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Iron oxide nanoparticles for magnetically-triggered healing of bituminous materials

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HIGHLIGHTS

- Iron oxide nanoparticles can rapidly heat bitumen through magnetic hyperthermia.
- Heating generated by the nanoparticles decreases the bitumen viscosity.
- Low bitumen viscosities allow for effective closure of micro-cracks.
- A nanoparticle crystallite size of 50 nm exhibits highest magnetic hysteresis losses.
- High hysteresis losses enables healing within only a few seconds.

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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-Fe_2O_3 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.

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 fibres.

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

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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 fibres added to asphalt concrete to promote local heating in the presence of an alternating magnetic field. Depending on the concentration of fibres, 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 millimetre-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 (γ-Fe_2O_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 (Fig. 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.

2. Materials and methods

2.1. Materials

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

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

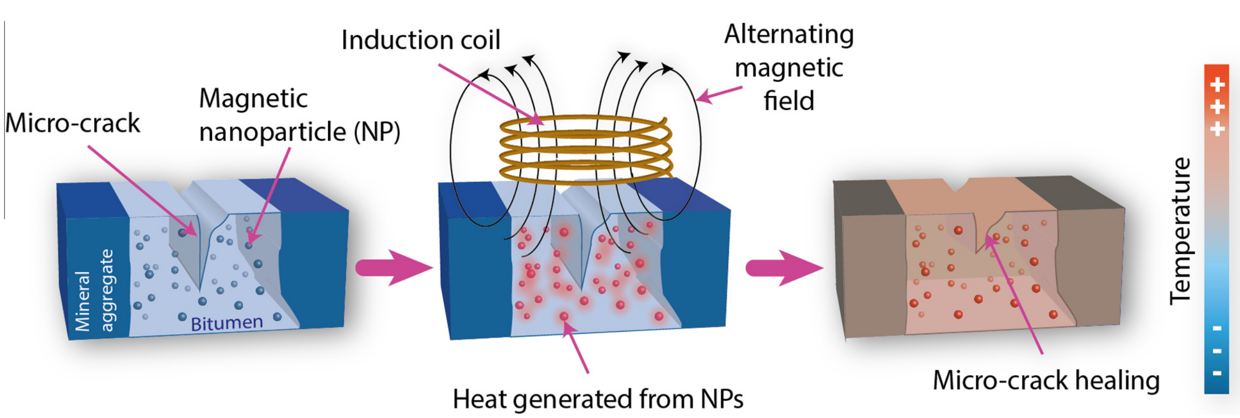

Fig. 1. Schematics illustrating the proposed crack healing method for bituminous materials using magnetic nanoparticles embedded in bitumen.