https://doi.org/10.1016/j.colsurfa.2019.01.021

The effect of multiwalled carbon nanotubes on the rheological behavior of bitumen

Cesare Oliviero Rossi[(1,*)], Valeria Loise[(1)], Alfonso Policicchio[(2)],Danilo Vuono[(3)]; Bagdat Teltayev[(4)], Andrea Gnisci[(5)] , Giacomo Messina[(5)] and Cesare Oliviero Rossi [(1)].

(1) Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 14/D, Rende (CS), 87036, Italy. tel./fax. +39 0984492045

(2) Department of Physics, University of Calabria, Via P. Bucci, Cubo 31C, Rende (CS), 87036, Italy

CNISM - National Interuniversity Consortium for the Physical Sciences of Matter, Italy

National Research Council, Institute of Nanotechnology (Nanotec) - UoS Cosenza, Via P. Bucci, Cubo 31C, Rende, CS, Italy

(3) Department of Environmental Engineering and Chemical Engineering, University of Calabria, 87036 Rende, CS, Italy

(4) Kazakhstan Highway Research Institute, Nurpeisova Str., 2A, Almaty 050061 Kazakhstan

(5) Department of Information Engineering, Infrastructure and Sustainable Energy, University "Mediterranea" of Reggio Calabria, Via Graziella, Loc. Feo di Vito, 89124 Reggio Calabria, Italy

Abstract

In the present study, we present the influence of addition of multi-walled carbon nanotubes (CNTs) on the microstructure and rheological behaviour of bitumen. Two different types of CNTs have been tested: the first, named Type 1, is obtained by laboratory synthesis through Catalytic Chemical Vapour Deposition (CCVD) technique, while the second one is a commercial one and it will be named asType 2. Both CNTs types were completely characterized thought Trasmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM) and micro-Raman spectroscopy to deep investigate both morphological, chemical and structural properties. Then, in order to understand the effect of the addition of CNT on bitumen, rheological analysis were performed through experiments in oscillatory regime.

1. Introduction

The extremely broad effort that the scientific community is putting on the so-called Nanoscience is mainly related to the comprehension of the nanometric size effects on the physico-chemical properties of the matter[1]. Both, organic and inorganic materials behave in a peculiar way when they are doped by nanostructures.

Connected to Nanoscience, Nanotechnology is the creation of useful materials, devices, and system through the control of matter on the nanometer scale and the exploitation of novel properties and phenomena developed at the length scale [2]. Since the discovery of fullerenes and nanotubes, nanostructure carbon-based materials occupy a strategic position in materials science and nanotechnology as one of the most promising and far-reaching systems.

In order to establish a link between nanostructure, mesostructure and material performances, production, characterization and manipulation techniques have to be developed and fully mastered down to the nanometric scale. In nanostructured carbon-based materials the physico-chemical properties are influenced by the pore dimension, surface morphology and local curvature [3,4].

Since the first discovery in 1991 [5] multi-walled carbon nanotubes (CNTs) have attracted enormous research attention in various scientific communities(Biological and biomedical research, Composite materials, Microelectronics, Solar cells, Energy storage) [6,7]. Cost often represented a limiting factor for the large scale applications of CNT-based technologies.Therefore, recent developments have demonstrated that it is possible to manufacture high quality CNTs at low prices. CNTs can be mass produced using Catalytic Chemical Vapor Deposition [5]. CNT based nanomaterials have advantages over conventional materials in various environmental and technological applications such as chemical functionalization and/or surface modification.

In last years, the standard imposed by companies operating in the bitumen becomes higher and higher consequently, the need for increasingly high performance and wear-resistant pavements push bitumen research exploring new materials. In this context, well fit the CNTs since they are well known for having extraordinary properties when they are incorporated to materials for cement production, compared to the low percentage of material added.

So,for these reasons, in this experimental workit was decided to test the bitumen modified with these kind of material.Our research aims to develop a bituminous binder that is able to improve rutting resistance potential and resistance to thermal cracking[8].In order to understand the effect induced by the CNTson the bitumen performance, two different types of nanotubes were investigated,inparticular a first type of CNTs labelled asType 1, which are laboratorysynthetized product characterized by the presence of defects on the structure and a morphology different from the second one labelled asType 2 which, on the contrary, are commercial materials usually characterized by a presence of carbon content >90%.A complete physical-chemistry analysis was performed on both types in order to characterize the CNTs and theirchemical and morphological differences were correlated with their rheological responses.

To this purpose the present paper reports on the results of careful rheologicalinvestigations that were done in the linear viscoelasticregion of the CNTs modified bitumen. Steady shear and dynamicshear test relaxation experiments were performed as well as AFM measurament to understand the effect of CNTs on the morphology of the bitumenous system.

2 Experimental

2.1. Materials

Carbon nanotubes identified as Type 1 samples are laboratory synthesized by Catalytic Chemical Vapour Deposition (CCVD) method using a Co-Fe based supported catalyst. In particular, 0.25 g of supported catalyst (Co 5 wt%–Fe 5 wt%/NaY) are spread on a 25 cm long quartz boat, made of a half tube of 3 cm in diameter. The boat is introduced into a quartz tube reactor of 4 cm in diameter and flushed with nitrogen (416 ml/min) for 5 min at 25°C. The reactor is introduced into a furnace preheated at 700°C (reaction temperature) [9] and the nitrogen flow is maintained for 10 min. A C_2H_4 flow of 800 ml/min is added to the N_2 flow for 20 min (reaction time). The C_2H_4 flow is replaced by a single N_2 flow of 416 ml/min, the reactor is removed from the furnace and the N_2 flow is maintained for 10 min. After cooling to 25°C, the boat is removed from the reactor and the product is collected [10].The obtained CNTs show a purity of 94 wt% and small presence of catalysts particles.

The second kind of CNTs, labelled as Type 2 and provided by Sigma Aldrich (cas number 308068-56-6, own diameter in the range 110-170 nm and length between 5 and 9 µm. The Carbon composition is > 90% and the density is 1.7 g/ml at 25°C. Multi walled carbon nanotubes were prepared by chemical vapor deposition (CVD).Finally, the pristine bitumen, with a penetration 50/70 sourced from Saudi Arabia, is supplied by Loprete Costruzioni Stradali (Terranova Sappo Minulio, Reggio Calabria, Italy).

The CNT-based bituminous samples is prepared by using a high shear mixing homogenizer (IKA model, USA). Firstly, bitumen is heated up to 150°C until it flowed fully, then 1% of the weight of the base bitumen of Type 1 (pristine and unpurified samples) or Type 2 is added to the melted bitumen under a high-speed shear mixer of 500 to 700 rpm/min. Furthermore, the mixture is kept under mechanical stirring at 150°C for 15 minutes in a closed beaker to avoid oxidation. After mixing, the resulting bitumen is poured into a small sealed can and then stored in a dark chamber thermostated at 25ºC to retain the obtained morphology.

2.2 CNTs characterization

To get a deep understanding of the analyzed system and correlate the chemical, structural and morphological features, different techniques were used. In particular, to investigate chemical, structural and morphological properties we performed systematic Trasmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and micro-Raman spectroscopy[11,12]

Trasmission electron images were recorded using a Philips CM10 using 100 V accelerating voltage in order to observe morphology changes in carbon nanotubes used as filler in the bituminous matrix samples.CNT samples were previously dispersed in ethanol, then placed on carbon gridsand dried before loading in the TEM apparata. Micrographs were recorded on a Gatan CCD camera and then analyzed by Digital Micrograph software.Phase structure of the samples was examined through XRD patterns measured on a Philips PW 1830 diffractometer using Cu Ka (40 kV, 40 mA) filtered radiation. Measurements were performed in reflection mode placing the sample powder on the special homemade sample holder. All analysis were acquired at room temperature (RT≅298K) and the patterns recorded in the 2-theta (2θ) range from 5° to 70°, in steps of 0.02° and counting time 1s per step. The effect related to the sample stage has been taken into account.

Raman spectra were collected using a HORIBA Scientific LabRAM HR Evolution micro-Raman spectrometerequipped with an integrated Olympus BX41 microscope 50x/0.50and a diode laser of 532 nm wavelength (2.33 eV), with incident power of 6.5 mW.The 500-3500 cm^{1} spectral range was investigated. Several different locations were sampled in each specimen on account of the possible lack of structural homogeneity[13]. The spectra collected were analysed using a commercially available spectroscopic analysis software package. Lorentzian bands, superimposed to a constant background, were used to fit the spectra. The wavenumber position, width (FWHM) and intensity of the bands were chosen by a least-square best-fit method.

In order to collect more informationabout composition and thermal stability of the CNT material, thermogravimetric analysiswere performed using a Perkin-Elmer TGA-6 Instrument, able to work inthe temperature range 20–800°C with a sensibility of 0.001 mgand a temperature rate of 5 °C/min.

2.3 Rheological characterization

The rheological properties of modified bitumens were investigated through Dynamic Shear Rheological (DSR) measurements. Dynamic experiments on bitumen samples were carried out using a controlled shear stress rheometer (SR5, Rheometric Scientific, USA) equipped with a parallel plate geometry (gap 2 mm, ϕ = 25 mm within the temperature range 25-150 °C) and a Peltier system (±0.1 °C) for temperature control.

Preliminary Standard stress sweep tests were performed in order to ensure that the rheological investigation is conducted in a linear viscoelastic region, thus making the measurement independent of the amplitude load applied. Temperature ramp tests (time cure)were carried out at 1 Hzwith heating rate of 1°C/min in the temperature range 25-120°C. Moreover, frequency sweep tests wereperformed from 25°C to 95°C in steps of 10°C. The applied stress was within the viscoelastic region.

Dynamic frequencysweep experiments were performed in a frequency range between 0.1 and 15.9 Hz. The small-amplitude dynamic tests provided information on the linear viscoelastic behaviour of materials through the determination of the complex shear modulus[14]:

$$G^*(\omega) = G'(\omega) + iG''(\omega) \qquad (1)$$

where G'(ω) is the in-phase (or storage) component and G"(ω) is the out-of-phase (or loss) component. G'(ω) is a measure of the reversible, elastic energy, while G"(ω) represents the irreversible viscous dissipation of the mechanical energy. The dependence of these quantities on the oscillating frequency gives rise to the so-called mechanical spectrum, allowing a the quantitative rheological characterization of studied materials.

According to the theory of the “weak-gel” model[15], the magnitude of complex modulus, G*, is expressed by:

$$|G^*(\omega)| = A\omega^{\frac{1}{z}} \qquad (2)$$

where A is a proper constant which can be interpreted as the “interaction strength” between the rheological units, that is a sort of amplitude of cooperative interactions.

3. Results and Discussion

3.1 Surface and Structure analysis

Figure 1 shows the results of the microstructural and morphological analyses carried out on the Type 1 (a) and Type 2(b) CNTs samples.TEM analysis reveals that both, commerial and laboratory CNTs, are multiwalled nanotubes.In particular the Type 1 are characterized by 20 µm of length and by diameters of ca. 17-20 nm while the Type 2 nanotubes have dimensions in the range 2-4 µm of length and diameters of ca. 50-120 nm. In addition, an in-depth analysis of the TEM images of the Type 1 sample, shows the presence of small trace of catalyst residuals or entanglement of nanotubes. The last is an indication that, even if the purification procedure adopted in the sample preparation is very effective sometimes, in in the laboratory nanotubes, it is possible to observe small trace of features related to catalyst residuals as later revealed also by the XRD analysis.

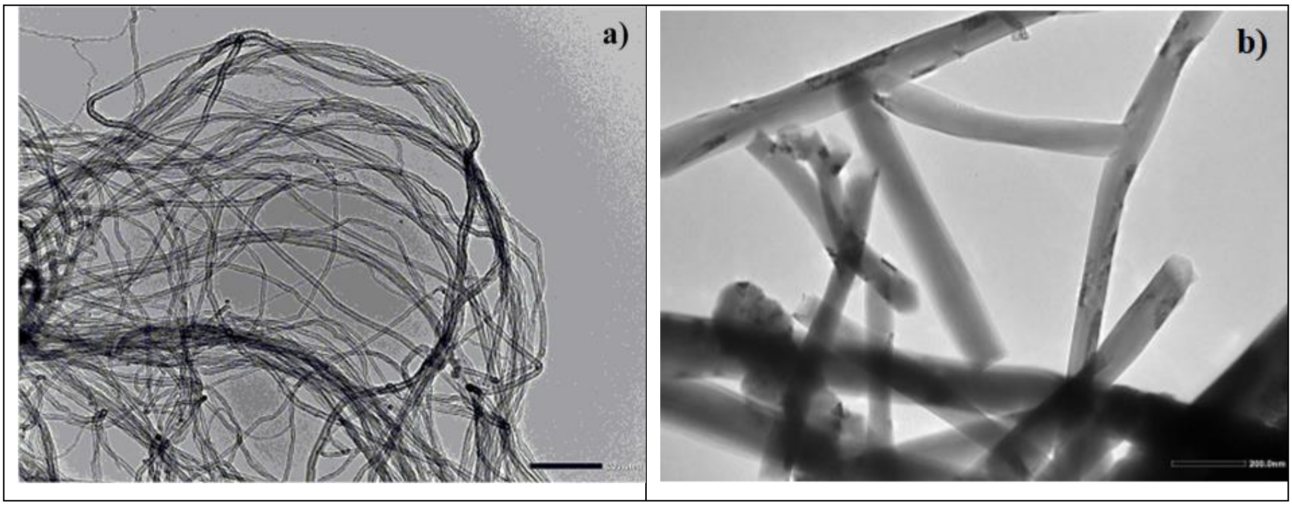
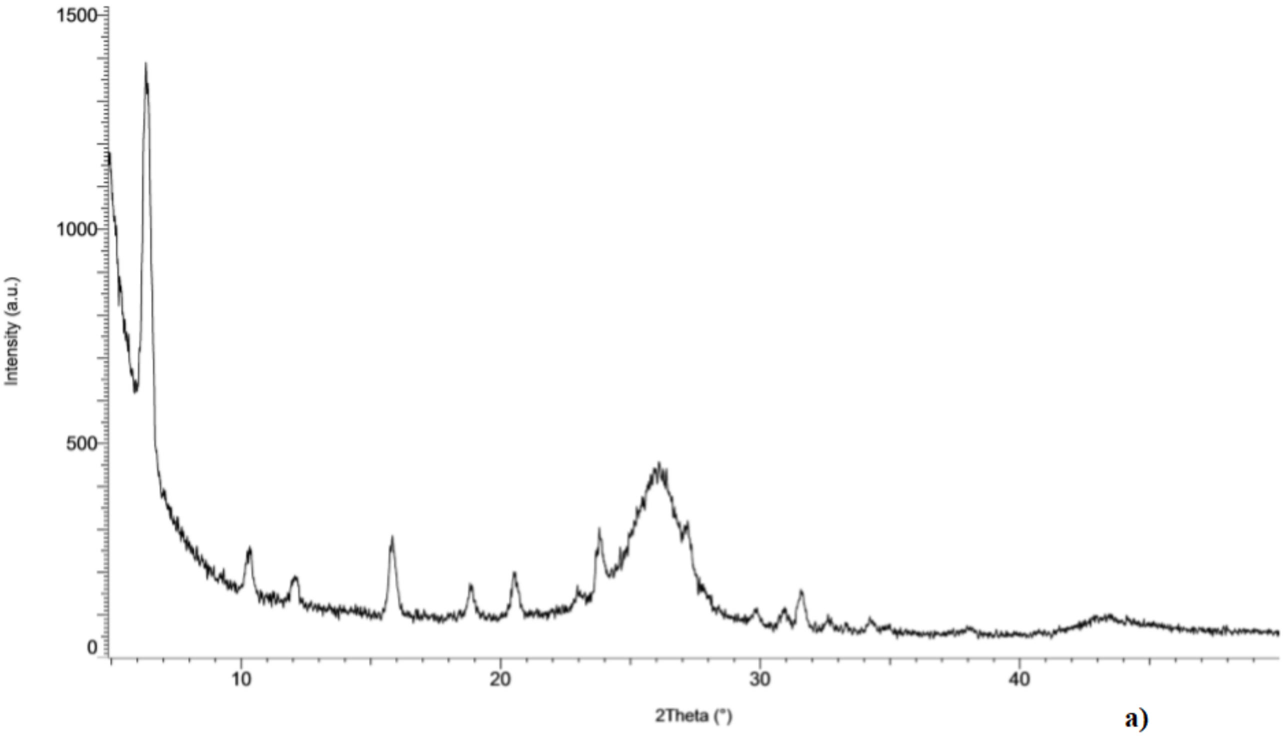


Figure 1.*TEM Image of a) Type 1 andb) Type 2 carbon nanotubes.*

Phase structure of the samples was identified via XRD analysis and reported below in Figure 2. The laboratory CNTs sample shows a wide peak centered at 2θ = 26.2°, denoting the typical graphitic structure of the nanotubes. Other interesting peaks are evident in the range 10-22° 2θ, probably due to the presence of catalysts nanoparticles. XRD pattern of Type 2 CNTs highlights a sharp peak at ca. 2θ = 26.5°, while no evidence of peaks due to the presence of catalyst is noted.



a)

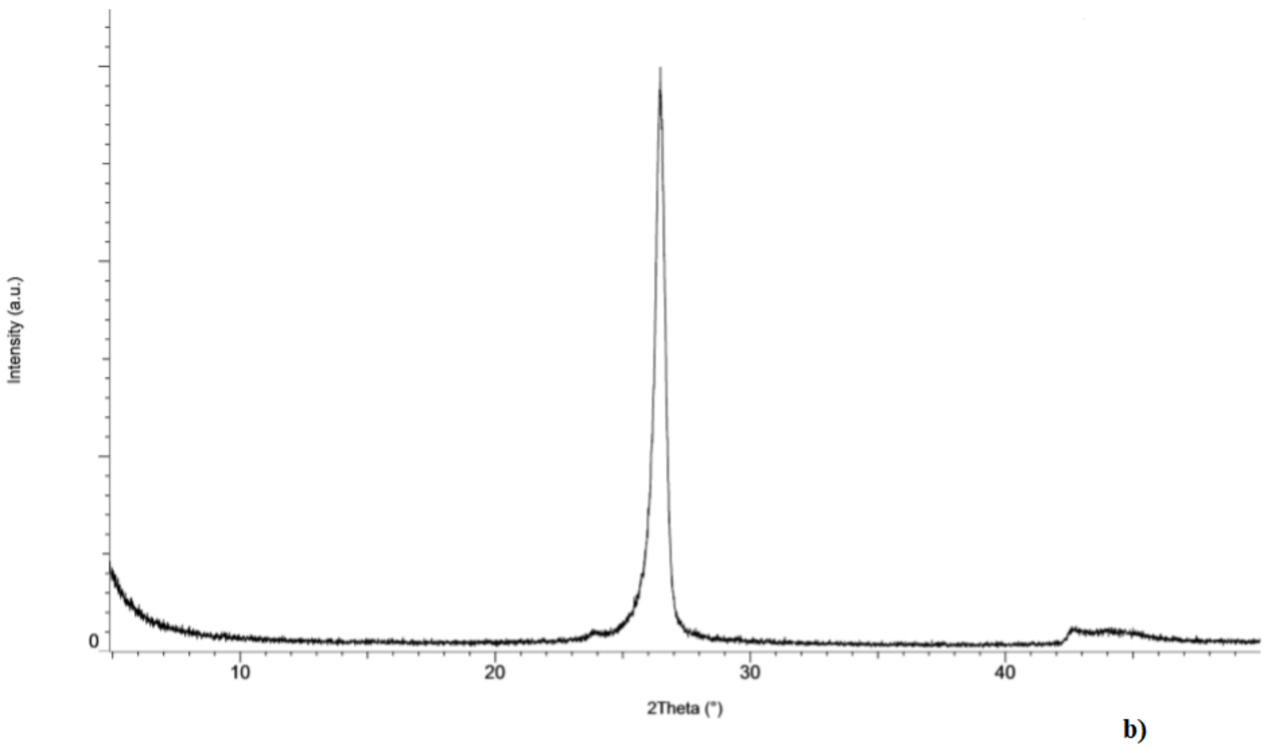


Figure 2. *XRD pattern of a) Type 1 and b) Type 2 CNT samples between 5 and 70 degrees.*

The crystalline quality of the samples was investigated by micro-Raman spectroscopy.Figure 3 compares the Raman spectra acquired ontheType 1 and Type 2 CNT samples. The main features are G-band at ~ 1570 cm^{-1} due to the stretching of all C-C pairs [16] the "disorder" D-band at ~ 1340 cm^{-1} due to the breathing mode of the C hexagonal rings [17, 18]and the 2D-band at ~ 2680 cm^{-1}originates from a double-resonance Raman process [19,20].The G- and 2D-band are the fingerprint of the graphitic crystalline arrangement and long-range order, respectively. The D-band is forbidden in perfect graphite and it becomes Raman active in presence of defects in the hexagonal network (e.g. distorted hexagonal rings, non-hexagonal rings, vacancies, grain boundary, substitutional heteroatoms) that break the crystalline translational symmetry of infinite graphene layers [17,18]. The laboratory-CNT Raman spectrum also shows the D'-band at ~1610cm^{-1} which,similarly to the D-band, is a disorder-activated double-resonance Raman feature and it is typical of disordered graphite and of MWCNTs [18,21].The evaluation of intensities ratio of D and G peaks (I_D/I_G) is commonly used to monitor the defect density, and its reciprocal (I_G/I_D) is taken as graphitization index for CNTs, while the intensities ratio of 2D and G peaks (I_{2D}/I_G) gives information about the long-range graphitic order [22].From Raman analysis, the I_D/I_G for Type 1 and Type 2 CNTsresult 0.8 and 0.2, respectively, pointing out a higher presence of defect in the Type 1 CNT and then a lesser crystalline quality. The I_{2D}/I_G are similar for both samples (0.6 and 0.5 for Type 1 and Type 2 CNT, respectively), with a packing degree probably due to the bundles organisation of CNTs.

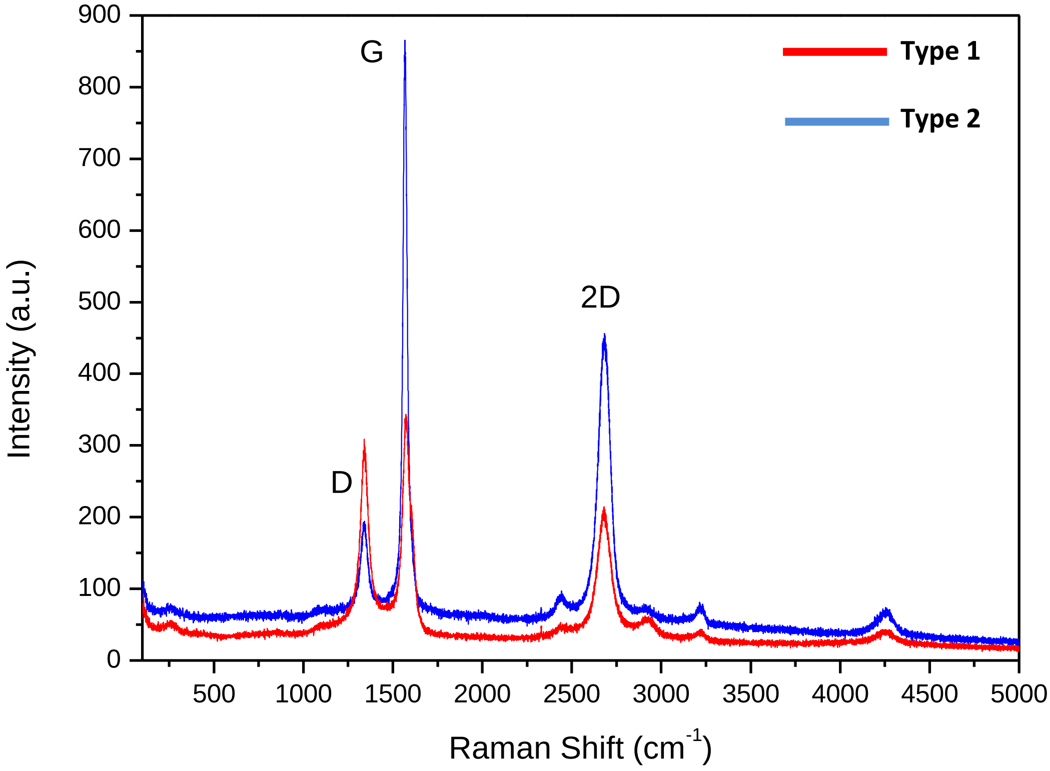


Figure 3.*Raman spectra of Type 1 and Type 2 CNT samples.*

The thermal analysis was performed to point out the quality of both CNTs.The results reported inFigure 4 shows the thermal behaviour of both Type 1 and Type 2 samples. Concerning Type 1 samples, it is evident a total weight loss of ca. 92% due to a single thermal phenomenon at ca. 550°C, a value very close to the purity of the CNTs obtained by CCVD.Concerning Type 2 samples it is evident a total weight loss of ca. 92% due to a single thermal phenomenon at ca. 600°C. This is an indication, confirming ourprevious hypothesis,that no amorphous regionsare present in the sample [23].A slight shift of thermal degradation temperature of Type 1, compared to that of type 2, could be related to a higher presence of defects affecting thermal stability, as previously hypothesised.

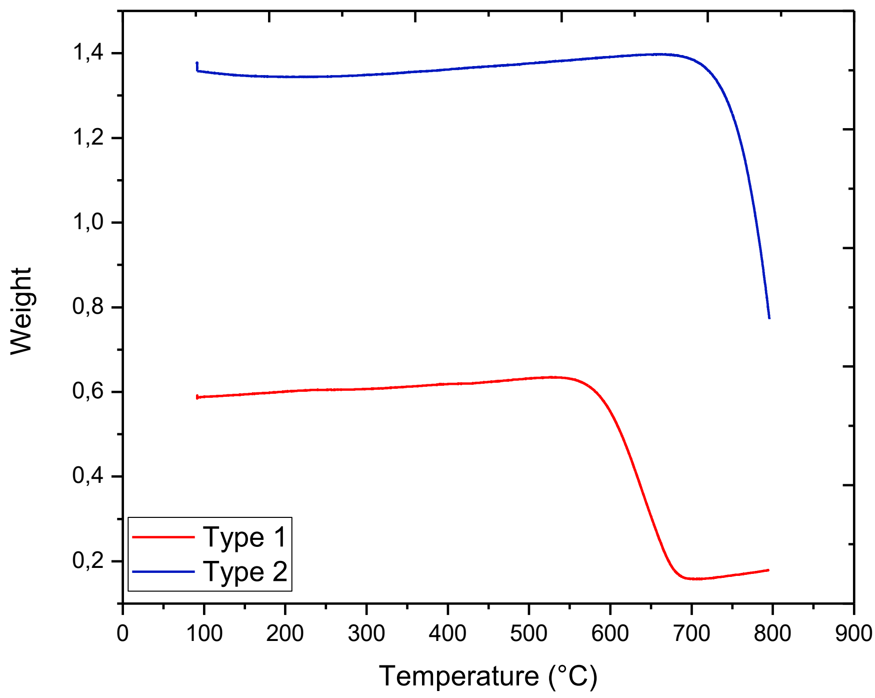
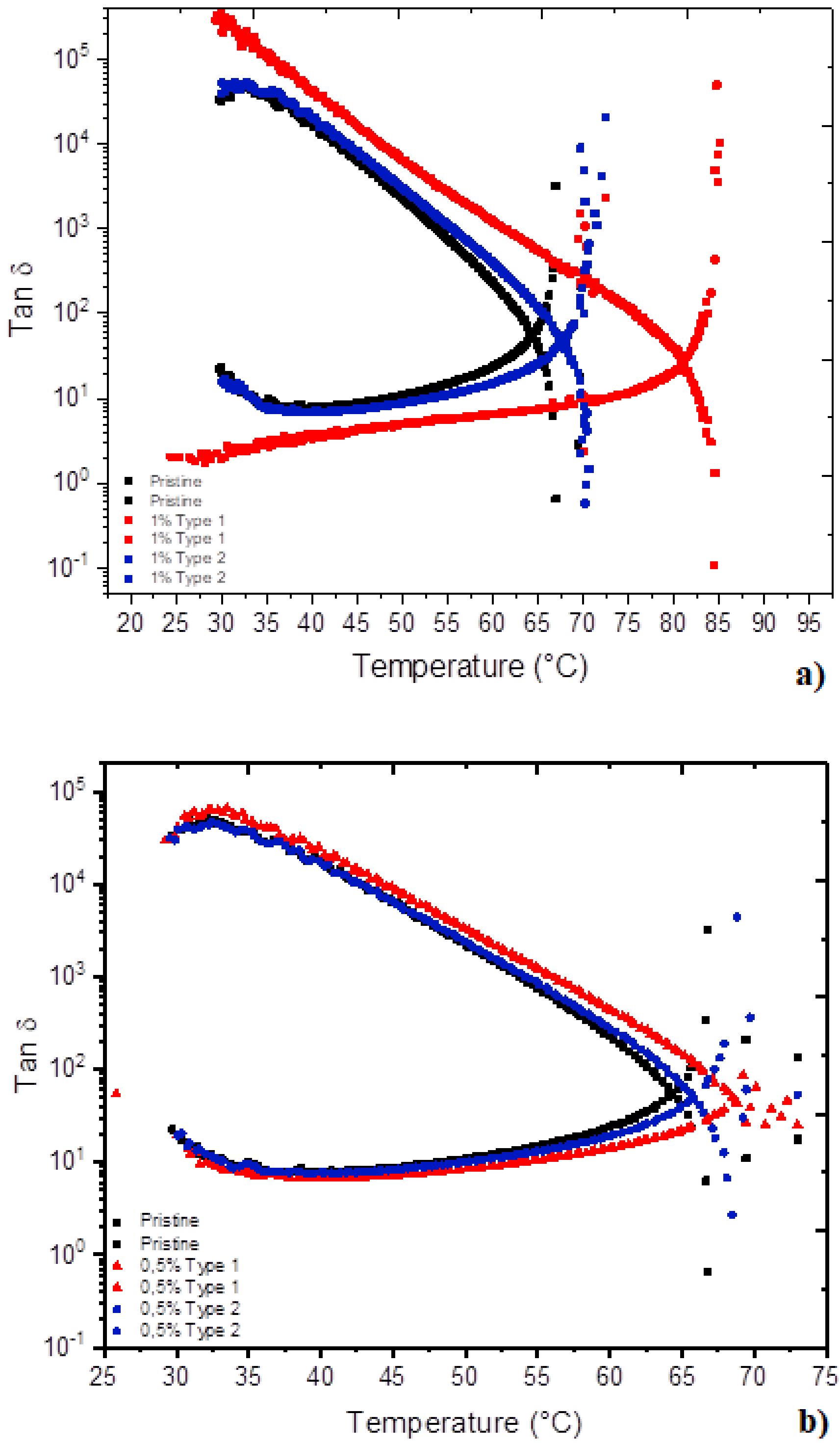


Figure 4.*TGA analysis of Type 1 CNTs sample and Type 2 CNTs sample.*

3.1 Rheology results of CNTs modified bitumen

In the present paragraph, the mechanical properties of bitumen modified by nanotubes are presented. The rheological analysis is crucial in order to understand if a addivive is effective shifting the transition from viscoelastic to liquid (higher than pristine bitumen as well as polymer modified bitumens).

Bitumen modified by Type 1 and 2 nanotubes are investigated by small stress dynamic rheology.Figure 5 illustrates the time cure tests of both the pristine and bitumens modified with CNTs (Type 1 and Type 2), to compare the rheological response of the tested systems. The effect of an inert filler CaCO3 (0.1-1 wt %) was also determined. As a general trend, the loss tangent increased and the storage modulus decreased as the temperature increased. However, the addition of CNTs to bitumen in form of solid powder dispersion provided a pronounced hardening effect for Type 1, manifested by a shift of the sol-transition temperature t* observed at higher temperature values compared to unmodified bitumen and Type 2 modified bitumen. In fact the addition of CNTs Type 2 shows only a moderate effect on the hardering effect.



Tan δ
Temperature (°C)
Pristine
Pristine
1% Type 1
1% Type 1
1% Type 2
1% Type 2
a)
Tan δ
Temperature (°C)
Pristine
Pristine
0,5% Type 1
0,5% Type 1
0,5% Type 2
0,5% Type 2
b)

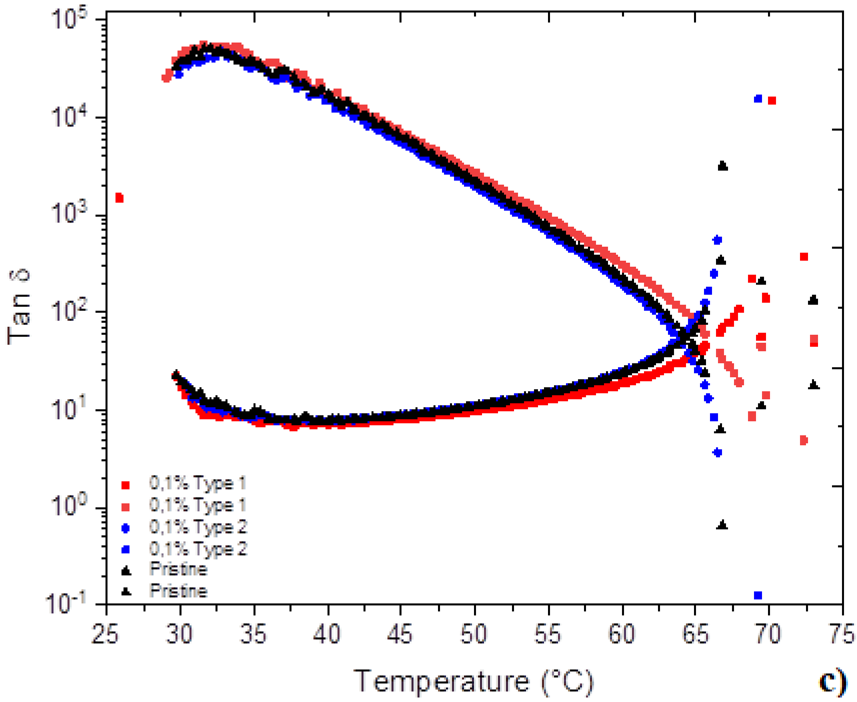


Figure 5. *Semi-log plot of temperature ramp tests for the fresh and modified bitumens formulated with: a) 1 wt%, b) 0.5 wt% and c) 0.1 wt% of Type 1 and Type 2. Left axis: storage modulus, G'(Pa). Right axis: loss tangent tanδ*

Time cure curves acquired for unmodified bitumen (both G′ and tanδ) were almost unaffected by the presence of inert filler ($CaCO_3$). It is worthy to note that the time cure test for the bitumen modified with CNTs Type 1 at 1 wt%shows a flattened behaviour of the loss tangent extending over a wide range of temperature before to diverge toward its limiting value t*. That peculiar mechanical response may be ascribed to a sort of viscoelastic buffering effect induced above a threshold amount of CNTs dispersed into bitumen. Similar rheological behaviours were observed for SBS modified bitumens [24].To better emphasize the differences between Type 1 and Type 2 modified systems, inFigure 6are illustrated theirlineartrend of t* vs additive contents (wt%). Both series of data follow linear trends as evidenced by the solid curves derived through linear fits. The efficiency as modifier agent could be easily identified in the bitumen samples mixed with Type 1 rather than withType 2, as evidenced by the higher slope. Figure 7 shows the mechanical spectra of the pristine bitumen and the one mixed with CNTs. The dynamic rheological response evidences a change only in the elastic modulus connected to the addition of CNTsin particular, it is more pronounced in the Type 1 sample.

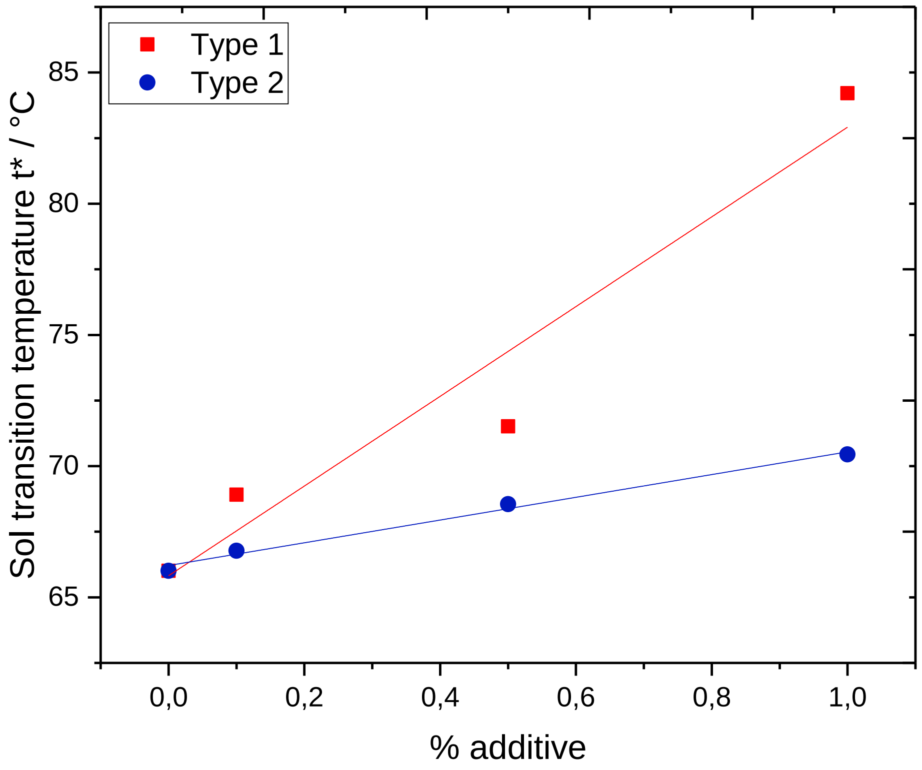


Figure 6. *Linear trends of t* vs % additive of bitumen modified with Type 1 and Type 2 CNTs*

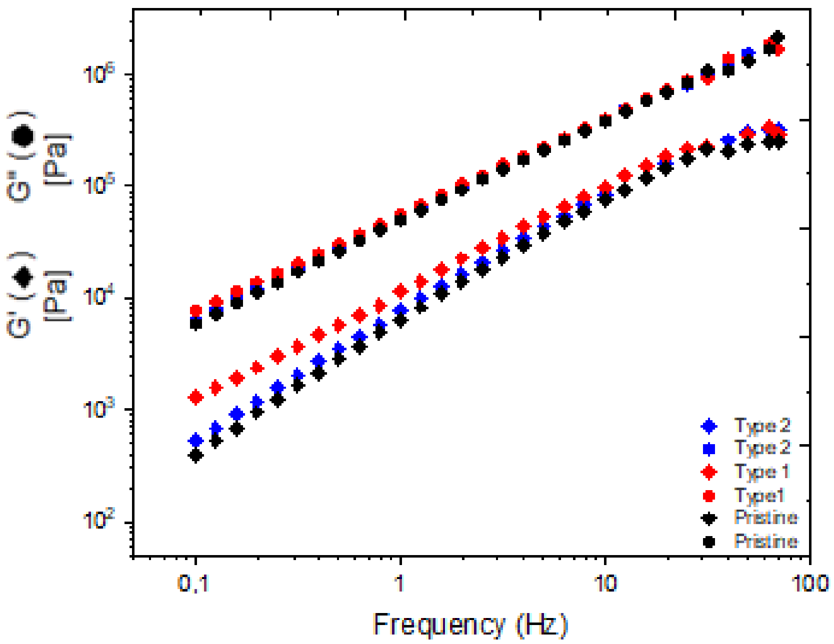


Figure 7*. Frequency sweep test of bitumen containing 1 wt % of type 1 and Type 2 CNTs at 45°C*

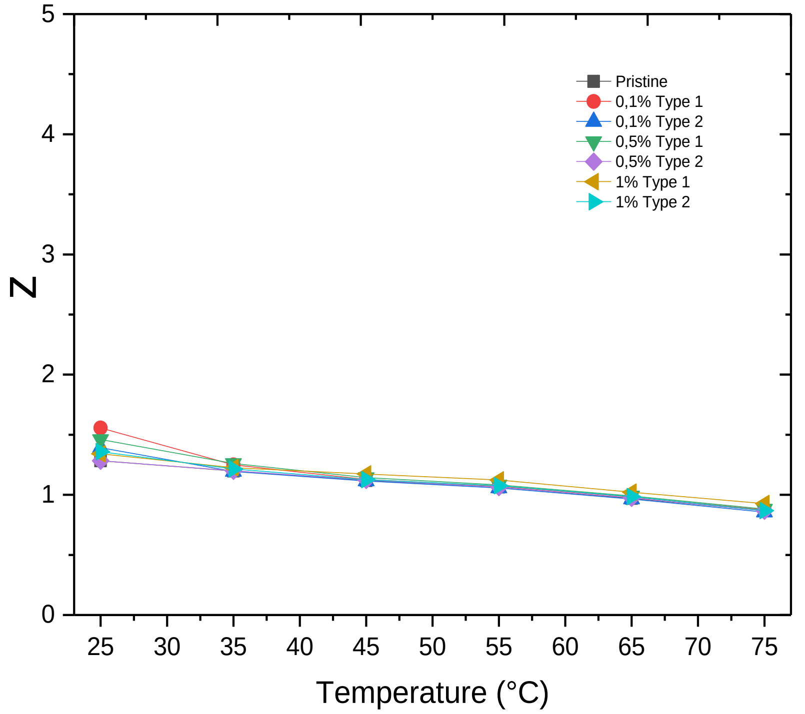
The Figure 8 shows the composition and temperature dependence of weak gel model parameters, z and A, as obtained by fitting the viscoelastic data to eqn. 2 for the Type 1 and Type 2 mixtures.

Both systems present a low flow coordination number, z, and high interaction strength values, A, in the investigated temperature range. Additionally, these data confirm the presence of the gel that becomes stronger with increasing CNTs concentration. It is worth noticing that:

- A values increase with CNTs concentration and they are higher for the mixtures containing type 1 CNTs;
- z values are close 1 evidencing a slight decreasing with increasing the temperature;

This means a hardening of the network but not an increasing of the flow units, which in turn means similar structural organization.

The rheological characterization clearly shows the effect of CNTs on the structural modification of the bitumen. The Type 1 is more affective and in our opinion can be ascribed to the higher number of the defects of the nanotubes. In principle, the hardening is due to the increase of the asphaltenes content or to creation of the network inside the bitumen. The defect can be an active center to link the asphaltene and turn on create a large network. Further experiments are needed to explore this hypothesis, but the present research is addressed to show the high potentiality of the nanomaterilas.



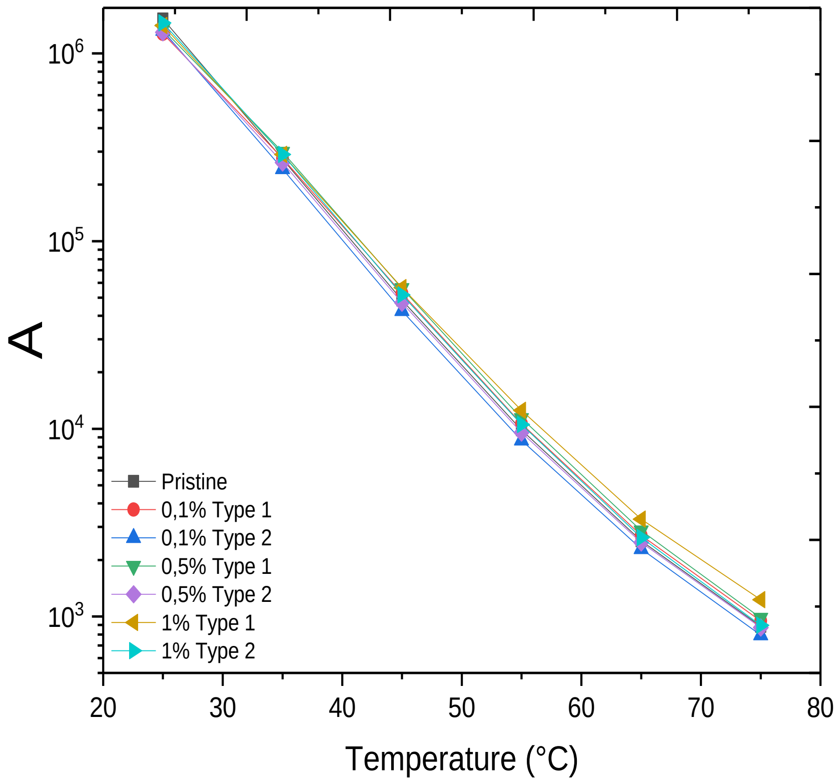


Figure 8. *Composition and temperature dependence of weak gel model parameters, z and A, for the Type 1 and Type 2 samples.*

4. Conclusion

The goal of the presented work was to understand, through a deep analysis, how the addition of carbon nanostructures could influence the properties of the commonly used bitumen. In particular, the interest was focused on carbon nanotubes (CNTs) and toward their improvement effects on the high temperature mechanical properties when used as additives in place of the common polymers actually utilized for this purpose. To do that, we made use of two different kind of CNTs, one synthetized on our laboratory (Type 1) and a second one commercially supplied (Type 2). Rheological analysis confirmed the positive role of CNTs acting as rheological modifiers, showing a better result using the laboratory CNTs than the analogous commercial ones. In particular, a minimum amount of CNTs (1 wt %) has been observed to shift the transition temperature of around 20°C. The differences between the two CNTs types, confirmed also by time cure rheological tests, was ascribed to the presence of different defects in the CNTs structures; presence confirmed by the several correlated physical chemistry techniques here presented. We think that the presented results could promote an alternative research field devoted to demonstrate the usefulness of nanotechnologies in the formulation of sustainable asphalt pavements.

5.Reference

[1] S. V. N. T. Kuchibhatla, A. S. Karakoti, D. Bera, S. Seal, One dimensional nanostructured materials, Progress in Materials Science 52 (2007) 699-913.

[2] S. Iijima, S. Saito, M. Yudasaka, Y. Miyamoto,Proceedings of the Tsukuba Symposium on Carbon Nanotube in Commemoration of the 10th Anniversary of its Discovery**,** Phys. B **323** (2002) 1-364.

[3] H. Ago, S. Imamura, T. Okazaki, T. Saito, M. Yumura, and M. Tsuji, CVD growth of single-walled carbon nanotubes with narrow diameter distribution over Fe/MgO catalyst and their fluorescence spectroscopy, The Journal of Phys. Chem. B **109** (2005) 10035 - 10041.

[4] H. Ago, K. Nakamura, S. Imamura, and M. Tsuji, Growth of Double-wall Carbon Nanotubes with Diameter-controlled Iron Oxide Nanoparticles Supported on MgO, Chem. Phys. Lett.**391** (2004) 308 - 313.

[5] F. Danafara, A. Fakhru’l-Razi, M. A. M. Salleh, D. R. Awang Biak, Fluidized bed catalytic chemical vapor deposition synthesis of carbon nanotubes - A review, Chem. Eng. Journal 155 (2009) 37–48.

[6] D. Vuono, E. Catizzone, A. Aloise, A. Policicchio, R. G. Agostino, M. Migliori, G. Giordano,Study of adsorption behavior of multi-walled carbon nanotubes towards dyes applied in textile applications, Advanced Science Letters 23 (6) (2017) 5851-5854.

[7] A. Policicchio, T. Caruso, R. G. Agostino, E. Maccallini, G. Chiarello, E. Colavita, V. Formoso, M. Castriota, E. Cazzanelli, Electronic, chemical and structural characterization of CNTs grown by SiC surface decomposition, Journal of Physics: Conference Series 100, PART 5 (2008) Article number 052093

[8] C. Oliviero Rossi, P. Caputo, V. Loise, D. Miriello, B. Teltayev, R. Angelico, Role of a food grade additive in the high temperature performance of modified bitumens, Colloids and Surface A 532 (2017) 618-624.

[9]V.N. Popov, Carbon Nanotubes: Properties and Application, Mater. Sci. Eng. R: Rep. 43 (3) (2004) 61–102.

[10] A. Policicchio, D. Vuono, T. Rugiero, P. De Luca, J. B. Nagy, Study of MWCNTs adsorption performances in gas processes, Journal of CO2 Utilization 10 (2015) 30–39.

[11] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I .Kallitsisa, C. Galiotisa, Chemical oxidation of multiwalled carbon nanotubes, Carbon 46 (6) (2008) 833-840.

[12] X. Zhao, Y Ando, Raman spectra and X-ray diffraction patterns of carbon nanotubes prepared by hydrogen arc discharge, Japanese journal of applied physics 37 (1998) 4846–4849.

[13] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy, Nano Lett. 10 (2010) 751–758.

[14] H. A. Barnes, J. F. Hutton, K. Walters, An Introduction to Rheology, Elsevier (1989)

[15] C. Oliviero Rossi, S. Ashimova, P. Calandra, M. P. De Santo, R. Angelico,Mechanical Resilience of Modified Bitumen at Different Cooling Rates: A Rheological and Atomic Force Microscopy Investigation, Appl. Sci. 7 (2017) 779.

[16] A. C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon,Phys. Rev. B 61 (2000) 14095-14107.

[17] H. Kuzmany, B. Burger, A. Thess, R. E. Smalley, Vibrational spectra of single wall carbon nanotubes, Carbon 36 (1998) 709-712.

[18] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes**,** Physics Reports 409 (2005) 47–99.

[19] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, Raman Spectrum of Graphene and Graphene Layers**,** Phys. Rev. Lett. 97(2006) 187401.

[20] L.M. Malarda, M.A. Pimentaa, G. Dresselhausb, M.S.Dresselhausc, Raman spectroscopy in graphene,Phys. Rep. 473 (2009) 51–87.

[21] S. Lee, J. W. Peng, C. H. Liu, Probing plasma-induced defect formation and oxidation in carbon nanotubes by Raman dispersion spectroscopy Carbon 47 (2009) 3488-3497.

[22] Y.A. Kim, T. Hayashi, K. Osawa, M.S. Dresselhaus, M. Endo, Annealing effect on disordered multi-wall carbon nanotubes, Chem. Phys. Lett. 380 (2003) 319-324.

[23] Y. Hsieh, Y. Chou, C. Lin, T. Hsieh, C. Shu, Thermal Analysis of Multi-walled Carbon Nanotubes by Kissinger's Corrected Kinetic Equation. Aerosol and Air Quality Research 10 (2010) 212-218.

[24] C. Oliviero Rossi, A. Spadafora, B. Teltayev, G. Izmailova, Y. Amerbayev, V. Bortolotti, Polymer Modified Bitumen: Rheological Properties and Structural Characterization, Colloid and Surface A 480 (2015) 390-397.