

H. Ajam,¹ P. Lastra-González,² B. Gómez-Meijide,¹ G. Airey,³ and A. Garcia¹

Self-Healing of Dense Asphalt Concrete by Two Different Approaches: Electromagnetic Induction and Infrared Radiation

Reference

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ABSTRACT

Self-healing of cracks in asphalt mixtures is a phenomenon that can be accelerated by reducing the viscosity of bitumen as it increases the capillarity flow through the cracks. One method to achieve this is by increasing temperature, which also produces a thermal expansion that contributes to the circulation of the bitumen through cracks. In the present paper, the healing performance of asphalt mixture heated using infrared heating to simulate the natural solar radiation, and induction heating, a new method to increase the temperature of asphalt pavements, were compared in terms of time and healing temperature. Healing was defined as the relationship between the 3-point bending strength of an asphalt beam before and after healing. The results show that both methods reach similar and satisfactory healing ratios at around 90 %. However, induction heating is more energy efficient because the effect is concentrated on the binder, instead of heating the whole mix. This can be translated into much shorter heating times to reach the same healing level. Finally, an optimum radiation energy was found, after which higher amounts of infrared radiation damage the properties of the healed material.


Keywords

self-healing, induction heating, infrared radiation, asphalt materials

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¹ Nottingham Transportation Engineering Centre [NTEC], Dept. of Civil Engineering, Univ. of Nottingham, Nottingham NG7 2RD, UK

² GITECO Research Group, Universidad de Cantabria. E.T.S. Ingenieros de Caminos, Canales y Puertos de Santander, Av. de los Castros s/n, 39005 Santander, Spain

³ Nottingham Transportation Engineering Centre [NTEC], Dept. of Civil Engineering, Univ. of Nottingham, Nottingham NG7 2RD, UK (Corresponding author), e-mail: gordon.airey@nottingham.ac.uk
 <http://orcid.org/0000-0002-2891-2517>

Introduction

Aggregate particles in asphalt materials are bonded together by asphalt bitumen, a complex visco-elasto-plastic liquid whose rheological properties, including the viscosity, depend to a great degree on its temperature [1]. When the temperature exceeds a critical value, so-called Newtonian temperature, bitumen starts flowing throughout the pores and capillaries of the material in an accelerated manner [2]. Under the same principle, micro-cracks produced in asphalt roads by traffic, weather exposure, etc. [3] can be quickly healed by simply increasing the temperature above the Newtonian temperature of the material [4], being the process more effective as the temperature increases [5].

To put this into practice, one of the most promising approaches is using induction heating technology [6,7], which involves the previous addition of electrically conductive fibers [8] or powder [9] into the asphalt mixture. When a given road contains these kinds of particles, they can be heated by simply applying an external varying electromagnetic field, which induces micro-currents and heats the particles through the Joule's effect [10]. The healing level that can be achieved by this method depends on the diameter, material composition, and length of the fibers [11]; it can also be predicted through the model proposed by Garcia et al. [12] based on the equilibrium of surface tension, gravity, and dissipation forces caused by the movement of bitumen against the walls of the crack.

It is also known that, besides the temperature, asphalt self-healing is mainly affected by intrinsic properties of the material, such as the viscosity [13] and chemical composition [14] of bitumen, type of aggregates [15], and compaction level of the mix [16]. However, roads placed in hot environments that are exposed for long times to temperatures higher than 70°C [17] are not perpetually healed. Instead, the cracks form and grow until some form of maintenance is required.

Throughout the present investigation, a comparison between the healing dynamics produced by electromagnetic induction and solar radiation (simulated by means of infrared lamps) was carried out to find answers to these questions and to

assess the effectiveness and energy efficiency of induction heating compared to the natural process of solar radiation. To obtain this, dense asphalt beams were manufactured containing steel grit as healing agents, and 3-point bending strength was tested before and after applying either an induction or infrared treatment on cracked samples. To compare both methods in a fair way, the concept of healing energy described by Gómez-Meijide et al. [18] was applied. Finally, the rheology of bitumen samples subjected to different radiation times was assessed to see to what extent the material aging affects the self-healing properties of asphalt materials.

Materials and Methods

DESCRIPTION OF MATERIALS

The asphalt samples used during the present investigation for the healing tests were produced with continuous and dense aggregate gradation with a target void content of 4.5 % (Fig. 1). The natural aggregate was limestone, whereas the conductive component was a metal grit with uniformed size of 1 mm. The latter was introduced into the mix by replacing part of the natural aggregate in this fraction. The volumetric content of metal grit in the mix was fixed at 4 % (11.2 % by weight). The selected binder was a 40/60 pen and the content was 4.7 %.

TEST SPECIMEN PREPARATION

The gradation was batched by blending samples of limestone with different gradations together with the metal grit. The asphalt concrete was mixed in a laboratory mixer at 160°C for 2 min, and then compacted as slabs by means of roller compactor until it reached the target void content of 4.5 %. The dimensions of the slabs were 310 × 310 × 50 mm³. Then, the slabs were cut by a radial saw blade suitable for concrete and stone materials, obtaining eight 150 × 70 × 50 mm³ prismatic samples from each slab. To see how this process affected the samples, the air void content was measured for a series of six samples, obtaining an average value of 4.70 % and a standard deviation of 0.56 %. Finally, a notch was cut at the midpoint from the central axis of the beams, with a thickness of about 2 mm and a depth of about 10 mm (Fig. 2).

TESTING OF ASPHALT SELF-HEALING

Although other possible characteristics in the non-destructive zone (e.g., recovery of stiffness or viscosity) were considered to study the self-healing capacity of the material, the present study was eventually carried out through the strength recovery on complete and brittle cracks (splitting the samples in two halves) to tests them under the most similar conditions possible (same crack area, position, etc.).

The samples were first tested under 3-point bending at -20°C to obtain a brittle and clean crack, while minimizing the effect of permanent deformations. The tests were carried out

FIG. 1 Aggregate gradation used for the present investigation.

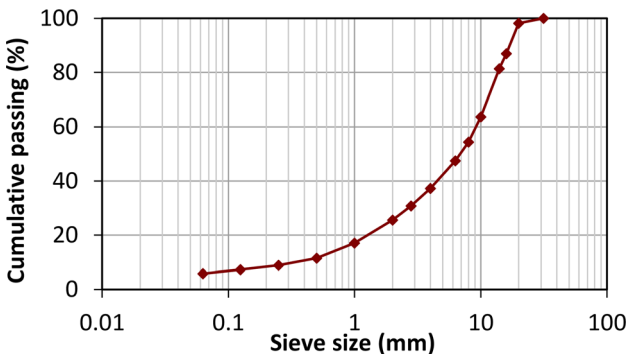
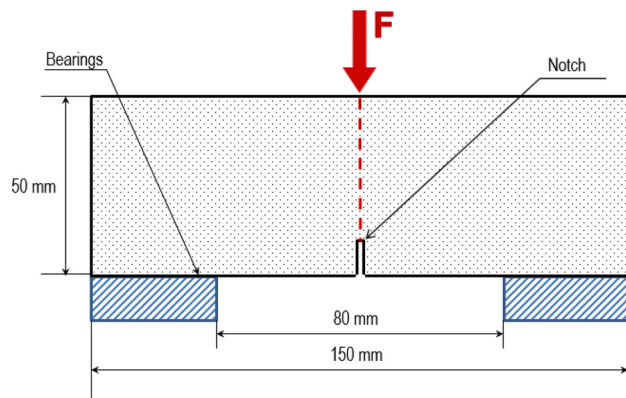


FIG. 2 Design of the 3-point bending test to break the samples.

under strain-controlled conditions, with an increasing load ramp at a deformation rate of 0.5 mm/min. During each test, a clear crack of approximately 200 μm width was produced, crossing vertically through the samples, from the notch to the load application point (**Fig. 2**).

Once the crack was produced and the sample was split in two different halves, they were put together again and healed by means of one of the following methods:

- (1) Induction heating: The samples were exposed to induction heating for 19 different times between 15 s and 240 s. No times longer than 240 s were used as the bitumen reached its burning temperature. The distance from the upper side of the sample to the coil was 1.5 cm, the current 80 A, frequency 348 kHz, and the power used 2800 W (**Fig. 3**, left).
- (2) Infrared radiation: To simulate the effect of the sun under controlled and steady conditions of temperature and radiation level over the whole testing time, the samples were placed under four infrared lamps at a distance of 30 cm. The samples were embedded in white porous sand (Catsan cat litter) with the exception of the upper

side to prevent them receiving infrared radiation from any other side and to avoid the deformation caused by high temperatures (**Fig. 3**, right). The samples were exposed to infrared heating for 42 different times between 5 min and 5760 min (96 h).

The temperature of the samples was constantly monitored by using an infrared camera for asphalt induction heating and thermocouples installed on the top and the bottom of the test specimens in the case of infrared heating.

Once the healing process was finished, the samples were cooled at -20°C and tested again under 3-point bending. The healing ratio (S) of asphalt samples was defined as the relationship between the ultimate force resisted by the test specimens during a 3-point bending test before being split into two halves, F_b , and the ultimate force measured for the same specimen and under the same conditions but when repeating the test after the healing process F_b :

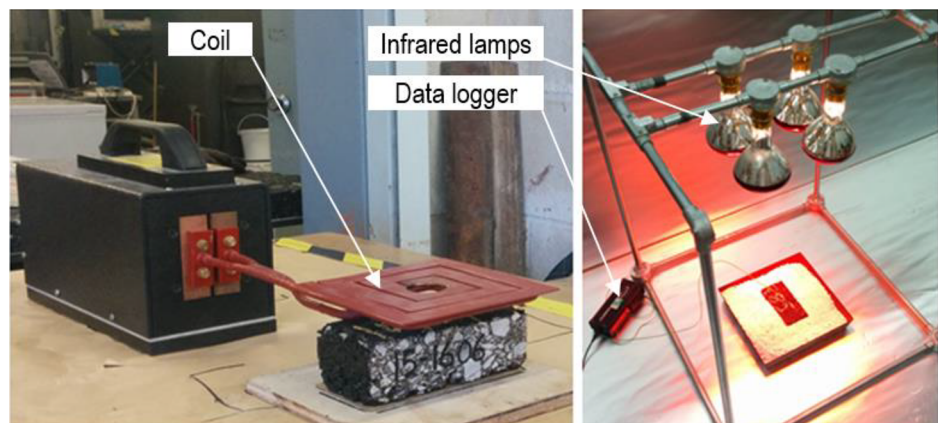
$$S(\tau) = \frac{F_b(\tau)}{F_i} \quad (1)$$

BITUMEN RHEOLOGY

Bitumen aging produced during the healing processes was studied by recovering, by rotary evaporator, the bitumen from five compacted samples of dense asphalt mix exposed to infrared radiation for 0 min, 200 min, 1 day, 2 days, and 4 days. The rheology of bitumen was examined using a dynamic shear rheometer (Bohlin Gemini HR nano), configured with 25-mm-diameter parallel plates with a gap between them of 1 mm. The range of oscillatory frequencies was between 0.1 Hz and 10 Hz and temperatures between 30°C and 70°C (at 5°C intervals). Constant strain of 1 % was fixed to ensure the linear viscoelastic behavior of the samples; complex viscosity (η^*) and complex modulus (G^*) were obtained for each frequency and temperature.

FIG. 3

Healing procedures by induction heating (left) and infrared radiation (right).



The corresponding curves of G^* versus frequency, obtained at different temperatures can be merged into a single smooth function by applying the principle of time-temperature superposition [19]. In the present investigation, the resulting master curves were constructed by fixing a reference temperature of 30°C and shifting the rest of the data by means of a shift factor. As a result, the complex modulus was mathematically modeled as the following sigmoidal function [20]:

$$\log|G^*| = \delta + \frac{\alpha}{1 + e^{\beta + \gamma(\log t_r)}} \quad (2)$$

where:

t_r = the reduced time of loading at the reference temperature,

δ = the minimum value of G^* ,

the sum $\delta + \alpha$ = the maximum value of G^* , and

the parameters β and γ = the shape of the sigmoidal function.

Data shifting is made by using a shift factor, whose form for a certain temperature of interest (T) is:

$$a(t) = \frac{t}{t_r} \quad (3)$$

where:

t = the time of loading at the desired temperature, and

t_r = the reduced time of loading at the reference temperature.

Theoretical Framework

Asphalt self-healing does not happen only during the heating periods, but also during cooling [2]. The analytical relationship between time and temperature can be obtained for heating and cooling stages by integrating Newton's law of heat transfer:

$$mc \frac{dT}{dt} = -kA(T - T_c) \quad (4)$$

where:

k = a heat transfer coefficient (s^{-1}), which depends of the area of the beams exposed to the environment, mass of the test samples, and specific heat capacity,

T (K) = the temperature of the sample,

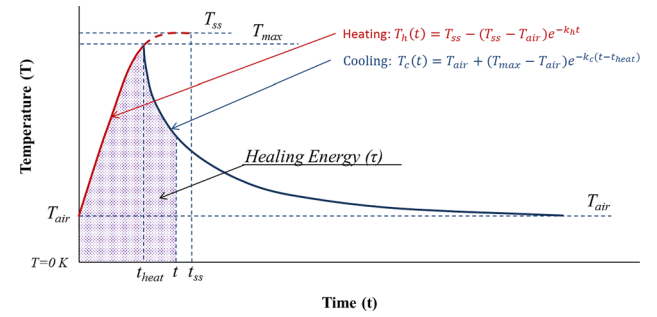
T_c (K) = a fixed temperature to which the sample temperature tends and that can be the ambient temperature (T_{air}) during cooling or the steady-state temperature reached by the sample during heating (T_{ss}),

m (g) = the mass of the sample, and

c (J/g °C) = the specific heat.

In Ref 18, the expressions of both heating and cooling curves were obtained (Fig. 4). In addition, the concept of healing energy was also developed in Ref 18 as the total area below the

FIG. 4 Healing energy as the area below the heating and cooling curves.



curves. Thus, considering a cooling process of 4 h at ambient temperature, this parameter (in K·s) can be calculated as:

$$\tau(t) = \tau_h(t_{heat}) + \tau_c(4h) \quad (5)$$

where:

$$\tau_h(t) = T_{ss} + \frac{T_{ss} - T_{air}}{k_h} (e^{-k_h t} - 1); \quad t < t_{heat} \quad (6)$$

$$\tau_c(t) = T_{air} \cdot (t - t_{heat}) + \frac{T_{max} - T_{air}}{k_c} (1 - e^{-k_c(t-t_{heat})}); \quad t > t_{heat} \quad (7)$$

where:

T_{air} = the ambient temperature,

T_{ss} = the steady-state temperature reached by asphalt mixture during heating, and

t_{heat} = the heating time of the test sample.

As the heating and cooling rates may differ during the heating and cooling periods, the heat transfer coefficient has been noted as k_h for the heating period and k_c for the cooling period. Both can be obtained by fitting the experimental temperature-time curves to these equations.

In addition, in Ref 2, a predictive model for the healing of asphalt materials was defined as follows:

$$S(\tau) = \frac{C_1}{F_0} \cdot e^{-D\tau} \left(-1 + e^{\frac{D\tau}{2}} \right)^2 \quad (8)$$

where:

$S(\tau)$ = the healing ratio or percentage of recovered strength after the healing treatment (%),

F_0 = the initial 3-point bending strength of the test samples (kN),

τ = the healing energy explained above (K·s), and

D and C_1 = parameters that can be calculated as:

$$D = \frac{\rho g r}{\beta} \quad (9)$$

$$C_1 = 8 \frac{\sigma_u \cdot C}{L \cdot H} \quad (10)$$

FIG. 5

Maximum temperature (°C) reached by the samples after different healing times.

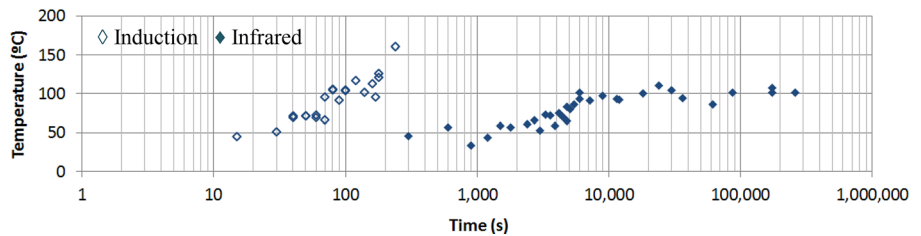
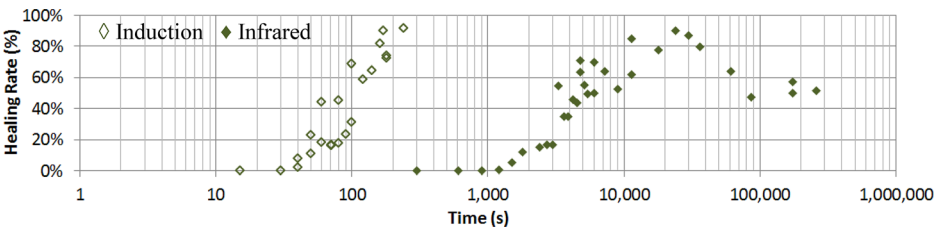


FIG. 7
Relationship between healing ratios (%) and healing time with different methods.



increases can always be translated into healing improvements. However, maintaining a steady temperature for longer times produces a detrimental effect on the healing. This behavior explains why roads exposed almost every day to sunlight and high temperatures (for instance, in desert climates) are not perpetually healed. Instead, there exists an optimal radiation point for asphalt self-healing. Once overcome, further radiation produces nothing but damage in the material.

To better understand this process, the input temperature and time were translated into healing energy (Eqs 5–7) and the healing model described in Eqs 8 to 10 was fitted to the experimental data. As can be seen in Fig. 8, the model provides an excellent fit during the increasing stage of the curves but it cannot predict the decreasing part. Because this model is based on equilibrium of surface tension, hydrostatic forces, and energy dissipation caused by friction, there must be at least another factor, different from these that affects asphalt self-healing.

In Fig. 8, it can also be seen that in terms of healing energy, a critical value exists, common for both methods that triggers the healing processes. However, after this point, the induction heating again resulted in a more efficient method, because it reaches higher healing levels with less energy.

The authors have found that a reason for the decrease of healing levels after reaching the steady-state temperature might be because of the aging of bitumen. To examine this, bitumen was extracted from test specimens exposed to infrared after 0 min, 200 min, 1 day, 2 days, and 4 days, and the rheology

and flow behavior index (n) (see Ref. [21]) were compared. The distance between the sample and the infrared lamps was set at 30 cm.

In previous research [11], it was described that the healing processes can only occur as long as the temperature of the material remains higher than a certain threshold defined as the Newtonian temperature of bitumen (T_{newt}). This critical temperature can be experimentally obtained through rheological tests and taking into account the following power law relationship [22]:

$$\eta^* = m \cdot |\omega|^{n-1} \tag{11}$$

where:

- ω = the frequency,
- η^* = the complex viscosity, and
- m and n = fitting parameters (n is known as the flow behavior index).

According to Ref 21, the behavior of the bitumen can be considered near-Newtonian when $0.9 \leq n < 1$. The correlation between n and the temperature can be seen in Fig. 9 and the master curves in Fig. 10 for samples of bitumen extracted from dense asphalt specimens subjected to infrared radiation of lamps situated at 30 cm above the samples and over periods of 0 min (control), 200 min (optimum healing results for dense mixtures at 30 cm) and 1, 2, and 4 days to analyze samples associated with the decreasing part of the healing curve (as seen in Fig. 8).

FIG. 8
Fitting of healing model to experimental data of healing by induction and infrared heating.

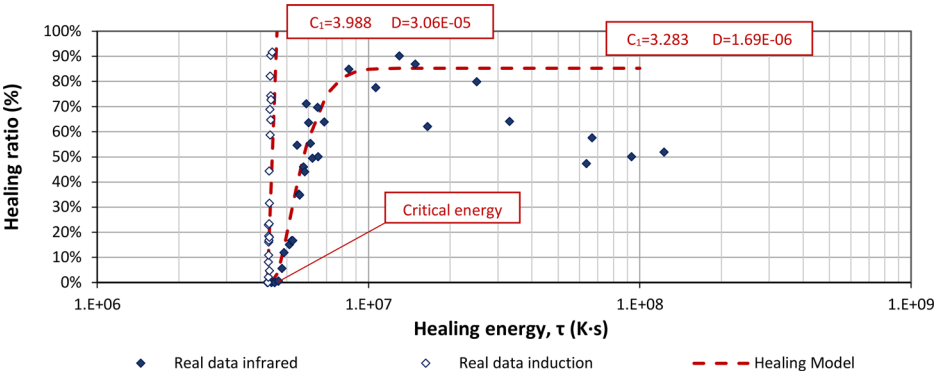
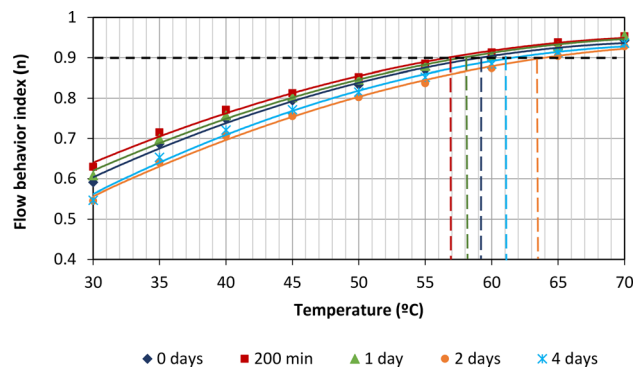


FIG. 9 Flow behavior index (n) of bitumen recovered from samples subjected to infrared radiation over different periods of time.



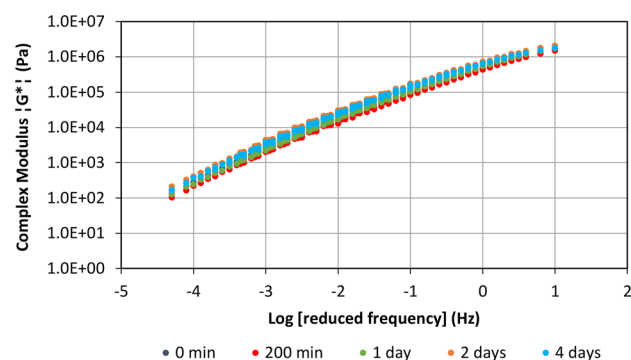
The results show that the rheological behavior of all the samples is very similar, not following a clear trend with the variations in the radiation time, and demonstrating values of Newtonian temperature that are significantly similar. All the T_{newt} -values ranked between 56.5°C and 64.0°C (average 59.8°C). Hence, although long-term factors that can affect the healing, such as traffic or aging in desert climates (which might result in stiffening of asphalt and increased cracking potential), the change of rheological properties caused by the infrared radiation cannot be considered as a substantial reason to explain the decreasing results obtained for the tested radiation times.

Conclusions

In the present experimental investigation, a comparison between two different methods to induce self-healing in asphalt mixture, induction, and infrared heating was performed. Furthermore, energy and healing models from previous research and based on surface tension, pressure, and energy dissipation forces because of friction were used to interpret the results. From this study, the following conclusions could be extracted:

- Induction heating applies the heat directly into the bitumen. Therefore, it is more efficient than infrared radiation and the healing times are much shorter.

FIG. 10 Master curves of bitumen recovered from samples subjected to infrared radiation over different periods of time.



- When applying infrared radiation, the temperature increased only until steady-state temperature (approximately 100°C) was reached. However, with induction heating, the temperature never stopped increasing with the heating time, reaching temperatures close to the flash-point of bitumen.
- Both methods produced similar and satisfactory healing ratios up to 90 %. However, the induction heating needed significantly less energy for self-healing.
- There is an optimal infrared radiation energy for asphalt self-healing. Once this value is exceeded, further infrared radiation damages the material. This explains why cracks that develop in roads of very warm and sunny environments do not heal during the warm seasons.
- With infrared heating, the healing level of cracks increases when they are subjected to increasing differential temperatures. However, new damage is produced when they are subjected to steady temperatures for long time periods. Because a steady-state temperature was not reached when using induction heating, the healing ratios never stopped increasing.
- The aging of the bitumen during the heating process did not result in a feasible explanation for this behavior. Based on the theoretical background considered for the present research, there must be at least another factor, different from surface tension, hydrostatic forces and energy dissipation because of friction that affects asphalt self-healing in a significant way.

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References

- [1] Read, J. and Whiteoak, D., *The Shell Bitumen Handbook*, Thomas Telford, London, 2003.

- [2] Garcia, A., Bueno, M., Norambuena-Contreras, J., and Partl, M. N., "Induction Healing of Dense Asphalt Concrete," *Constr. Build. Mater.*, Vol. 49, 2013, pp. 1–7, <http://dx.doi.org/10.1016/j.conbuildmat.2013.07.105>
- [3] Menozzi, A., Garcia, A., Partl, M. N., Tebaldi, G., and Schuetz, P., "Induction Healing of Fatigue Damage in Asphalt Test Samples," *Constr. Build. Mater.*, Vol. 74, 2015, pp. 162–168, <http://dx.doi.org/10.1016/j.conbuildmat.2014.10.034>
- [4] Garcia, A., Bueno, M., Norambuena-Contreras, J., and Partl, M. N., "Single and Multiple Healing of Porous and Dense Asphalt Concrete," *J. Intell. Mater. Syst. Struct.*, Vol. 26, No. 4, 2015, pp. 425–433, <http://dx.doi.org/10.1177/1045389X14529029>
- [5] Dai, Q., Wang, Z., and Mohd Hasan, M. R., "Investigation of Induction Healing Effects on Electrically Conductive Asphalt Mastic and Asphalt Concrete Beams Through Fracture-Healing Tests," *Constr. Build. Mater.*, Vol. 49, 2013, pp. 729–737, <http://dx.doi.org/10.1016/j.conbuildmat.2013.08.089>
- [6] Ayar, P., Moreno-Navarro, F., and Rubio-Gamez, M. C., "The Healing Capability of Asphalt Pavements: A State of the Art Review," *J. Clean. Prod.*, Vol. 113, 2016, pp. 28–40, <http://dx.doi.org/10.1016/j.jclepro.2015.12.034>
- [7] Garcia, A., Schlangen, E., and van de Ven, M., "Two Ways of Closing Cracks on Asphalt Concrete Pavements: Microcapsules and Induction Heating," *Key Eng. Mater.*, Vols. 417–418, 2010, pp. 573–576.
- [8] Garcia, A., Bueno, M., Norambuena-Contreras, J., Partl, M. N., and Schuetz, P., "Uniformity and Mechanical Properties of Dense Asphalt Concrete With Steel Wool Fibres," *Constr. Build. Mater.*, Vol. 43, 2013, pp. 107–117, <http://dx.doi.org/10.1016/j.conbuildmat.2013.01.030>
- [9] Apostolidis, P., Liu, X., Scarpas, A., Kasbergen, C., and van de Ven, M. F. C., "Advanced Evaluation of Asphalt Mortar for Induction Healing Purposes," *Constr. Build. Mater.*, Vol. 126, 2016, pp. 9–25, <http://dx.doi.org/10.1016/j.conbuildmat.2016.09.011>
- [10] Liu, Q., Garcia, A., Schlangen, E., and van de Ven, M., "Induction Healing of Asphalt Mastic and Porous Asphalt Concrete," *Constr. Build. Mater.*, Vol. 25, No. 9, 2011, pp. 3746–3752, <http://dx.doi.org/10.1016/j.conbuildmat.2011.04.016>
- [11] Garcia, A., "Self-Healing of Open Cracks in Asphalt Mastic," *Fuel*, Vol. 93, 2012, pp. 264–272, <http://dx.doi.org/10.1016/j.fuel.2011.09.009>
- [12] Garcia, A., Schlangen, E., van de Ven, M., and Liu, Q., "A Simple Model to Define Induction Heating in Asphalt Mastic," *Constr. Build. Mater.*, Vol. 31, 2012, pp. 38–46, <http://dx.doi.org/10.1016/j.conbuildmat.2011.12.046>
- [13] Pauli, A. T., "Chemomechanics of Damage Accumulation and Damage-Recovery Healing in Bituminous Asphalt Binders," Ph.D. thesis, TU Delft, Delft, Netherlands, 2014.
- [14] Qiu, J., "Self-Healing of Asphalt Mixtures, Towards a Better Understanding," Ph.D. thesis, TU Delft, Delft, Netherlands, 2012.
- [15] Apeagyei, A. K., Grenfell, J. R. A., and Airey, G. D., "Observation of Reversible Moisture Damage in Asphalt Mixtures," *Constr. Build. Mater.*, Vol. 60, 2014, pp. 73–80, <http://dx.doi.org/10.1016/j.conbuildmat.2014.02.033>
- [16] Garcia, A., Schlangen, E., van de Ven, M., and van Vliet, D., "Induction Heating of Mastic Containing Conductive Fibers and Fillers," *Mater. Struct.*, Vol. 44, No. 2, 2011, pp. 499–508, <http://dx.doi.org/10.1617/s11527-010-9644-2>
- [17] Ongel, A. and Harvey, J. T., "Analysis of 30 Years of Pavement Temperatures Using the Enhanced Integrated Climate Model (EICM)," *UCPRC-RR-2004/05*, Pavement Research Center, Institute of Transportation Studies, University of California Berkeley, University of California Davis, Berkeley/Davis, CA.
- [18] Gómez-Meijide, B., Ajam, H., Lastra-González, P., and Garcia, A., "Effect of Air Voids Content on Asphalt Self-Healing via Induction and Infrared Heating," *Constr. Build. Mater.*, Vol. 126, 2016, pp. 957–966, <http://dx.doi.org/10.1016/j.conbuildmat.2016.09.115>
- [19] National Center for Asphalt Technology at Auburn University (NCAT), "Hot Mix Asphalt Materials," *Mixture Design and Construction*, 3rd ed., Lanham, MD, NAPA Research and Education Foundation, 2009.
- [20] Witczak, M. W. and Bari, J., "Development of a Master Curve (E^*) Database for Lime Modified Asphaltic Mixtures," *Research Project*, Arizona State University, Tempe, AZ, 2004.
- [21] Heyes, D. M., Mitchell, P. J., and Visscher, P. B., "Viscoelasticity and Near-Newtonian Behaviour of Concentrated Dispersions by Brownian Dynamics Simulations," *Trends Colloid Interf. Sci.*, Vol. 97, 1994, pp. 179–182, <http://dx.doi.org/10.1007/bfb0115161>
- [22] Sung, Y. T., Kum, C. K., Lee, H. S., Kim, J. S., Yoon, H. G., and Kim, W. N., "Effects of Crystallinity and Crosslinking on the Thermal and Rheological Properties of Ethylene Vinyl Acetate Copolymer," *Polymer*, Vol. 46, No. 25, 2005, pp. 11844–11848, <http://dx.doi.org/10.1016/j.polymer.2005.09.080>