Self-healing of asphalt mixes, containing conductive modified bitumen, using microwave heating

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ABSTRACT

In this paper we propose the use of carbon nanotubes as new additives for bituminous materials suitable for microwave radiation heating. As self-healing rates of asphalt pavement increase with temperature, these microwave absorbing materials facilitate crack healing.
Different modified bitumens, were prepared using high shearing rates to ensure adequate dispersion. Carbon nanotube content and irradiation time were optimized measuring the temperature-time profile for a selected set of specimens and an exhaustive study of the rheological properties of the modified bitumens was carried out.
Different tests performed both on the modified binders and on asphalt mixes using microwave irradiation confirm that high healing rates are obtained with low additive contents.
Results showed in this paper have been obtained in the development of the MAMCE project, granted by the Spanish "Ministerio de Economía y Competitividad", call "Innpacto 2011".

Keywords: Asphalt, Durability, Healing, Maintenance

1. INTRODUCTION

Carbon nanotubes are allotropes of carbon, such as diamond, graphite or fullerenes. Its structure can be considered from a graphene sheet rolled on itself, and depending on the degree of rolling, and how the original sheet is formed can result nanotubes with different diameters and internal geometry. Nanotubes are categorized as single-walled (SWNTs) when formed by a unique tube and multi-walled (MWNTs) when formed by multiple concentric tubes. This structure confers electrical, mechanical and thermal properties to these materials that make them very valuable for different technological applications [1].

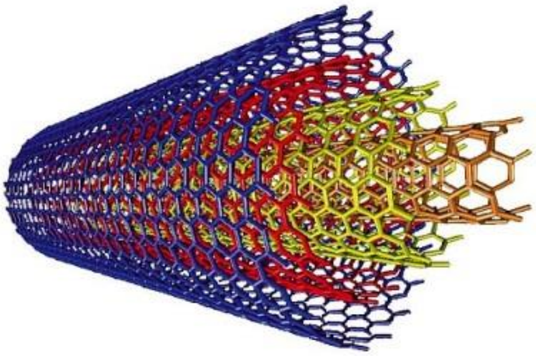


Figure 1: Multi-Walled Nanotube Structure

So far their study as possible paving materials has focused on improving the mechanical properties of the binders and asphalt mixes, but in this project we wanted to take advantage of other properties that these materials can bring to the road to find new areas of application.

Specifically, in this article we expose how the modification of bitumen with MWNTs turns them into electrical semiconductor materials which, by applying a microwave source, [2] can be heated in a controlled, rapid and homogeneous way.

It is well known that the bitumen has a great self-healing capacity because of their chemical complexity, allowing repairing the damage that occurs during their service and restoring functionality. However, under usual road conditions this ability to self-repair proves to be insufficient, and damage will accumulate until the material is fatigued. [3,4]

In recent years there has been great interest in developing systems that accelerate and improve the intrinsic self-healing ability of the bitumen in order to increase the durability of roads and controlled asphalt heating is one of the most used approaches. [5]

The use of this property allows us to heat only the binder, so that we could tune its temperature, saving energy and preventing accelerated aging.

In short, if we have an asphalt mix made with a binder with semiconducting properties, capable of generating heat in a controlled way when absorbing microwave radiation, we can accelerate its own self-healing process repairing cracks and extending its life.

2. BITUMEN MODIFICATION WITH CARBON NANOTUBES

In the study of the production of dispersions of nanotubes in bitumen different variables (temperature manufacturing, speed and time of agitation and content and type of nanotubes) were taken into account.

The initial tests were performed over a B 150/200 bitumen with MWNTs contents between 0.1 and 5%, and allow us to establish the blending conditions that would ensure a homogeneous dispersion of the nanotubes in the bituminous matrix, with total absence of aggregates, which is essential to achieve the electrical properties we were looking for. [6]

Rheological results (Figure 2) show small variations in the properties at temperatures studied in the DSR, which becomes in a very large increase in viscosity at higher temperatures, leading to materials with very high viscosities.

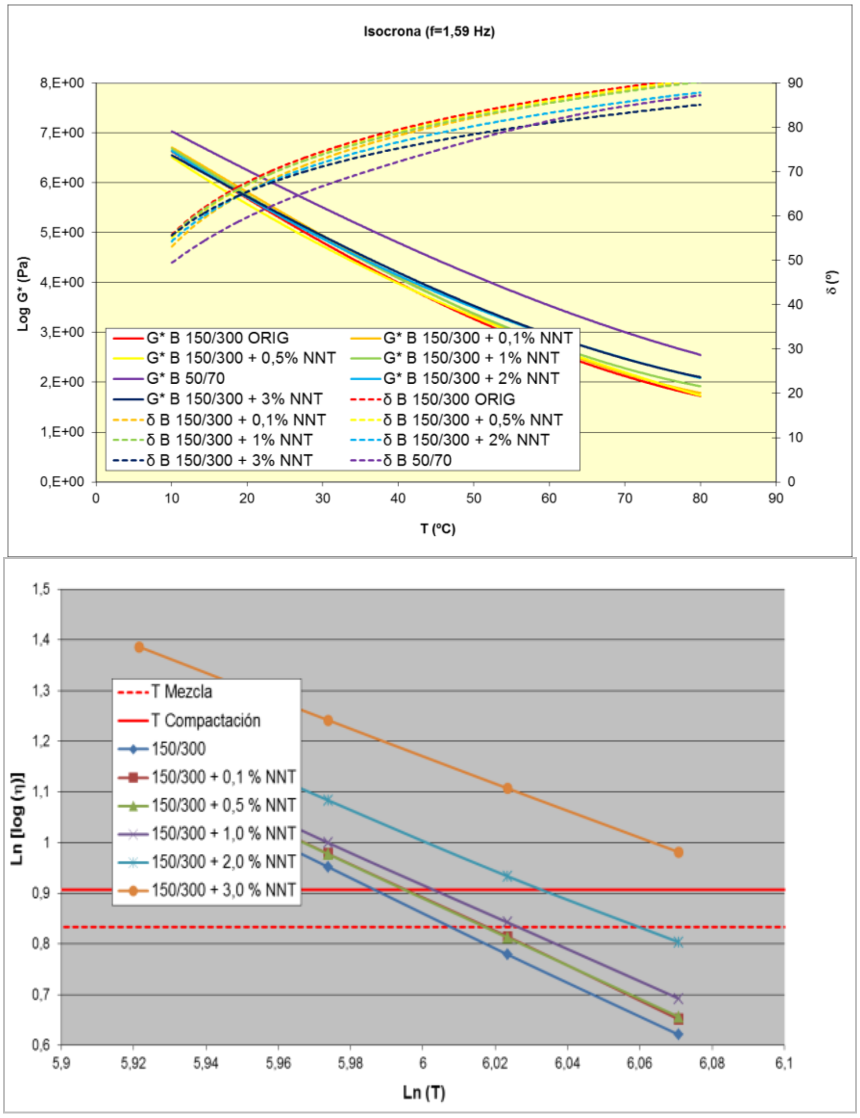


Figure 2: Rheological properties of MWNTs dispersions in bitumen.

A scanning electron microscope (SEM) was used to verify that a good dispersion of nanotubes was obtained. Images obtained on the above mixtures (Figure 3) show a good dispersion of carbon nanotubes in the bituminous matrix used where no aggregations but isolated nanotubes were observed.

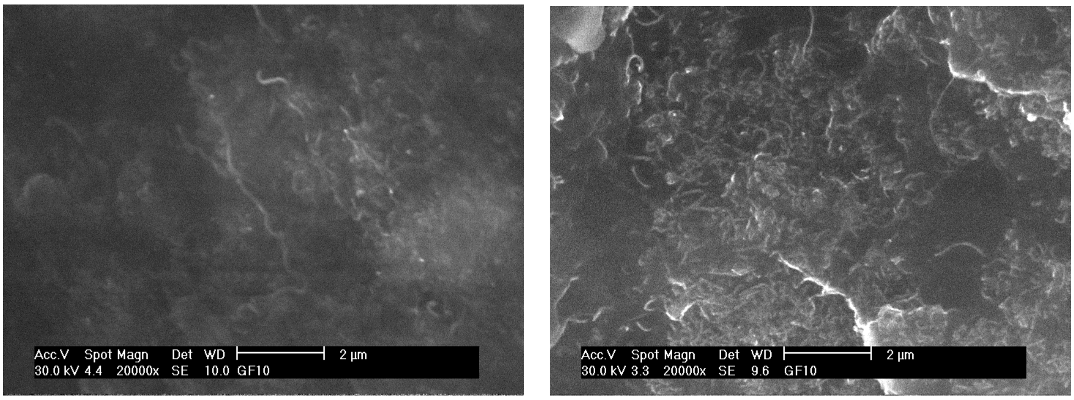


Figure 3: SEM pictures of MWNTs dispersions in bitumen.

Once the conditions of nanotubes dispersion were established, the next step was the development of MWNTs modified bitumen suitable to be used in asphalt mixes. Different percentages of bitumen B 50/70 and B 70/100 were combined with different rates (1, 2 and 3%) of two types of MWNTs (G and B). To characterize the samples both, empirical tests of consistency and rheological tests were used. Resistance to aging of these materials was also studied using accelerated aging tests (RTFOT) and subsequent evaluation of the evolution of their properties.

In Figure 4 the results obtained for multiple batches are presented. As expected, for the original binder, the penetration values decrease when the nanotubes content increases while the softening point increase, although, as already observed in previous studies, the changes are lower than expected.

A decrease in thermal susceptibility when increasing the percentage of MWNTs, reflected in a decrease in penetration indexes, is observed.

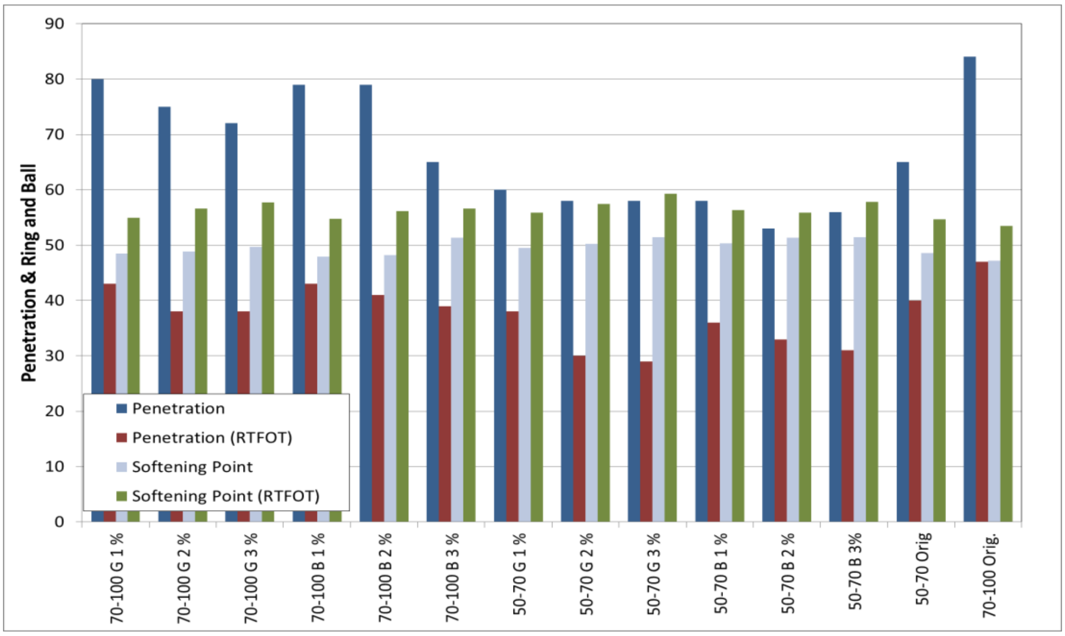


Figure 4: Empirical tests results for MWNTs modified bitumen.

Regarding resistance to aging, changes in the properties are similar to those observed in the original binders, and no changes are observed in the results of the change in mass, so one can infer that the modification does not influence significantly in the aging behavior of the materials studied.

We must also mention that the results obtained in all cases result in bitumen that complies with the current European specifications for road bitumen contained in EN 12591.

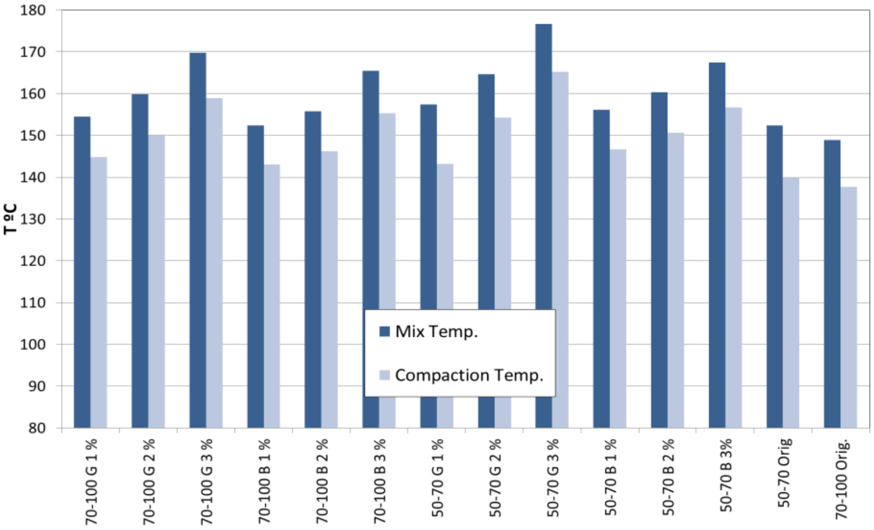


Figure 5: Mixing and compaction temperatures for MWNTs modified bitumen.

As was the case with the B 150/300 mixtures, the influence of the content of nanotubes is magnified as temperature increases, leading to materials with very high viscosities and low thermal susceptibility. So looking at calculated temperatures for mixing (T @ visc = 200 mPa.s) and compaction (T @ visc = 300 mPa.s) of the manufactured binders (see table below) it is observed how this temperatures increase up to 24 ºC compared with the original ones, but in any case, these temperatures are within the usual ranges of those for binders use in roads.
The study of the rheological properties of the binders was performed by temperature and frequency sweeps using a dynamic shear rheometer (Figure 6). The results show once again that adding nanotubes do not produce significant

changes in the rheological properties measured between 10 and 80 ° C, so an appropriate behavior as a binder for asphalt mixtures was expected for all of them.

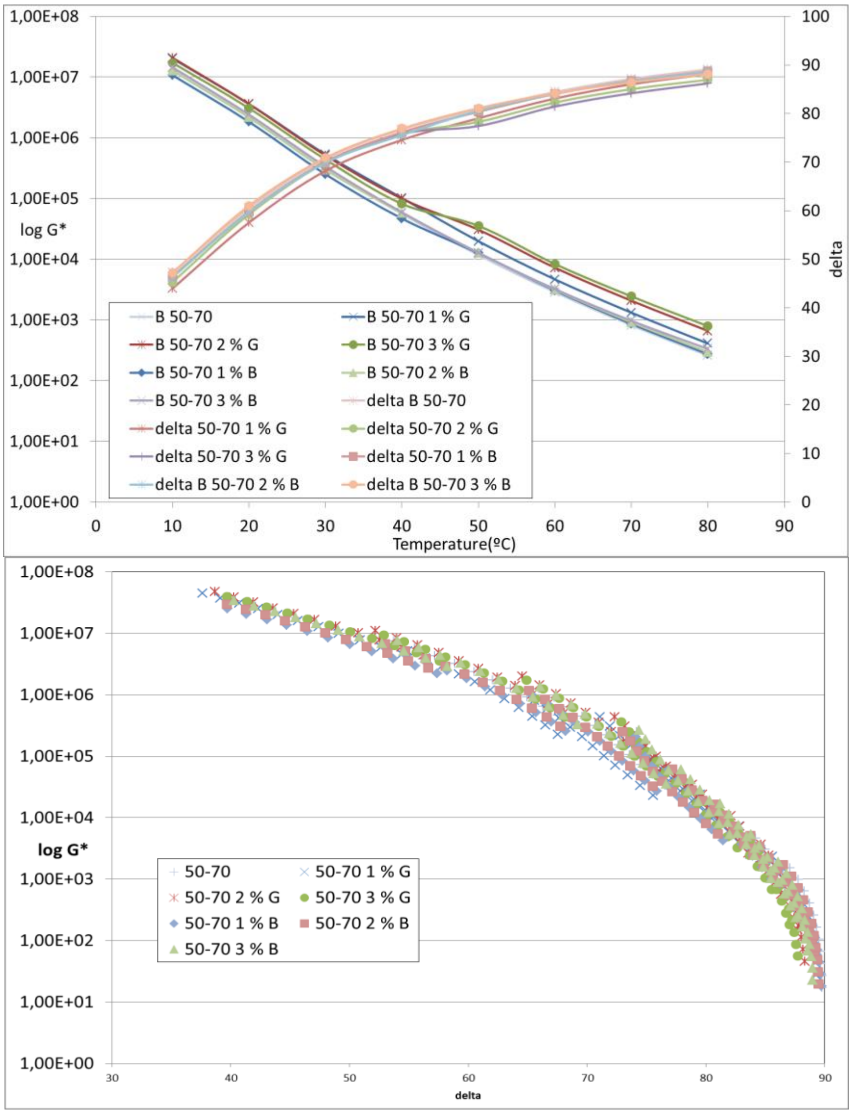


Figure 6: Rheological Properties for MWNTs modified bitumen.

Finally, changes on the electrical behavior of bitumen with the addition of different percentages of MWNTs were studied and an evolution from insulator to semiconductor, with conductivity values exceeding 3.10 Sm^{-1}, was observed (Figure 7).

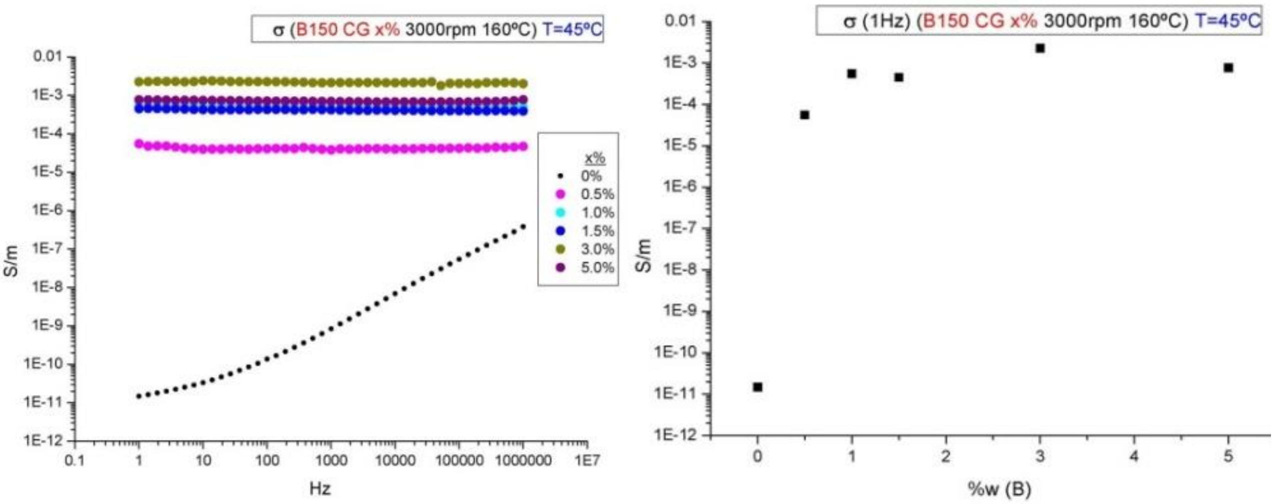


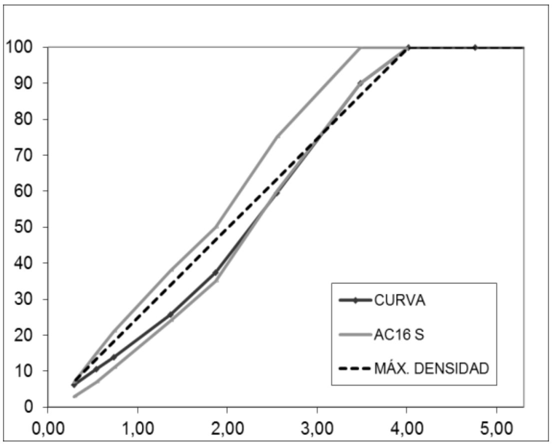
Figure 7: Electrical Properties for MWNTs modified bitumen.

The conductivity of the dispersion increases with MWNTs concentration, approaching to a horizontal asymptotic limit meaning that percolation of material has been reached at a concentration of approximately 3% by weight with a conductivity value of 2.2 x 10-3 Sm-1, which should allow a controlled heating of the material by applying microwave waves.

3. ASPHALT CONCRETE WITH CARBON NANOTUBES MODIFIED BITUMENS.

The next step was to evaluate the performance of asphalt mixes manufactured with the MWNTs modified binders described above.

The study was performed over an asphalt concrete AC16 S (EN 13108-1) with a 4.7% of binder content, usually used as reference in in Cepsa studies (Figure 8), manufactured with conventional B 50/70 and with B 50/70 modified with 3% of nanotubes.



UNE Sieve (mm)	Grading Envelope (% Passing)	
	AC 16S	Used
22	100	100
16	90 – 100	90
8	60 – 75	59
4	35 - 50	37.4
2	24 – 38	25.8
0.5	11 – 21	13.8
0.25	7 – 15	10.6
0.063	3 – 7	6.2

Figure 8: Agregrate Grading.

Asphalt concrete performance was studied using the Marshall test (EN 12697-30) as well as evaluating rigidity modulus (EN 12697-26, annex C) and water sensitivity (EN 12697-12).

Results obtained in the Marshall test (Table 1), on specimens compacted with 75 blows per side at 160-165 ° C, are within expected for this type of mixtures and shows no significant differences in terms of the bitumen used, with or without MWNTs.

Table 1: Marshall Test Results.

	B 50/70	B 50/70 + 3 % MWNTs
Marshall Stability (KN)	13.0	12.3
Flow (mm)	2.6	2.6
Density (g/cm^3)	2.368	2.308

The same conclusion is obtained by comparing the results of modulus (Table 2), in line with the binder results which showed no significant changes in their rheological behavior at performance temperatures when modified with MWNTs.

Table 2: Rigidity Modulus Results.

	B 50/70	B 50/70 + 3 % MWNTs
Modulus (10Hz, 20ºC)	7533 MPa	7279 MPa

However, significant differences were found when performing the water sensitivity test (Table 4). Although the Indirect Tensile Strength (ITS) results obtained on the dry specimens are similar, the results obtained in the wet specimens of the MWNTs modified binder asphalt were too low giving a 51% ratio that does not comply the minimum value specified for these mixes, and is well below the 78% obtained with a conventional bitumen.

Table 3: Water Sensitivity Results.

	B 50/70	B 50/70 + 3 % MWNTs
ITS Dry Specimens (MPa)	2.362 MPa	2.120 MPa
ITS Wet Specimens (MPa)	1.849 MPa	1.086 MPa
Ratio (%)	78 %	51 %

The explanation for this result should be in the high specific surface area of the MWNTs, which modify the binder-filler relationship producing dry bitumen mixes. The appearance of the mix, clearly indicates a lack of bitumen, requiring the use of more open mixes allowing the use of larger bitumen contents.

4. POLYMER MODIFIED BITUMEN MODIFICATION WITH CARBON NANOTUBES

Due to Cepsa's previous experience in anti-cracking mixes with high content of highly modified PMB (> 6,5 %) [7], we decided to use this approach to overcome the bad results obtained in the water sensitivity test, instead of modify the aggregate grading and increase the content of conventional bitumen.

A highly modified PMB, with a 3 % of MWNTs, high viscosity to prevent bitumen drainage during manufacture and with exceptional mechanical properties, so that the mixture has a good mechanical behavior, was designed. The results of its characterization are summarized in Table 4.

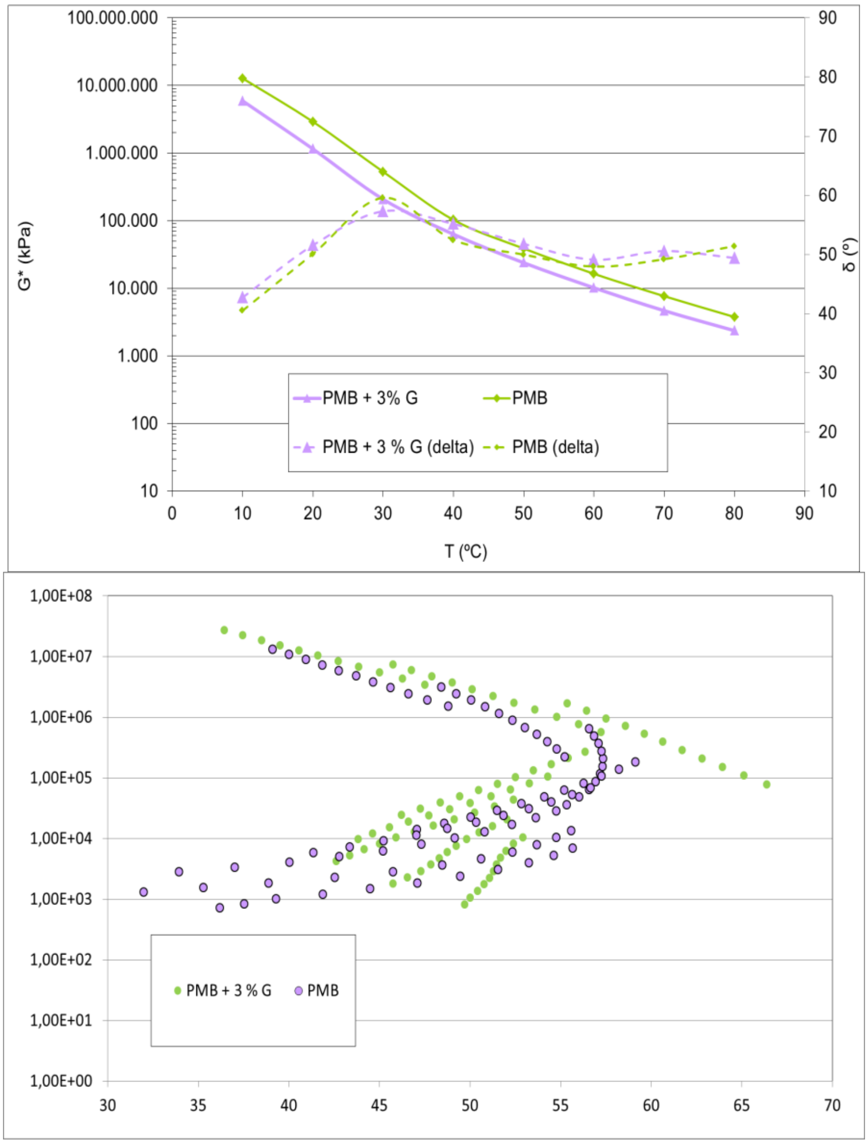


Figure 9: Rheological Properties for MWNTs modified PMB.

In Figure 9, the rheological properties of the designed binder compared to a similar binder with no MWNTs are collected. In line with what was observed in the rheological study of conventional binders, it can be concluded that the addition of nanotubes does not produce significant changes in the rheological properties measured between 10 and 80 ° C.

Table 4: Empirical tests results for MWNTs modified PMB.

Property	Test Method	Unit	Value
Original Binder			
Penetration (25 ºC; 100 g; 5s)	EN-1426	0.1 mm	49
Softening Point	EN-1427	ºC	93.8
Elastic Recovery (25 ºC)	EN-13398	%	97
Flash Point	EN-2592	ºC	264
Force-Ductility (5ºC)	EN-13589 EN-13703	J/cm^2	5.33
Viscosity			
140 ºC		mPa.s	2790
160 ºC		mPa.s	1103
180 ºC		mPa.s	470
RTFOT residue			
Change of Mass	EN-12607-1	%	0.29
Retained Penetration (25 ºC; 100 g; 5 s)	EN-1426	%	80
Increase in Softening Point	EN-1427	ºC	1.3

Discontinuous mixtures with the aggregate grading shown in Figure 10 and a high content (6-7 %) of the highly modified PMB with a 3 % of MNWTs were manufactured.

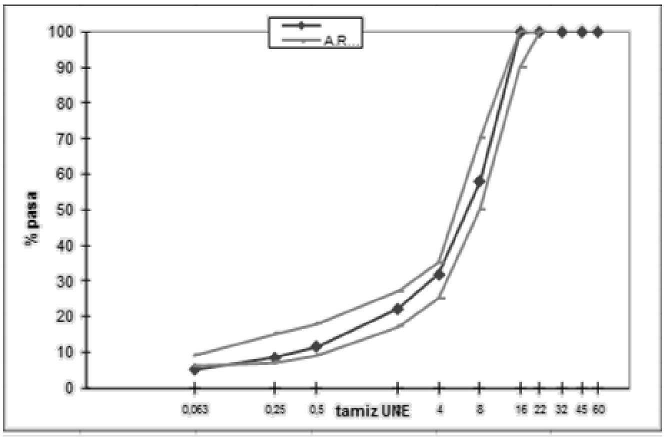


Figure 10: Aggregate Grading.

In the following table some of the characteristic values determined in this mixture are shown. It should be noted how, the higher binder content used in those mixtures, has solved the problem with the water sensitivity test occurred in conventional mixtures, resulting mixtures with good characteristics and virtually identical to those obtained when highly modified PMBs with no MNWTs are used. Note that due to the different nature of the mixes used, additional test (wheel tracking and bitumen drainage) were done in order to evaluate its performance.

Table 5: Mix results.

Property	Unit	Value
Marshall Stability (KN)	KN	13
Water Sensitivity: **ITS Dry Specimens (MPa)** **Ratio ITS_W/ITS_D (%)**	 MPa %	 2,23 94
Wheel Tracking Test **V 105-120 (7 %)**	 mm/min	 $< 6.10^{-3}$
Bitumen Drainage **7 % @ 190 ºC**	 %	 0

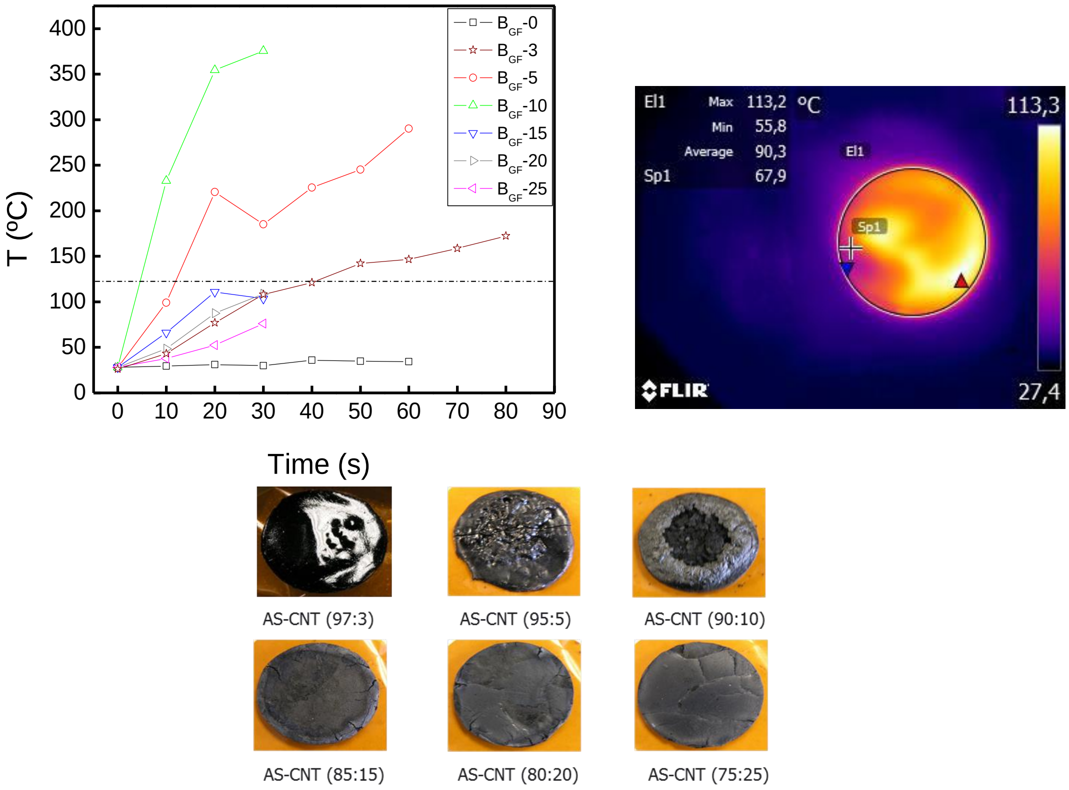
5. SELF-HEALING ASPHALT MIXES.

As mentioned in the introduction, improving and accelerating bitumen self-healing property, due to controlled and localized heating, is one of the uses arising from the new properties that nanotubes provide to bitumen, and should have direct application in roads.

5.1 Microwave Heating.

To evaluate the warming caused by the application of a microwave source on MWNTs bitumen, circular films with a 4 cm diameter and 3.7 mm of thickness were prepared and heated by applying microwaves for different periods of time with a power of 1.27 kW and a frequency of 2.45 GHz. The temperature increase was measured with an infrared pyrometer.

The results obtained are shown in Figure 11. For the sample with no MWNTs, temperature does not change in the time interval studied; however, in samples with high percentage of MWNTs a linear temperature increase versus time is shown with a slope that increases with the MWNTs quantity until a 10 % content and decreases with higher MWNTs contents.



AS-CNT (97:3)
AS-CNT (95:5)
AS-CNT (90:10)
AS-CNT (85:15)
AS-CNT (80:20)
AS-CNT (75:25)

Figure 11: Temperature Variation of Bitumen with Different MWNTs Content vs. Radiation Time.

These results are explained by the fact that the carbon nanotubes form a percolation network in the bitumen matrix in which they are interconnected. Therefore, besides increasing the dielectric loss against electromagnetic waves, also increase losses due to eddy currents and improves the absorbance of the material so that very high temperatures are reached in short time. Samples with 5 and 10% of MWNTs temperature exceeds 200 °C in only 10-20 seconds and continues to increase at higher irradiation times

On the other side, on samples with high content of MWNTs, the dominant effect is the reflection so that incident radiation is totally reflected on the surface and does not penetrate into the material so as a consequence, despite increasing carbon nanotube content, heating decreases with percentages greater than 10%.

Taking these data into account, the optimum composition seems to be around 3% of MWNTs, for which a linear variation of warming with the irradiation is obtained and temperatures of 80 °C and 100 °C are reached in only 20 and 30 seconds respectively.

This optimal percentage of MWNTs is within the range at which binders with suitable rheological properties for road use are obtained.

The study was repeated on test specimens of asphalt mix made with bitumen modified with different percentages of MWNTs (0 to 3%) and results shown in Figure 12 were obtained.

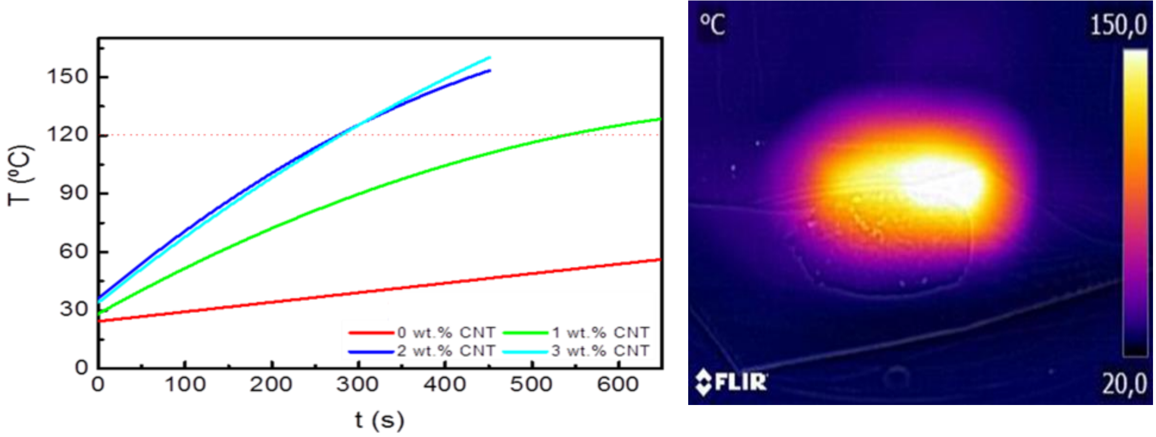


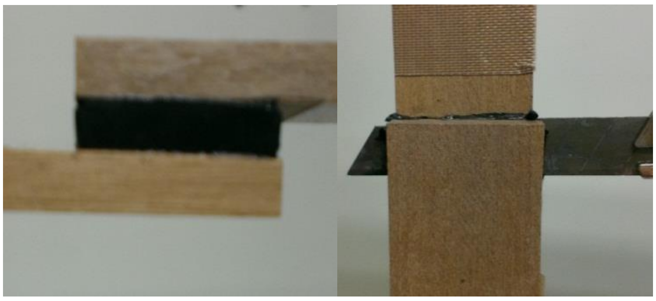
Figure 12: Temperature Variation of Asphalt mixes with Different MWNTs Content vs. Radiation Time.

The estimated self-heailing (80-100 ºC) temperature was reached in the samples with 1% of MWNTs in 300 seconds, while for samples with 2 and 3% of MWNTs, was achieved in just 150 seconds.

5.2 Self-Healing.

Finally, different tests were performed to evaluate directly the self-healing ability of the designed materials, bitumen and asphalt.

To evaluate binder performance, a tensile test was conducted on a fixed weight of sample poured between two sets of woods (3,8x20x19,5 mm) (Figure 13). Fifteen samples were prepared for each composition; a third of the samples were tested as they were, and a slit simulating the formation of a crack (0,3x10x19,5 mm dimensions) was performed on the rest with a blade. Finally, half of these samples were heated by microwave for 20 seconds and allowed to cool to room temperature. With this procedure three groups of samples were obtained: five original, five cracked and five heated by microwaves.



(a) (b)

Figure 13: Self-Healing Bitumen Test.

The tensile test results are shown in Figure 14. The tensile strength at break of the lap joint vs. the amount of MWNTs is plotted in the first graphic while on the second the whole curves of the sample with 3% MWNTs content are plotted. The results indicate that radiation heals cracks, recovering and even improving initial values.

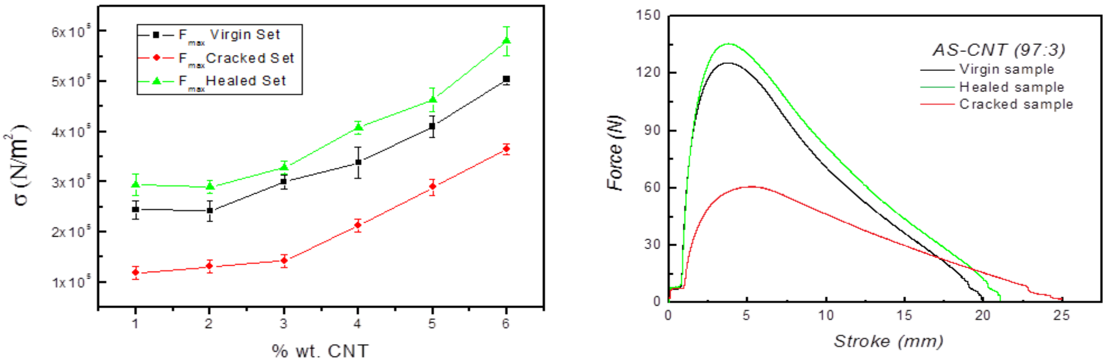


Figure 14: Self-Healing Bitumen Test Results.

To asses self-healing on asphalt, Marshall specimens compacted with 50 blows per side of the mixture described in section 4 (Figure 10) were manufactured with the highly modified PMB, both with and without 3% MWNTs.

The specimens were tested by indirect tensile break at 20 °C and, subsequently, heated and recompacted in the Marshall stability breaking head applying a load of 1 KN for 30 seconds (Figure 15). These operations were repeated some times to see the evolution of the specimens after various in cycles of breaking and recompaction.

Figure 15: Self-Healing Asphalt Test.

Preheating was performed differently according to the binder composition, with or without MWNTs content:

- Mixtures containing MWNTs, were heated by applying microwave for 180 seconds, reaching temperatures between 90 and 100 °C.
- Mixtures with no MWNTs were heated in oven at 100 °C for 3 hours in order to assure that the specimens reached, homogenously, similar temperatures as the mixes heated with microwaves.

Table 6 shows the results obtained, expressed as a percentage of the initial Indirect Tensile Strength.

Table 6: ITS Ratio of Healed Asphalt.

	Original	Ratio after Recompaction		
		1	2	3
MWNTs modified Asphalt	100%	90%	85%	79%
Conventional Asphalt	100%	77%	66%	-

Results obtained on MWNTs modified Asphalt show how, after only 180 seconds of heating by microwaves, 90 % of the initial strength is recovered, demonstrating the existence of an accelerated self-healing induced process. Furthermore, this process can be repeated more than once, showing good results, around 80 % of initial ITS, after the third breaking test.

On the other side, conventional asphalt with no MWNTs, shows a lower recovered strength (< 80%) even when they are heated for 3 hours.

Additional test evaluating the contribution of the induced self-healing on the asphalt fatigue behavior are underway.

5. CONCLUSIONS.

Paving grade and polymer modified bitumen, with different contents of MWNTs (1-3%) and complying the current specifications for use in bituminous mixtures, have been developed.

Bitumen modified with MWNTs has a change in its electrical behavior from insulator to semiconductor with conductivity values greater than 10^{-3} Sm^{-1}.

Asphalt concrete manufactured with MWNTs modified binders show problems on water sensitivity due to the high specific surface area of the MWNTs.

Discontinuous mixtures, with high content (>6 %) of highly modified PMB with a 3 % of MNWTs, showed good properties to be used in roads.

Both MWNTs modified bitumen and asphalt made with it, can be heated in a controlled, rapid and homogenous way by applying a microwave source.

This heating can be used to accelerate the self-healing processes, naturally present in the bitumen, which should result in greater durability of asphalt mixtures made with them.

ACKNOWLEDGEMENTS

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