 particles. From 0°C until approximately 25°C the crack remains sharp due to the absence of flow in this type of bitumen for this temperature range (Stage A). At about 25°C the bitumen melts and eventually flows, enabling high capillary forces acting on strongly curved surfaces to eventually fill up the cracks produced by indentation. This leads to a clear change in the crack morphology, which is readily evident by the wider projected opening of the crack when observed from the top (Stage B in Figure 8c). Eventually, cracks are gradually filled up with adjacent bitumen material (Stage C) until complete closure (Stage D). Similar behaviour is observed for cracks in composites containing NP13 and NP219 particles, albeit at a slower rate. This indicates that crack healing requires an increase in temperature that is sufficient to fluidize the bitumen and enable capillary-driven flow into the cracks.

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485 **Figure 8.** Crack closure behaviour of bitumen composites containing iron oxide nanoparticles
 486 when exposed to an alternating magnetic field. (a) Scheme illustrating the crack produced on
 487 the surface of a bitumen sample through Vickers indentation at -20 °C. (b) Temperature
 488 change of bitumen samples containing 1 vol% of NP50 nanoparticles during the magnetically-
 489 triggered healing process using an AMF with $\mu_0 H_{\max} = 30$ mT and $f = 298$ kHz. (c) Crack
 490 morphologies during the magnetically-triggered healing process. Purple arrows show the
 491 initial location of cracks. The difference in contrast between pictures is due to presence of
 492 water in the initial sample, which evaporated while the temperature was increased.

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7. Conclusions

We developed a method to rapidly heat bitumen by stimulating a low volume fraction of pre-embedded iron oxide nanoparticles using an external alternating magnetic field. The high thermal response achieved through this hyperthermia effect enables a fast decrease of the bitumen viscosity, allowing for effective closing of micro-cracks in bituminous materials. Besides their remarkable magnetic properties, the homogeneous spatial distribution of the nanoparticles achieved by adsorbing oleic acid on their surface provides a convenient path to generate a uniform temperature increase throughout the material. As an example, we exploited the magnetic properties of three different types of iron oxide nanoparticles differing in size and composition to generate heat in bitumen. For all studied nanoparticles, a direct correlation was observed between the energy dissipation measured from magnetization curves and the power loss estimated from macroscopic heating experiments on nanoparticle-bitumen composites. Because nanoparticles with average crystallite size of 50 nm exhibit the highest magnetic hysteresis losses, this powder is the most efficient in quickly increasing the temperature of the bitumen specimens. Finally, we showed that radial cracks generated by Vickers indentation of bitumen samples at low temperature could be healed within only a few seconds using the proposed hyperthermia effect. Our strategy to rapidly decrease the viscosity of a viscoelastic binder such as bitumen by means of pre-embedded iron oxide nanoparticles can be considered a major step towards the ultimate goal of providing an efficient on-demand crack healing method for bituminous materials. Since this research is only focused on proving the principle, upscaling and the simplification of the mixing procedure should be addressed in future studies.

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