

GRAPHENE EMBEDDED BITUMINOUS ROADS: A NEW LOOK INTO THE DESIGN OF COMPLEX NANOCOMPOSITES

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Abstract

The chemistry of bitumen and the percentage of asphaltene can vary significantly depending on external and internal factors such as the source and method of bitumen extraction. This makes graphene embedded bitumen a complex ternary phase system. Within the framework of this paper, we focus on the phase stability and particle interaction between graphene and asphaltene in order to optimize the process of tailoring the microstructure of graphene embedded bitumen to improve the gas barrier and mechanical properties. We use characterization techniques such as rotational-rheometer, DSC, chemical titration and road engineering standards such as RTFOT and penetration-grade to study the critical-clustering-concentration, phase behavior and the impact of embedding graphene to manufacturing process of asphalt. Phase separation and agglomeration of dissimilar nanoparticles was observed when graphene embedded bitumen (1 % vol) was subjected to RTFOT, increasing the change in viscosity by around 13 % when compared to 10 % in std. bitumen. Hence this paper aspires to provide a brief look into tailoring of nanocomposites with dissimilar nanoparticles and embedding nanoparticles such as graphene into complex matrices.

Keywords: Graphene, material design, bitumen, material characterization, dissimilar nanoparticles

1. INTRODUCTION

Carbon based nanoparticles have been of interest to researchers for decades. Carbon allotropes such as graphene have been embedded in various matrices to improve the material property such as gas-barrier, thermal-conductivity and tensile-strength of the parent material. One such material is bitumen, for the reason that nearly 70 % of all global road is made of asphalt (bitumen + aggregate) [1]. Bitumen is a petroleum byproduct with complex chemistry, contains naturally occurring nanoparticles known as asphaltene [2]. There are global attempts by researchers from various fields to modify the properties of bitumen using nanoparticles. They most often aim to improve material properties such as thermal conductivity, electrical conductivity, tensile strength, rutting resistance, chemical aging and fatigue.

The two key strategies widely used are to either directly incorporate the additive to bitumen or enhance the polymer that is used in the polymer modified bitumen (PMBs). This paper does not intend to review existing works by other researchers, because Yang et al. and Fang et al. have reviewed near 100 such works by researchers in this field [3][4]. For the current study the assumptions formed by other authors, for their publications, are of interest.

Firstly, before attempting to study the mechanism of incorporating nanomaterial into bitumen it is important to define bitumen, its microstructure and properties. The true microstructure of bitumen is still widely debated but it is well established that bitumen can be divided based on various factors such as acidity, polarity, solubility and molecular weight. Separating bitumen fractions based on its solubility is the most widely used and well-established method [2]. Using this method bitumen is divided into Saturates, Aromatics, Resins and Asphaltenes. The most common and simple model that is followed to explain the arrangement of these 4 fractions is the sol-type or gel-type [2].

Yen et al. derived from x-ray diffraction that asphaltene exists as nanosheets about 8 layers [5] thick. Some well cited works, such as the one by Jahromi et al., assume bitumen to be a complex polymer with asphaltene existing as particles that are larger than 10 nm [6]. In their paper, Jahromi et al. illustrate a diagram in which nanoparticles adhere perpendicular to the asphaltene surface. This is contradictory to the assumption that asphaltene is nanometers in length and a few layers thick [2]. In another work, Yu et al. provide a model where nanoparticles are dispersed in a bitumen matrix with random orientation [7].

Arguably, in the two aforementioned papers and similar works by other researchers, the authors have assumed the behavior of bitumen as that of a viscoelastic solid-matrix rather than a viscoelastic liquid, hence assuming nanoparticle embedded bitumen to be a nanocomposite. Nanoparticle embedded bitumen should not be treated as a nanocomposite in the same way as incorporating materials such as fillers or Portland cement into bitumen, during the design of asphalt, does not categorize the newly modified bitumen as composite. Thus, modified bitumen cannot be categorized as a composite.

This paper aspires to study the first strategy and understand the underlying mechanism and limitations of directly incorporating nanoparticles into bitumen. Two critical assumptions are made during this study. Firstly, Yen's interpretation of asphaltene is considered and hence asphaltene is assumed to exist as nanoparticles and bitumen is treated as colloidal system [5]. It was shown by Induchoodan et al. that there exists a critical concentration above which nanoparticles began to agglomerate in polymer matrix [8]. Hence, the second assumption is that there must exist a critical concentration that restricts further addition of nanoparticles into bitumen and this concentration should be below the limitation predicted by Induchoodan et al for a homogenous matrix.

2. METHOD

2.1. Materials

M-grade XGNP graphene nanoplatelets (GNP) was used for the study. The GNP has a surface area of 120-160 m²g⁻¹, thickness of 6-8 nm, density of 2.2 gcm⁻³ and diameter of 25 µm. XGNP was purchased from XGScience. 70/100 grade bitumen was supplied by Skanska for the studies. Analytical grade N-Heptane was purchased from Sigma Aldrich.

2.2. Sample Preparation

XGNP was further exfoliated using shear-mixer but no chemical modification was performed on the material. Graphene and bitumen were blended using a shear mixer with 4-blade setup. Graphene was sputter coated with gold for a duration of 60 seconds while asphaltene precipitate was sputter coated with palladium for a duration of 30 seconds.

2.3. Experimental Setup

Anton paar MSR302 with a 25 mm plate-plate setup with a gap of 1 mm and temperature controller was used for the rheological studies. Oscillation test was performed on all samples with a shear strain from 0.01 to 0.16 at a constant frequency of 10 rad/s and the experiments were repeated from a temperature range of 40 °C to 70 °C with a step increment of 6 °C. For the thermal oxidation of bitumen, a rolling thin film oven test (RTFOT) was performed. Two 35 g samples for each type of bitumen was prepared and subjected to 163 °C for 85 mins in an aerobic environment with a constant air supply of 4000 ml/min and the entire setup was in constant rotation at a rate of 15 rpm.

Chemical extraction of asphaltene from bitumen was performed by dissolving bitumen in N-Heptane. The solution was stirred at 1000 rpm for 1 hour and then centrifuged using a Sigma 4-16 at 4500 rpm for 15 mins

in two 30 ml sample holders. The solution was decanted after the centrifugation. This was repeated 3 times and the precipitate was air dried. After which, Graphene and asphaltene were observed under a FEG-SEM.

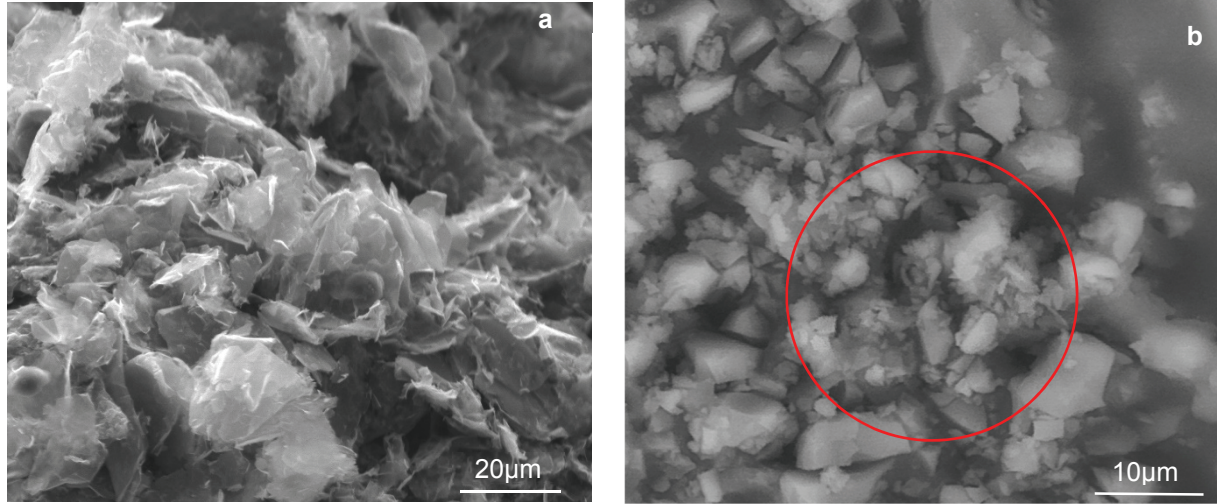


Figure 1 SEM image of a) exfoliated graphene flakes.
b) agglomerated asphaltene particles after chemical extraction from bitumen

3. HYPOTHESIS

Asphaltene should in theory have a diameter of 1-2 nm [2]. This goes to show that there are pre-existing nanoparticles in bitumen and many papers that were reviewed by Yang et al. and Fang et al. [3,4] do not account for these nanoparticles. This further implies that bitumen must not be considered as a uniform binder, polymer i.e. matrix in a conventional sense, but rather as a complex colloidal system with existing nanoparticles. Hence, adding unmodified graphene to bitumen makes the mixture an $n+1$ phase system, where $n>0$. For simplification, bitumen is assumed to be a simple two-phase colloidal system, i.e. $n=2$, we assign bitumen with a hard phase and liquid phase. The hard phase being n -heptane insoluble asphaltene, and the rest of the fractions are considered as a homogeneous liquid phase.

$$\phi_{\text{tot}} = \phi_{\text{lp}} + \phi_{\text{hp}} \quad (1)$$

Where ϕ_{tot} is the total volume fraction of the system and $\phi_{\text{tot}} = 1$. ϕ_{lp} and ϕ_{hp} are the volume fraction of liquid and solid phase respectively. By adding graphene to this system (ϕ_{gr} , volume fraction of graphene), it has gone to being $n=3$. Due to the similar dimensions and interactive forces that both graphene and asphaltene exert, there must be a common upper limit to the amount of graphene that can be added, because the two families of nanoparticles could form agglomerates with each other. This upper limit is represented by ϕ' , where ϕ' is the volume fraction beyond which nanoparticles in bitumen start to form agglomerates. Hence, there must exist an optimal ratio of graphene to asphaltene for a nanomodified bituminous system.

$$\text{i.e. } \phi_{\text{tot}} = \phi_{\text{lp}} + \phi_{\text{hp}} + \phi_{\text{gr}} \quad (2)$$

$$\text{where } \phi_{\text{hp}} + \phi_{\text{gr}} < \phi'$$

Furthermore, the volume fraction of asphaltene in bitumen increases during processing of asphalt and this increase has to be accounted during calculation. When bitumen is subjected to elevated temperatures, i.e. above 130°C, the rate of thermal oxidation of bitumen increases, this phenomenon is called short term aging. During short term aging, asphaltene fraction in bitumen increases, due to the chemical process that leads to the production of asphaltene from resins [2].

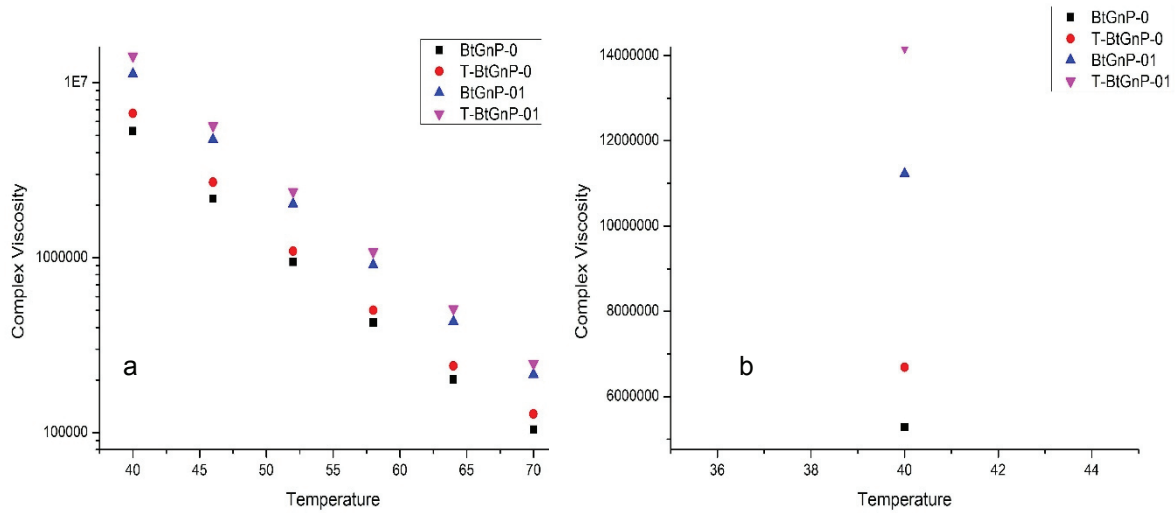


Figure 2 a) Log of complex viscosity vs temperature for neat binder and graphene embedded bitumen, before and after thermal oxidation. BtGnP – 0 and T – BtGnP – 0 are neat binder before and after thermal oxidation and T – BtGnP – 0 and T – BtGnP – 01 are graphene embedded bitumen, before and after thermal oxidation. b) Complex viscosity vs temperature of neat binder and graphene embedded bitumen, before and after thermal oxidation, at 40°C.

4. RESULTS AND DISCUSSION

(Figure 1) shows graphene sheets and asphaltene particles. It is evident from Figure 1b that asphaltene appears to be an independent hard phase, ϕ_{hp} . Asphaltene precipitates are circled red to differentiate it from the background. Asphaltene starts to precipitate when N-heptane introduced to bitumen. As the ratio of N-heptane to bitumen is increased the amount of asphaltene precipitated increases until it reaches a saturation point [2]. The precipitate is often obtained as an agglomerate and this is observed in Figure 1b.

During the rheological study bitumen was tested within its linear viscoelastic region and the properties were studied. During this study the complex viscosity (η^*) was measured instead of the shear viscosity (η), because at low frequency the viscous viscosity (η') component of the complex viscosity is approximately equal to the shear viscosity.

$$\eta^* = \eta' + i\eta'' \quad (3)$$

$$\eta'_{\omega \rightarrow 0} = \eta \quad (4)$$

This is true because at lower temperatures the contribution of the imaginary viscosity (η'') is neglectable and η^* is similar to the η' , as shown by Li et al. [9]. Since the working frequency is 10 radians the condition is applied and η^* is studied to understand the hypothesis.

$$\eta^*_{\omega \rightarrow 0} = \eta \quad (5)$$

In this study the nomenclature BtGnP shall stand for bitumen embedded with graphene and following the digits represent the volume of graphene in bitumen. The prefix 'T' shall be used to describe any material that has been thermally oxidized and should not be confused with temperature. Neat binder, which is bitumen with no graphene (BtGnP – 0), and graphene embedded bitumen with 1 % volume of graphene (BtGnP – 01) were thermally oxidized, compared and studied.

Graphene, asphaltene and graphene embedded bitumen were successfully characterized. BtGnP – 01 exhibited immediate signs of agglomerations. Considering $\eta^*_{BtGnP-01}$ and $\eta^*_{T-BtGnP-01}$ as the complex

viscosities before and after RTFOT of BtGnP – 01 and similarly $\eta_{\text{BtGnP}-0}^*$ and $\eta_{\text{T-BtGnP}-0}^*$ as the complex viscosities before and after RTFOT for BtGnP – 0, we can plot a graph with \log of η^* as abscissa and temperature (T) as the ordinate, as shown in **(Figure 2 a)**. It is immediately observed that there is a larger increase in complex viscosity of GnP-01 when compared to BtGnP – 0 after thermal oxidation by RTFOT. Upon further observation, it is evident that η^* for BtGnP – 01 increased by 12.21-14.65 % while η^* for BtGnP – 0 increased by only 10.31 %, **(Figure 2b)**.

Rheological studies of polymers have shown that the size of the molecules/particles has a direct relationship to the viscosity of the material. The larger the particle size the higher is the viscosity [10] and Induchoodan et al. showed that increasing the volume fraction of the nanoparticles leads to an increase in the viscosity of the nanocomposite [8]. So, both neat binder and graphene embedded bitumen should show an increase in the viscosity after RTFOT.

In both BtGnP – 0 and BtGnP – 01, there is an increase in asphaltene concentration. Thus, the contribution of ϕ_{hp} must be similar and ϕ_{gr} is fixed, and its contribution is observed in the difference between $\eta_{\text{BtGnP}-01}^*$ and $\eta_{\text{BtGnP}-0}^*$. Thus, the increase in the complex viscosity of BtGnP – 01 after RTFOT can be related to the agglomeration of graphene and asphaltene. Therefore, the total volume of nanoparticles $\phi_{\text{hp}} + \phi_{\text{gr}}$ has exceeded ϕ' , and hence

$$\eta_{\text{T-BtGnP}-01}^* - \eta_{\text{BtGnP}-01}^* > \eta_{\text{T-BtGnP}-0}^* - \eta_{\text{BtGnP}-0}^* \quad (6)$$

This goes to validate the hypothesis proposed in this paper. Thus, while directly incorporating nanofillers such as graphene into bitumen the total volume fraction ϕ' , for graphene and asphaltene, must be accounted rather than ϕ_{gr} only.

5. CONCLUSION

Bitumen is considered to be a colloidal solution. Asphaltene and graphene were shown to be dissimilar nanoparticles. An upper limit ϕ' was predicted for bitumen, beyond which graphene and asphaltene start to agglomerate with each other. This was experimentally determined by thermally oxidizing bitumen, both with and without graphene, and comparing their respective complex viscosities.

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REFERENCE

- [1] Introduction, in: HUNTER, Robert, SELF, Andy and READ, John. *Shell Bitumen Handbook (6th Edition)* - 4.2.2 More Complex Models, pp. 05-10.
- [2] Constitution and Structure of Bitumens, in: HUNTER, Robert, SELF, Andy and READ, John. *Shell Bitumen Handbook (6th Edition)* - 4.2.2 More Complex Models, pp. 54-57.
- [3] YANG, Jun and TIGHE, Susan A Review of Advances of Nanotechnology in Asphalt Mixtures. *Procedia - Social and Behavioural Sciences*. 2013. vol. 96, no. 2, pp. 1269-1276.
- [4] FANG, Changqing, RUIEN, Liu, and SHAOLONG, Yan, Nanomaterials Applied in Asphalt Modification: A Review, *Journal of Materials Science & Technology*. 2013. vol. 29, pp. 589-594.
- [5] DICKIE, John P and YEN, Teh Fu, Macrostructures of the Asphaltic Fractions by Various Instrumental Methods, *Analytical Chemistry*. 1967, vol.39, pp. 1847-1852
- [6] JAHROMI, Saeed and KHODAI, Ali, Effects of Nanoclay on Rheological Properties of Bitumen Binder, *Construction and Building Materials*. 2009, vol. 23, pp. 2894-2904

- [7] YU, Jian-Ying, FENG, Peng-Cheng, ZHANG, Heng-Long, and WU, Shao-Peng, Effect of Organo-Montmorillonite on Aging Properties of Asphalt, *Construction and Building Materials*. 2009, Vol. 23, pp. 2636-2640
- [8] INDUCHOODAN, Govindan and KÁDÁR, Roland, Tailoring Polymer Nanocomposite Microstructure by Controlling Orientation, Dispersion and Exfoliation of GnP in LDPE via Extrusion Flow, *Annual Transactions of the Nordic Rheology Society*. 2016, vol. 26, pp. 187-191
- [9] LI, Shu-Ping, ZHAO, Ge and CHEN, Hong-Yuan, The Relationship between Steady Shear Viscosity and Complex Viscosity, *Journal of Dispersion Science and technology*. 2006, vol.26, pp. 415-419
- [10] RICHARDS, John, Viscosity and the Shapes of Macromolecules, *Journal of Chemical Education*. 1993, vol. 70, pp. 685-689