

# Investigation of the Rheological Properties of Asphalt Binder Containing Graphene Nanoplatelets

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**Norwegian University of Science and Technology**  
**Department of Civil and Transport Engineering**

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of Asphalt Binder Containing Graphene Nanoplatelets

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Norwegian University of  
Science and Technology

## Forord

Denne masteroppgave ble gjennomført i samarbeid med NTNU faggruppe Veg, transport og geomatikk. Målet med oppgaven var å undersøke effekten av grafen som additiv til bindemiddel, prosjektet ble utført i løpet av våren og sommeren 2015.

Det er mange som fortjener takk til sin faglige og moralsk støtte gjennom min arbeid og utdanning i siste to årene. Jeg vil først takke Inge Hoff, Sara Anastasio og Helge Mork for god, konstruktiv og målrettet veiledning i løpet av prosessen. En stor takk til mine kolleger Lisbeth Johansen, Kine Nilssen, Andreas Kjosavik og Carl Thodesen for hjelp med laboratoriearbeid, faglig rådgivning og sosialbidrag. Takk til alle ansatte ved NTNU og SINTEF for fremstilling av et godt arbeidsmiljø og sin støtte.

Til sist en stor takk til mine foreldre og min kjære Vildana for støtte på hjemmebanen.

Trondheim, 08.02.2016

Haris Brcic

## Sammendrag

Årlig produksjon av asfalt i Norge er ca. 6 millioner tonn per år med det total verdi ca. 5 milliarder kroner. En stor del av dette beløpet er for reasfaltering av det eksisterende vegnettet. Ofte er grunnen for tidlig reasfaltering for storr spor og sprekker i asflatdekker. For å redusere muligheten for spordannelse og oppsprekking av asfaltdekker med ett av to oppfylles: økning strekkfasthet av asfaltblanding (1) eller å øke fleksibiliteten (2). Dette kan oppnås ved å forandre bindemiddelegenskaper ved anvendelse av additiver. Grafen er et nytt produkt, som nylig ble oppdaget av to forskere ved Universitet i Manchester. Det antas at grafen har et stort potensial i mange områder. Grafen har blitt brukt som tilsetningsstoff til sement i betongindustrien med suksess. Produsenter av grafen markedsfører bruk av grafen i bindemiddel, men få resultater er tilgjengelig til nå.

Denne masteroppgave har som mål å undersøke effekten av grafen i vegbitumen, ved bruk av Superpave PG-klassifisering.

Resultantene viser at tilsetning av grafen forbedrer mostand mot permanent deformasjon for blandinger med grafeninnehold 2% og over. Lavtemperaturegenskaper holder seg innenfor samme PG klasse, men beregnet brudd temperatur viser at bindemiddel blir stivere og dette blir påvirker lavtemperatur egenskaper.

## **Summary**

Annual production of asphalt in Norway is about 6 million tons per year, in total values about 5 billion NOK. A large part of this amount is for repaving existing road network. Often reasons for early repaving are rutting and cracking damages of pavements. In order to reduce potential for rutting and cracking of the asphalt pavements one of two objectives must be accomplished: increase mixture tensile strength (1) or increase mixture flexibility (2). This can be achieved by altering binder properties by using additives. Graphene is a new product, recently discovered by two scientist in University of Manchester. Graphene is believed to have a great potential in many applications, in civil engineering successfully used as additive to cement. Producers of graphene largely promote use of graphene in binder but few results are available until now.

This master thesis aims to investigate effect of graphene on bitumen by using Superpave PG-classification.

Results show that graphene modified binders have improved resistance to permanent deformation when mixed added 2% or more graphene. Low temperature properties remain within the same PG class but calculated failing temperature shows that the binder becomes stiffer then reference binder and therefore more prone to low temperature cracks.

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## Abbreviations

ASTM	=	American Society for Testing and Materials
BBR	=	Bending beam rheometer
CNT	=	Carbon Nanotubes
DSR	=	Dynamic shear rheometer
J <sub>nr</sub>	=	Unrecoverable creep compliance
G*	=	Complex modulus
GO	=	Graphene Oxide
HMA	=	Hot Mix of Asphalt
J <sub>n</sub> r	=	Non-recoverable creep compliance
m	=	Master curve slope
MSCRT	=	Multiple Stress Creep and Recovery Test
PAV	=	Pressure Aging Vessel
PG	=	Performance Grade
R	=	Elastic Recovery
rpm	=	Revolutions per minute
RTFO	=	Rolling Thin Film Oven
S	=	Creep stiffness
SSA	=	Specific Surface Area
sin	=	Sine function
SHRP	=	Strategic Highway Research Program
$\delta$	=	Phase angle
$\mu$	=	lateral contraction

## 1. Introduction

Norway is a country with about 93.000 km public roads divided in different categories from national to local significates, 50% of traffic accrues on 11% of road network. A large distance between dense populated south, west coast divided by fjords and high mountains and far north, a large, but low populated area with many low-traffic roads and small roads are some one of the diversities who makes this country unique in terms of road building and managing.

Many countries are facing increased traffic volume, loads and tire pressure, who is often reason for increased rutting and cracking of roads. Climate has also great importance especially for countries such as Norway, where major climate variations throughout the year play a big role in pavements lifetime. Use of fossil fuels has led to increased CO<sub>2</sub> levels in atmosphere, this affects climate globally and makes it more difficult to predict future conditions. Most of the scenarios suggest that the weather in future will be more unstable and extreme with milder winters on average (3).

Asphalt pavements performance is largely dependent of binder type and its properties to resist high and low temperatures in combination to heavy traffic loads trough the pavements lifetime. Some binders require modification to meet specifications. Binder modifications have been practiced in past 50 years or so with significant increase in past decade because of the following factors: increased demand of HMA pavements, specifications given from road authorities, environmental and economic issues, etc. (4).

Asphalt pavements are classified as flexible pavements because the total pavement structure deflects under loading. A stiffer binder can withstand higher temperature but is more prone to low temperature cracking, while a softer binder will perform better in cold climates but deform at higher temperatures. A balance between these properties when choosing the type of asphalt binder is critical to meet the road administration requirements for asphalt pavements throughout its service life. Polymer modifiers, crumb rubber and hydrated lime are widely used additives in the asphalt industry that have ability to improve the performance and hence the lifespan of the bituminous material.

Among other emerging technologies, graphene has been used in concrete applications (5), (6) and it is reported that graphene can contribute increase in comprehensive strength of concrete for 50% by using CNT (7), increase compressive and flexural strengths when added into cement (8), increase in elastic module of concrete by 35% (9), increase in load capacity for 47% and fracture toughness for 25% (10), and it is believed to have a great potential in many applications as well as in asphalt pavements (11), (12) (13).

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities (12). Few illustrative examples are given in Figure 1. Deepening of its type graphene can be hydrophobic or hydrophilic, with different tensile strength, volume and purity depending of production method.

The producers of this nanotechnology promote the use of graphene in asphalt mixtures however, no data on its actual performance is currently available. This thesis aims therefore to investigate the effect of this particular additive on the rheology of the bitumen depending on its content and its homogeneity level.

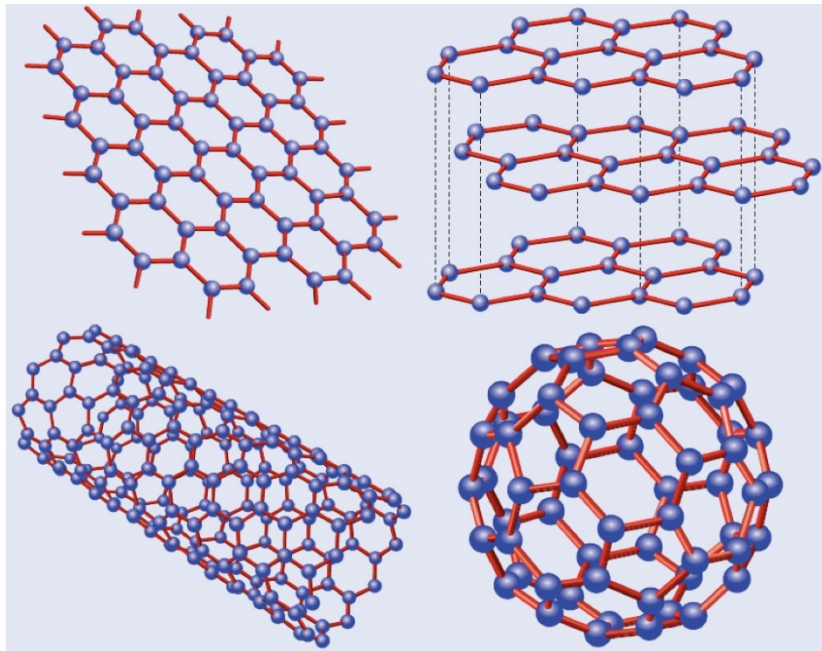


Figure 1: Graphene illustration (15)

*Graphene and its descendants: top right: graphene; top left: graphite = stacked graphene; bottom right: nanotube=rolled graphene; bottom left: fullerene=wrapped graphene. Picture taken from; [www.graphene.nus.edu.sg](http://www.graphene.nus.edu.sg).*

## 2. Scope of Research

This research investigate asphalt binder properties with graphene as an additive. The Dynamic Shear Rheometer or DSR can be used to provide an approximation of the graphene effect after given mixing time on the rheology of the graphene-modified binder compared to reference binder.

The main objective of this research can be summarized as follows:

- To compare the effect of the graphene when mixed with bitumen trough the change in  $G^*$  of the binder by testing in *DSR*
- Change in stiffness after testing in *BBR*

The research was done in following steps:

1. Mixing bitumen with graphene in 6, 15, 20, 26, 30 and 40 minutes in percentages of 1%, 1.5% and 2%.
2. Determining the high temperature properties of the unaged binder with and without graphene using *DSR*.
3. Determining the high temperature properties and elastic recovery after subjecting to artificial short term aging *RTFOT* using *DSR* and *MSCR* test.
4. Determining intermediate temperature and fatigue properties after subjecting to artificial long term aging *PAV* using *DSR*.
5. Determining low temperature properties and crack resistance after *PAV* aging using *BBR*.

### 3. Materials - finding the right graphene type

Graphene is a new material, recently discovered by two scientist in 2003 in University of Manchester when they discovered a way to separate flakes from graphite to create flakes which were just one atom thick. Six years after they had isolated graphene for the first time their work was rewarded with Nobel Prize in physics (14). This two dimensional material is believed to have a great potential in many applications. Graphene has been used successfully as an additive to cement. Nanomaterials have been identified as the strength and durability enhancers of cementitious composites provided that the nanomaterials are well dispersed (5). Some producers promote use of graphene as additive to bitumen but few results are published until now. As referred in first chapter, the graphene used in concrete can increase compressive strength, elastic module, fracture toughness and load capacity.

A lack of specific data on graphene as additive to binder when choosing graphene type has made my task difficult in the beginning. The properties of different graphene types are presented in Table 1 (except graphene nanoplatelets) as reported by (5). Graphene types currently available on marked where not well described as in Table 1 when it comes to properties relevant for material for use in civil engineering.

Material	Elastic modulus (GPa)	Tensile strength (GPa)	Density (kg/m <sup>3</sup> )	Diameter thickness (nm)	Surface area (m <sup>2</sup> /g)
Graphene	1000	~130	2200	~0.08	2600
GO	23-42	~0.13	1800	~0.67	700-1500
CNTs	950	11-63	1330	15-40	70-400
Carbon fiber	7-400	0.4-5	1770	6000-20000	0.134
Graphene Nanoplatelets	-	5	1000	2-10	20-40

Table 1: Material properties of typical fillers, *reference (5)*

As can be seen from the Table 1, some of the properties vary with several orders of magnitude. However, it is not obvious how the different properties will influence on binder performance. High prices of graphene due to its new production technology has limited the possibilities of testing on large scale in this study. Graphene oxide or *GO* has been evaluated as possible graphene type but abandoned in order to avoid premature aging of bitumen due to oxidation that can lead to stiff and brittle binder more prone to fatigue and low temperature cracking in early stage of pavements lifetime. The high price of *GO* would have also limited the research to only few tests.

Graphene nanoplatelets have been chosen based on properties as purity, specific surface area and tensile strength on one hand and price on another. Specific surface area or *SSA* is area of a material per unit of mass, a finer material tends to have larger surface area and vice versa. Being the weight equal an additive with larger *SSA* is supposed to have higher interaction with other materials. Graphene possesses a higher elastic modulus and tensile strength when compared to any other material. Therefore, if assumed that the continuous graphene sheet is evenly distributed through the binder as reinforcing material, it should strengthen the binder in terms of tensile and flexural strengths or prevent large cracks propagation with a dense system of microcracks, shown from cement and concrete experiences.

According to the producer, this type of graphene can improve composites tensile strength, stiffness, corrosion resistance, abrasion resistance and anti-static electricity and lubricant properties (15).

Nanoplatelets offered a good compromise as starting point for my research, thickness 2~10nm and "diameter" of ~5 $\mu$ m give these platelets an aspect ratio of ~1000, and therefore good strengthening characteristics. Considering graphene properties and asking price by choosing Graphene nanoplatelets, I was able to produce and test several mixtures when compared to other graphene types. The characteristics of "Graphene Nanoplatelets" (2-10nm) are given in Table 2.

<b>Bulk Characteristics</b>				
Appearance	Carbon Content	Bulk Density	Water Content	Residual Impurities
Black and Grey Powder	>99.5%	~0.10 g/ml	<0.5 wt%	<0.5 wt%
<b>Physical Properties</b>				
Diameter	Thickness	Specific Surface Area	Electrical Conductivity	Tensile Strength
~5 $\mu\text{m}$	2-10 nm	20-40 $\text{m}^2/\text{g}$	80000 S/m	5 Gpa
Structure Features: The layered structure is as same as graphite crystal				

Table 2 Graphene technical data sheet

Graphene nanoplatelets are hydrophobic and phobic to most polar solvents, possibility of mixing graphene first with surfactant and then dispersing in binder was considered but abandoned due to lack of necessary equipment.

Bitumen is a collection of polar and non-polar molecules. The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the non-polar materials (16). Since graphene nanoplatelets are considered as hydrophobic it is expected that graphene will react with the non-polar groups of bitumen binder.

In order to confirm graphene volume a simplified measurement has taken where 1g of graphene is poured in test tube and compared with same weight of hydrated lime whose Specific Surface Areal is between 15-20 $\text{m}^2/\text{g}$ . Relationship after this measurement was that Graphene nanoplatelets has five times larger Specific Surface Area than referent hydrated lime (Figure 2).

It would be ideal to compare effect of graphene with several binder types for instance a soft, normal and stiff binder for conditions in Norway, by that comparing effect on low and high temperature properties. Because of the limited amount of graphene I was able to use only one type of binder. In central Norway most common binder type used on medium trafficked roads is 70/100 penetration graded or PG 64-22, which makes it a logical first choice and easy accessible binder.





Figure 2: Volume: hydrated lime 1gram vs graphene 1gram.

Since no indication were given from the graphene producers, a first trial was made with a 2% by weight content of additive in the bitumen. The percentage was afterwards varied in order to individuate the area of use.

## **4. Test procedures**

This chapter is summary of available binder test methods and authors conclusions based on findings after literature review. The chapter also provides a description of the work in different stages of this study, the experimental plan to complete the proposed research and the procedures employed to accomplish the objectives of the research.

### **4.1 Binder test methods**

Current test methods used in European specifications are empirical in nature and not suited for the development of rational performance-based relationships between binder and mixture properties. Binder properties are mostly being investigated and described by conducting penetration and viscosity testing or rheology testing. Research shows that penetration graded and viscosity graded binders are limited in their ability to fully characterize asphalt binder for use in *HMA* pavements (17).

Rheology is the study of flow, widely used to explain the elastic and viscous behavior of bitumen, when subjected to a stress (18-19). Complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) are considered to be the fundamental rheological parameters, normally measured from a device known as Dynamic Shear Rheometer (*DSR*) (20). A number of studies has been conducted to investigate asphalt binder rheology (21). Performance graded tests are developed as part of the SHRP research program during late 80s and early 90s of past century in United States. Superpave research effort under SHRP program have introduced PG tests and specifications to address *HMA* pavement performance. It addresses three main causes of deteriorating of a pavement, which are rutting-related permanent deformation, traffic-induced fatigue cracking and low-temperature thermal cracking (22).

Following this logic, the *PG* tests were chosen including *DSR* and Bending Beam Rheometer (*BBR*) on fresh, Rolling Thin Film Oven Test (*RTFOT*) and Pressure Aging Vessel (*PAV*) aged bitumen.

Testing was done for different binder content and conditioning state: original, short term aged and long term aged binder by performing *PG* grading of graphene-modified binder and comparing to properties of reference binder.

The fundamental material properties of binders related to these modes were identified by measuring stiffness module “*S*” a parallel to E-modulus who contains elastic and viscous deformations, in order to model behavior of viscoelastic materials such as bitumen. The performance grades, or *PG*, in the Superpave binder specifications are based on  $T_{max}$  who is the maximum average 7 days pavement temperature and  $T_{min}$  lowest cracking temperature of binder. The long-term aged binder is also tested for its resistance to fatigue cracking by using *DSR*. The properties of the binder change rapidly at high temperatures or during the asphalt production and the paving of the road. The binder properties change during service life mostly through oxidation. Superpave uses *RTFOT* to simulate short-term bitumen aging, during production and paving phase and *PAV* to simulate long-term bitumen aging that should simulate aging on the field. An old bitumen becomes more stiff and brittle by that more prone to low temperature cracking and fatigue failure. According to this, *DSR* test are conducted to evaluate resistance to rutting on original-unaged binder and *RTFOT* while binder resistance to low temperature cracking is tested on *BBR* and *DTT* after aging on *RTFOT* and *PAV*. Fatigue cracking properties are also tested on binder after *RTFOT* and *PAV* aging (23).

Experience has shown that test methods used for conventional or unmodified binders do not adequately characterize rutting for modified binders. In order to better understand effect of modification an *MSCR* test method has been introduced. *MSCRT* provides a more accurate measure of rutting resistance by taking into account properties of modified binder. The test method measures two values; *J<sub>nr</sub>* or non-recoverable creep compliance, and *R*, the elastic Recovery at two stress levels (24).

## 4.2 Binder blending

There is no available literature or research about blending graphene with the bitumen, therefore I turned to the field of cement and concrete materials who used successfully graphene as additive. Nanomaterials have been identified as strength and durability enhancers of cementitious composites if the nanomaterials are well dispersed (25). Depending on the graphene type, different methods of blending and dispersing have been applied and different effects achieved. The main influence of nanoparticles when added to cement is increased hydration rate (26,27) where 1D nano fiber and 2D nano sheet not only accelerate hydration but also reinforce the cement matrix from their large aspect ratios (28,29). *GO* sheets are hydrophilic and highly dispersible in water, also highly reactive *GO* nanomaterial and can exhibit a lower elastic modulus and tensile strength (30). Some graphene types are dispersed in water and mixed on 120rpm before adding to cement (31), Yousefi recommended dispersing nanoparticles in lime-saturated water followed by ultrasonication, prior to mixing with cement (32). The idea of dispersing graphene in surfactant and ultrasonication was abandoned due to lack of equipment for dispersing and mixing. Graphene nanoplatelets unlike *GO* are hydrophobic or phobic to most polar solvents, based on that I concluded that mixing with solvent prior to adding to binder without being able to predict the outcome could take unwanted turn and therefore abandoned.

Simplified blending approach was selected and performed by IKA mixer with maximum speed of 530 rpm. The intention was to not use maximum blending speed to avoid lost on nanoplatelets who could be thrown away from the metal container when high shear mixing is applied and to simulate the mixing process in asphalt plant by blending graphene with binder on lower speeds. The binder was heated in a metal container in average 400grams by mix at a temperature 160°C. After preheating the binder was placed in the oven with an attached shear mixer where graphene was added by hand pouring it into the metal container, short after pouring the mixing propeller was lowered in approximately middle of the metal container. the amount of graphene added was 1%, 1,5% and 2% mixed in different time intervals from 6 to 40 minutes (Figure 3).

Due to high specific surface area, graphene has shown to be difficult to mix with bitumen without appropriate dosing equipment for contents of 2% graphene or more. The high specific surface area of graphene and volume of metal container has set blending limitations. In additions to mixing with IKA mixer, a portion of hand mixing was required when mixed 2% by weight of graphene after 6 minutes in order to blend layer of graphene on top of the binder. Graphene 2% have been mixed at higher speed (300rpm) then 1% and 1,5% (150rpm).

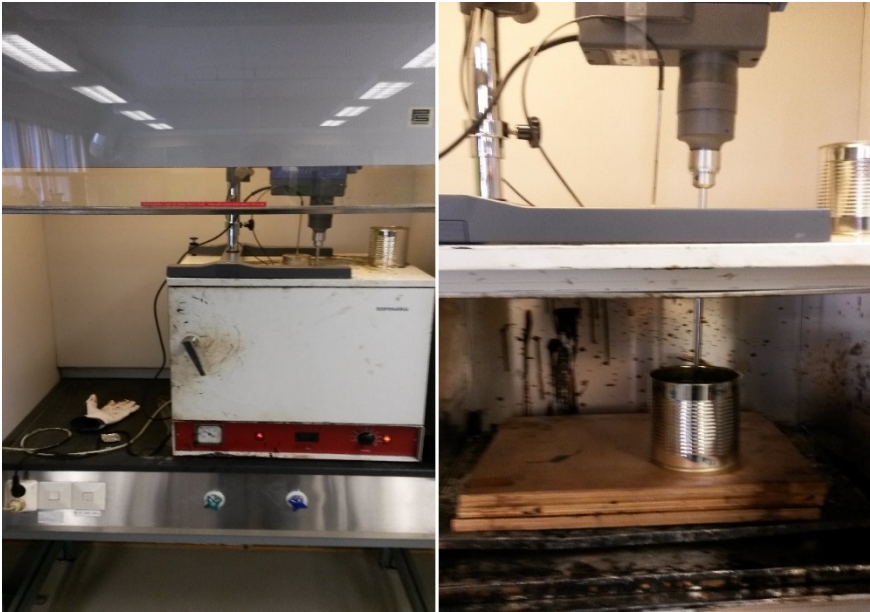


Figure 3: Blending oven with mixer

Some blending had visible traces of graphene lumps after mixing or after making *DSR* samples, in particular the blendings with 2% graphene after 6 minutes mixing and 1% graphene after 20 minutes of mixing on low speed (150rpm) (Figure 4).

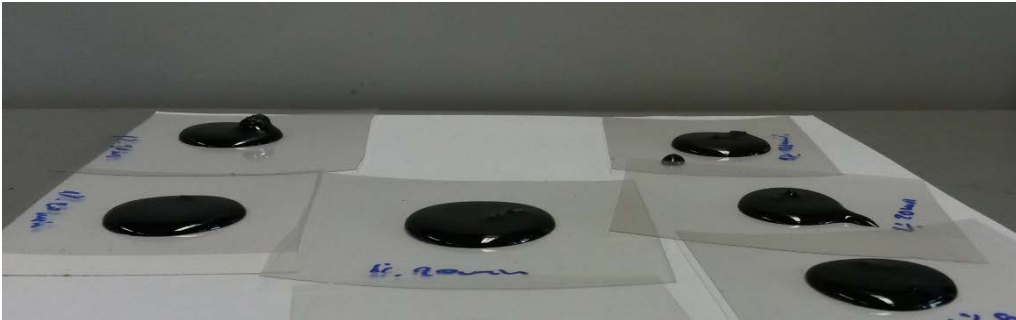


Figure 4: DSR samples with lumps

### 4.3 Dynamic Shear Rheometer

DSR is apparatus used to characterize the viscous and elastic behaviour of bituminous binders at medium and high temperature. This characterization is used in in the Superpave *PG* binder specifications, where *DSR* measures the complex modulus  $G^*$  and phase angel  $\delta$ , complex shear modulus can be considered the samples total resistance to deformation when repeatedly sheared while phase angel ( $\delta$ ) is delay between applied shear stress and resulting strain (Figure 5). Relation  $G^*/\sin(\delta)$  is found to correlate well with rutting resistance at high temperature, while the relation  $G^*\sin(\delta)$  is found to correlate well with fatigue resistance at intermediate temperatures. As described earlier, the test is performed on both original and aged binder (Table 3).

The *PG* grading was performed in accordance to NS-EN 14770 (33).

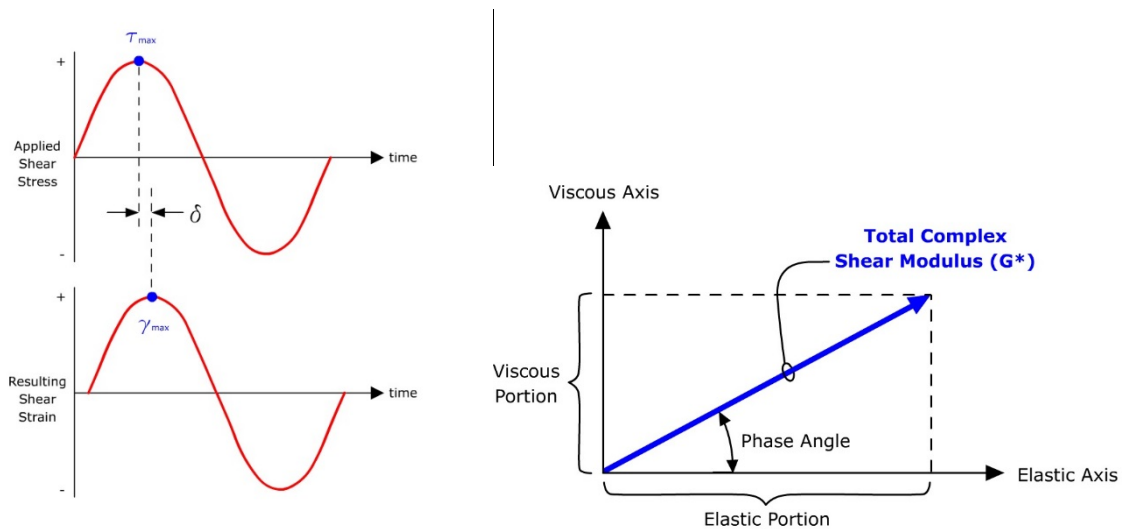


Figure 5: DSR curves and complex modulus  $G^*$  - *pavementinactive.com*

Conditioning	Threshold	Spindle size	Gap opening
Original binder	$G^*/\sin(\delta) > 1kPa$	25 mm	1 mm
RTFOT-aged	$G^*/\sin(\delta) > 2.2kPa$	25 mm	1 mm
PAV-aged	$G^*\sin(\delta) < 5MPa$	8 mm	2 mm

Table 3: *PG* grading overview

#### 4.4 Multiple Stress Creep and Recovery test

MSCR test is an additional test implemented by *DSR*, this test method is originally developed for polymer modified binders. MSCRT is latest improvement to the Superpave PG Asphalt Binder specification, developed and mostly used in USA. This new test provide the user with a new high temperature binder specification that more accurately indicate the rutting performance. A major benefit with this test is that eliminates the need to run tests such as elastic recovery, toughness and ductility. MSCR test uses the well-established creep and recovery concept to evaluate the binders potential for permanent deformation. A one second creep load is applied on the binder sample. After load is removed, the sample is allowed to recover for 9 seconds (34) Figure 6. The two main parameters of *MSCRT* are elastic response  $R$  and non-recoverable creep compliance  $J_{nr}$  of modified binder by subjecting binder to 10 repeated stress and relaxation levels first at 0,100 kPa and then at 3200 kPa. Test is performed on Rolling thin oven film test (*RTFOT*) aged binder at highest passing temperature for *DSR* test. Polymer modification curve is introduced to distinct between different modified binder types and classify them in to categories:

1.  $J_{nr} = 2.0 - 4.0 =$  Standard
2.  $J_{nr} = 1.0 - 2.0 =$  Heavy
3.  $J_{nr} = 0.5 - 1.0 =$  Very Heavy
4.  $J_{nr} = 0.25 - 0.5 =$  Extreme

The material response in the MSCR test is significantly different than the response in the existing PG tests. In the PG system, the high temperature parameter,  $G^*/\sin\delta$ , is measured by applying an oscillating load to the binder at very low strain. Due to the low strain level, the PG high temperature parameter doesn't accurately represent the ability of polymer modified binders to resist rutting. Under the very low levels of stress and strain present in dynamic modulus testing, the polymer network is never really activated. In the existing PG specification the polymer is really only measured as a filler that stiffens the asphalt. In the MSCR test, higher levels of stress and strain are applied to the binder, better representing what occurs in an actual pavement. By using the higher levels of stress and strain in the MSCR test, the response of the asphalt binder captures not only the stiffening effects of the polymer, but also the delayed elastic effects (34).

The MSCRT has been used to test and rank SBS and SB polymers, elvaloy, crumb rubber, latex and chemically modified binders. Categorization of the binder with graphene itself was not objective in this case, but polymer modification curve was useful for comparison with the other modified the binders. Test was performed in accordance to ASTM D7-405-10a standard (35).

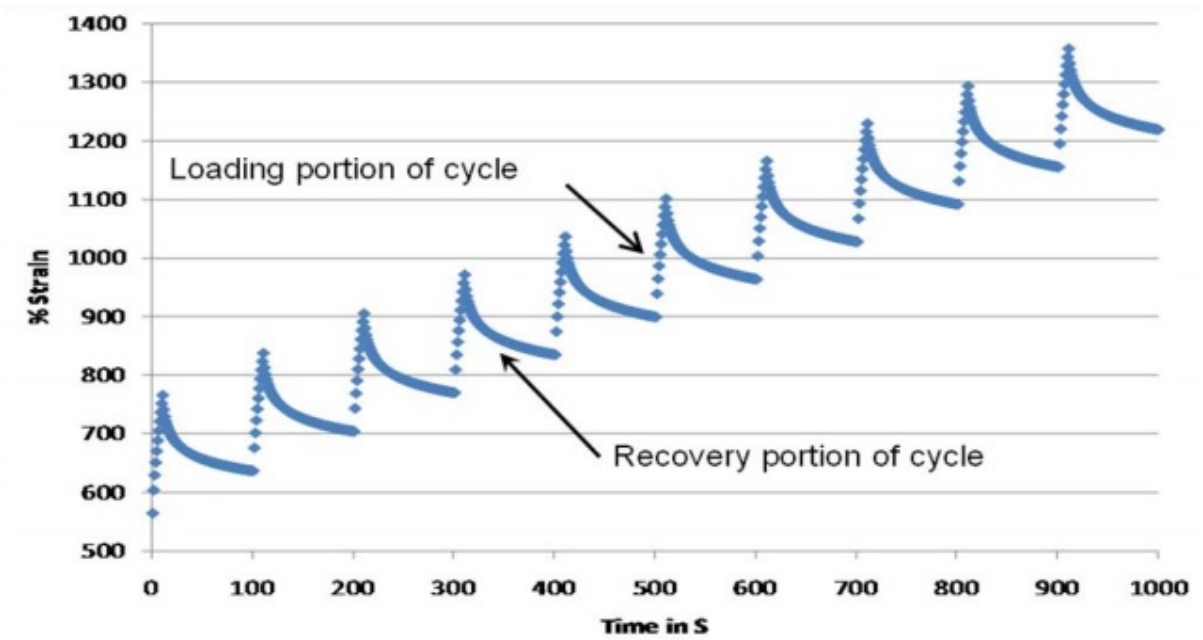


Figure 6: Example for modified binder response to repeated loading, (34).

MSCRT non-recoverable creep compliance is calculated as follows:

$$J_{nr} = \frac{\text{Unrecovered Shear Strain}}{\text{Applied Shear Stress}}$$

MSCRT recovery is calculated as follows:

$$\text{Recovery} = 100\% * \frac{\text{Peak Strain} - \text{Unrecovered Strain}}{\text{Peak Strain}}$$



## 4.5 Binder aging

The properties of binder change rapidly during mixing in the asphalt plant and during compaction. The binder characteristics change also during pavement lifetime at lower temperatures due to oxidation. The Superpave binder specifications uses two types of aging procedures to simulate these two types of aging. Rolling thin oven film test or *RTFOT* simulates aging after asphalt production and paving (36). The *RTFOT* procedure takes unaged binder samples in cylindrical glass bottles and places these bottles in a rotating carriage within an oven. The carriage rotates within the oven while the 163°C temperature ages the samples for 85 minutes. The *RTFOT* has problems with highly viscous binders (some polymer modified asphalt binders and PG 70-XX and higher) because they do not flow properly in the bottles as they are rotated (37). After *RTFOT* aging is completed a part of binder intended for DSR testing is removed, the rest of binder is subjected to Pressure aging vessel or PAV (40). The PAV is intended to simulate long-term aging of the binder by subjecting the binder to high air pressure and temperatures (38).

## 4.6 Bending Beam Rheometer

When the temperatures drops, asphalt pavements contracts and builds up internal stresses. If this contraction occurs fast enough the pavement may crack because it does not have time to relax. These types of cracks are typically called a thermal cracks they are often transversal to driving direction on road. A binder should be soft and able to quickly relax during strain at low temperatures in order to resist cracking when the temperature falls. The *BBR* test used to determine binders resistance to low temperature cracking determines the creep rate ( $m$ ) is defined as the slope of log-stiffness vs. log-time (60 seconds). The observed deflection and creep stiffness are calculated as function of time, as illustrated in Figure 7 (picture taken from pavementinteractove.com). The creep stiffness is inversely proportional to the deflection. The test is performed at plus 10°C above minimum temperature. Samples used for *BBR* are after PAV-aging (39).

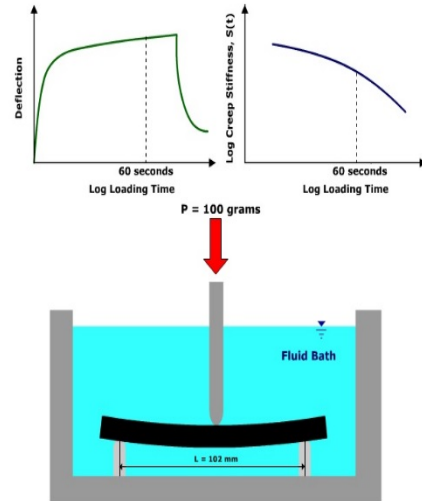
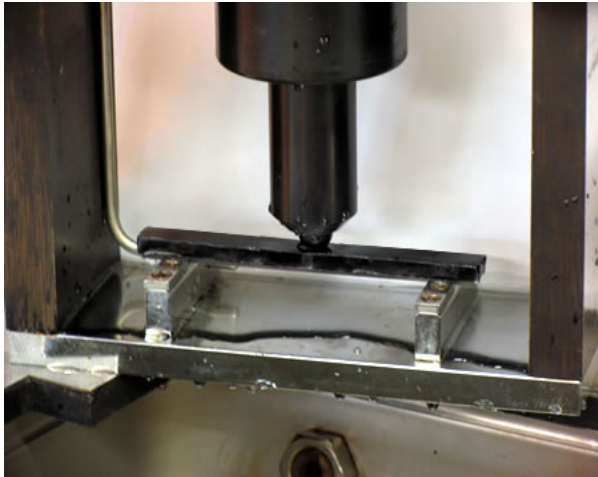


Figure 7: Illustration and schematic overview of BBR - *pavementinteractive.com*

The binder stiffness should not exceed  $S > 300 \text{ MPa}$  after 60 s and the creep rate  $m$  should be  $m < 0.3$  at 60 s. The stiffness of the binder after 60 s at given temperature plus  $10^\circ\text{C}$  is comparable to the stiffness of the binder after 2h at same temperature, if the binder is in the linear viscoelastic region.

## 5. Results

Unmodified binder of 70/100 penetration grade was used as reference binder and mixed with graphene nanoplatelets in percentages of 1%, 1.5% and 2%. Table 4 shows failure temperatures and *PG*-grading according *ASTM* specifications (20), failure temperatures are interpolated. Note that the *BBR* results are based only on one samples per temperature.

<b>Binder</b>	<b>Mixing time (min)</b>	<b>Original (°C) Average)</b>	<b>CI*</b>	<b>RTFO (°C) Average)</b>	<b>CI*</b>	<b>PAV (°C) Average)</b>	<b>CI*</b>	<b>BBR (°C)</b>	<b>PG</b>
<b>Reference</b>	0	65,1	0,4	64,9	0,3	20,5	2,9	-17,5	<b>64-22</b>
<b>Graphene 1% LS</b>	15	68,3	0,8	67,8	0,5	21,4	1,0	-15,7	<b>64-22</b>
<b>Graphene 1%</b>	40	68,4	1,2	69,0	2,2	21,3	1,7	-14,8	<b>64-22</b>
<b>Graphene 1,5%</b>	15	70,5	5,9	69,1	0,4	16,2	25,7	-16,2	<b>64-22</b>
<b>Graphene 1%</b>	15	67,1	0,4	69,3	0,3	21,1	1,7	-15,8	<b>64-22</b>
<b>Graphene 1%</b>	30	68,2	1,2	68,9	0,3	19,5	3,4	-13,1	<b>64-22</b>
<b>Graphene 2%</b>	6	109,7	92,8	-	-	22,7	4,9	-13,0	-
<b>Graphene 2%</b>	15	71,6	0,6	75,2	0,3	18,1	14,0	-15,7	<b>70-22</b>
<b>Graphene 2%</b>	25	71,7	7,0	73,4	1,2	22,2	0,6	-12,6	<b>70-22</b>

Table 4: Failure temperatures and *PG*-grading (CI – Confidence Interval).

*BBR* results are uncomplete, temperature are based only on one sample per temperature due to materials limitations.

## 5.1 Dynamic Shear rheometer

The DSR results are shown as complex modulus  $G^*$  and phase angle  $\delta$  at all test temperatures. In Figure 8 two sets of samples are presented separately from the others because of inhomogeneity within the samples due to insufficient mixing time: Graphene 1% 20 minutes mixing time and Graphene 2% after 6 minutes of mixing time had visible lumps on DSR samples. However, samples without lumps from these two groups (1%-20min and 2%-6min) were chosen and tested at DSR. Mixes with graphene are presented compared to results after mixing original binder for 15 minutes without any additives. These mixes are marked as *Mixing time 15min LS* or Low Mixing Speed (150 rpm) and *Mixing time 15min NS* or Normal Mixing Speed (300 rpm). Mixing effect in form of  $G^*/\sin\delta$  is visible in Figure 9. Note that Mixing time 15 LS and NS are shifted on 14 and 16min (dark blue and brown points) in order to have better overview on Figure 8.

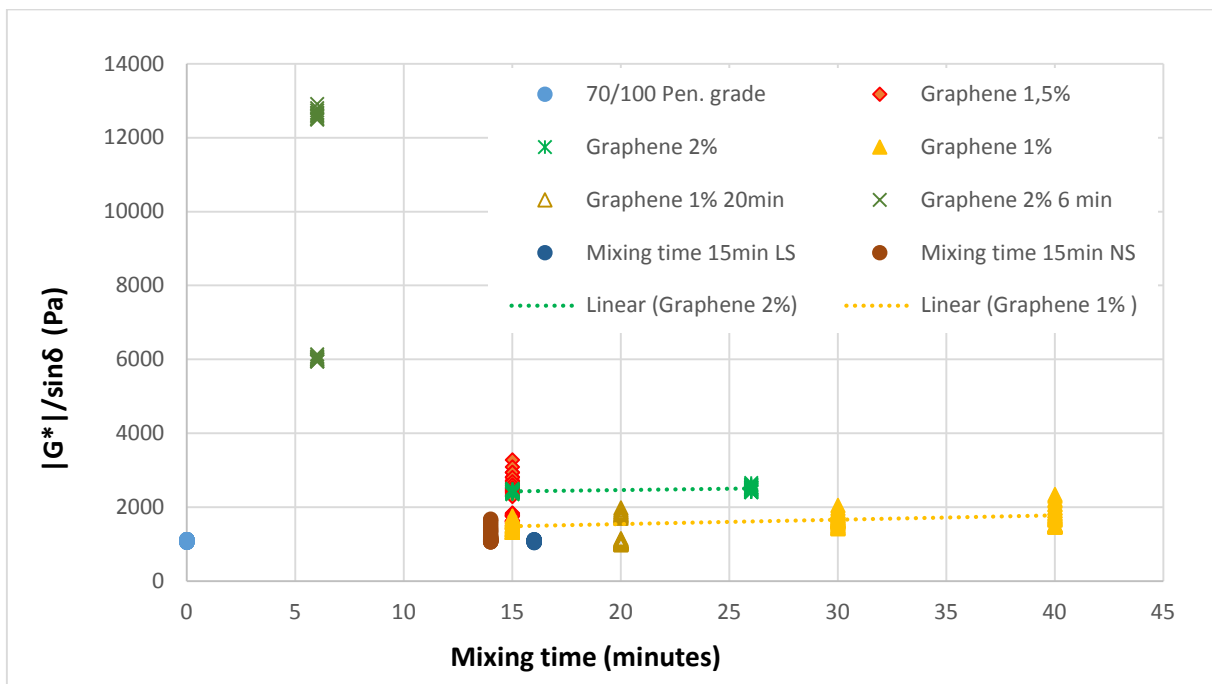


Figure 8: DSR results for unaged binder at 64°C.

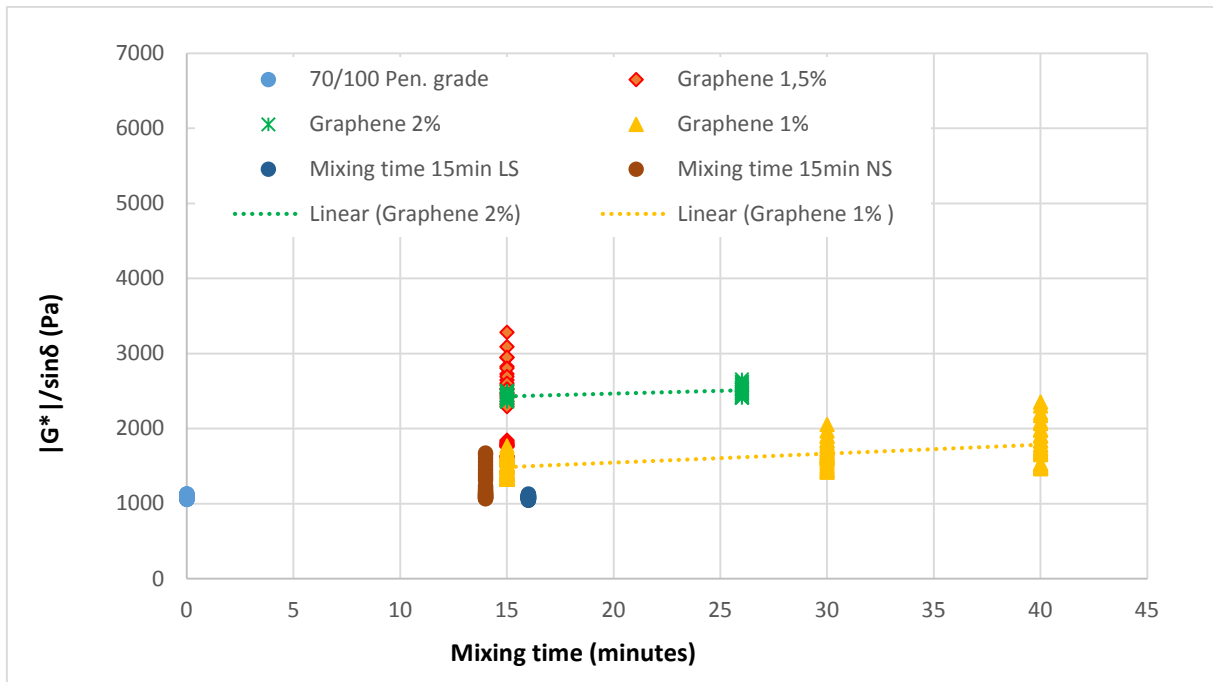


Figure 9: DSR result for unaged binder at 64°C without inhomogeneous samples.

Figure 10 shows DSR results for RTFOT samples at 64°C. All sample groups without visible lumps.  $G^*/\sin(\delta)$  for graphene 2% after 15min and 26min is presented at 64°C for better compression although they have passed 70°C. Due to insufficient material, group Graphene 2% after 6min mixing was not tested after RTFOT aging.

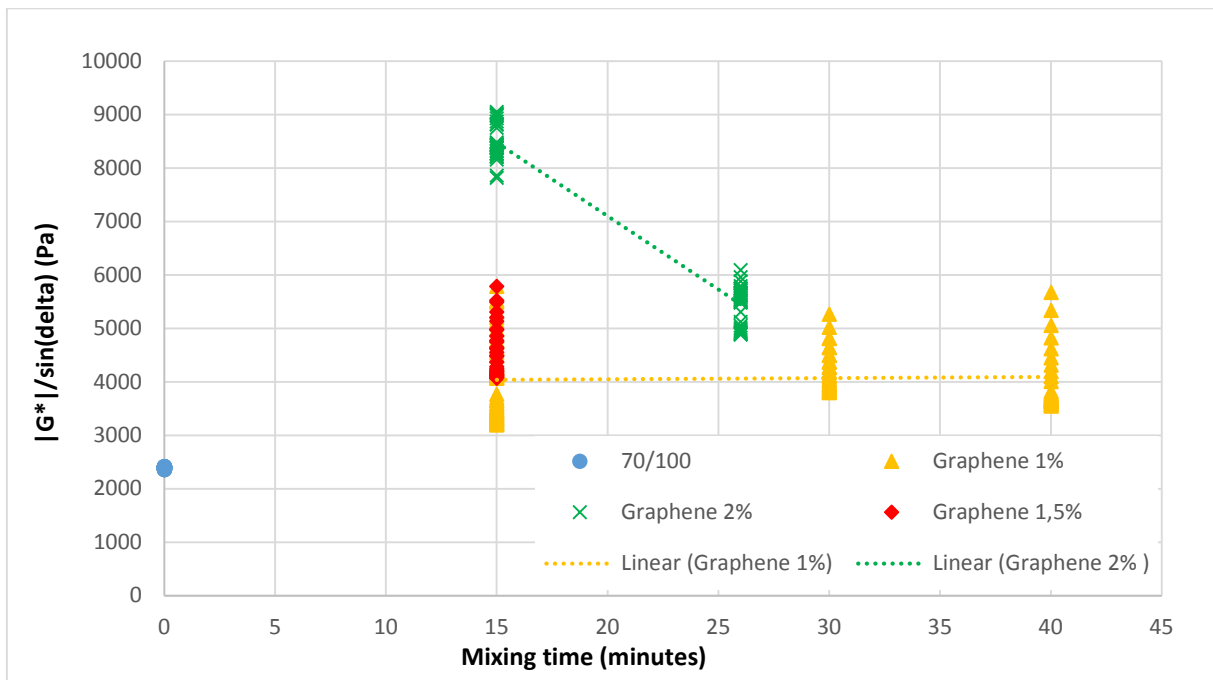


Figure 10: DSR results for RTFOT aged binder at 64°C.

Results after *PAV DSR* of all graphene groups compared to reference binder are widely spread. Sign that graphene is not mixed good enough (Figure 11).

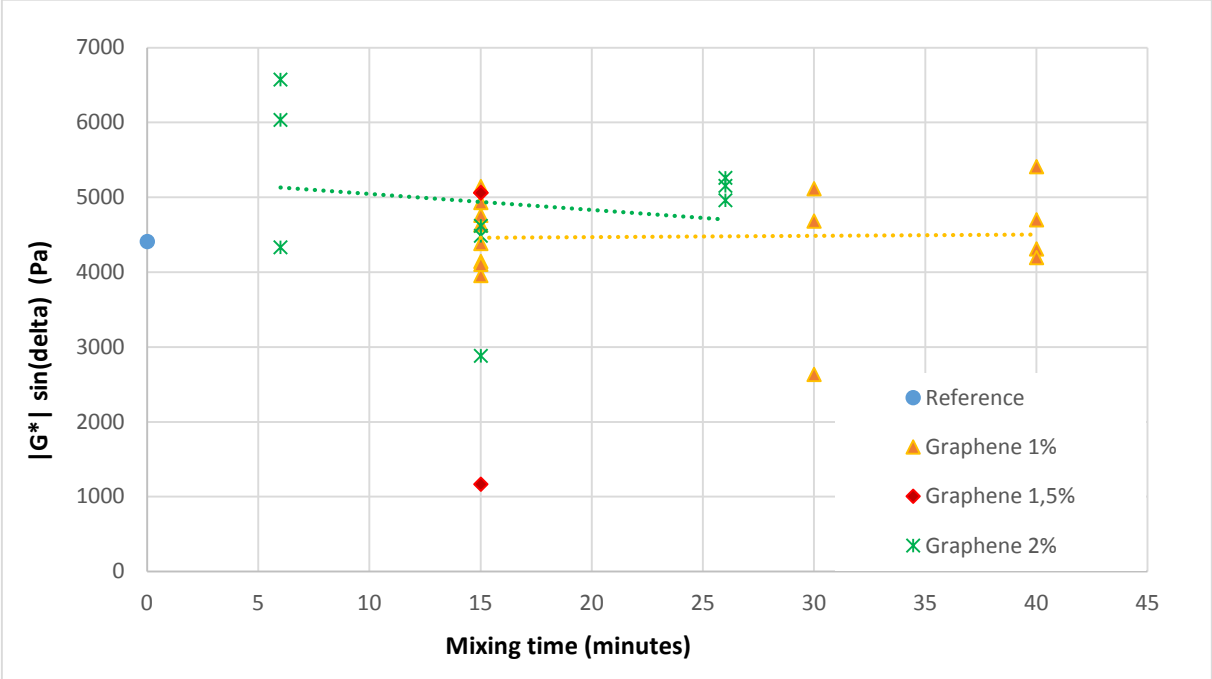


Figure 11: DSR results for PAV-aged binder at 22°C.

## 5.2 Multiple Stress Creep Recovery

*MSCR* test results are given for the non-recoverable creep compliance  $J_{nr}$  (Figure 12) and creep recovery  $R$ , Figure 13 for shear stress of 3,2kPa. The test has been carried out at the highest passing temperature during the *PG*-grading on *RTFOT* aged binder. The reference binder has therefore been tested at a different temperature compared to the samples containing graphene, see Table 4. Two key parameters are evaluated after *MSCR* test,  $J_{nr}$  and % $R$  and plotted on polymer modification curve for comparison. The results are presented in Figures 12 to 14.

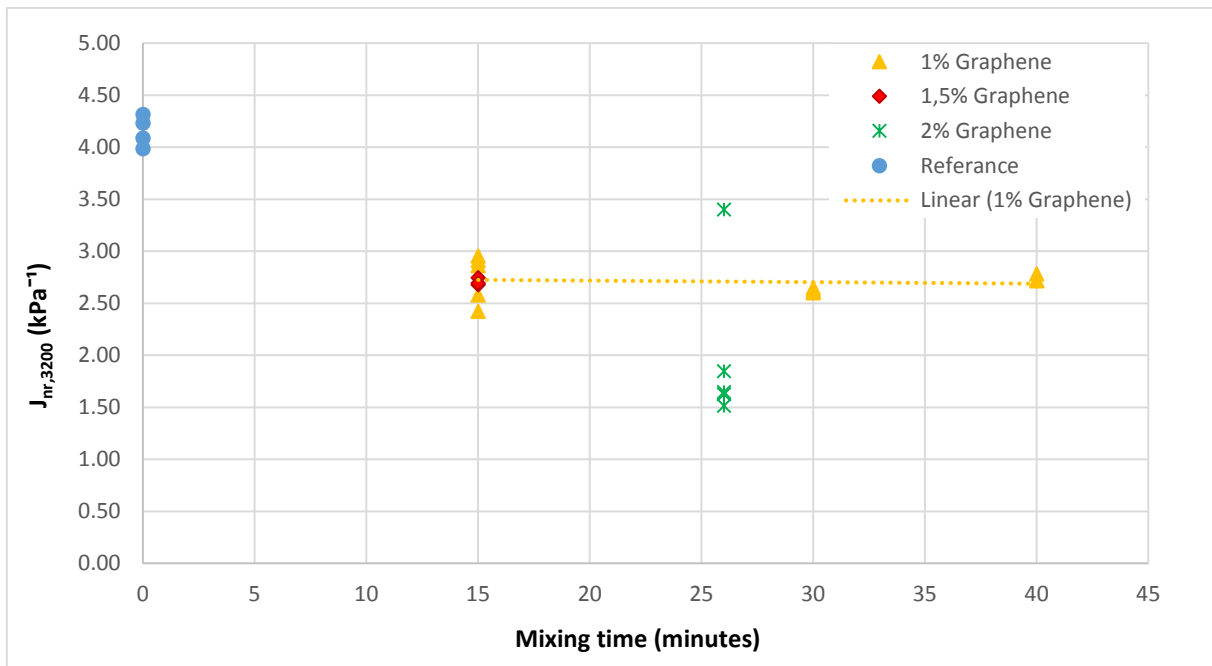


Figure 12: *MSCR* Non-recoverable creep compliance  $J_{nr,3200}$

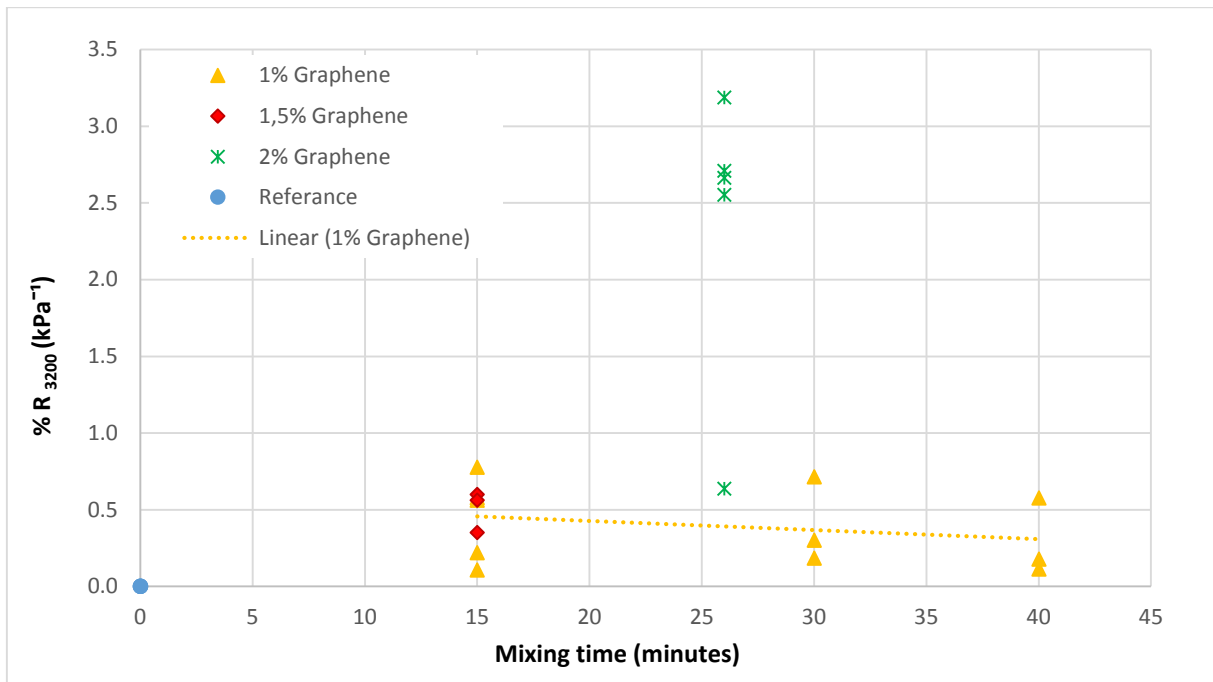


Figure 13: MSCR percent creep recovery at 3,2kPa

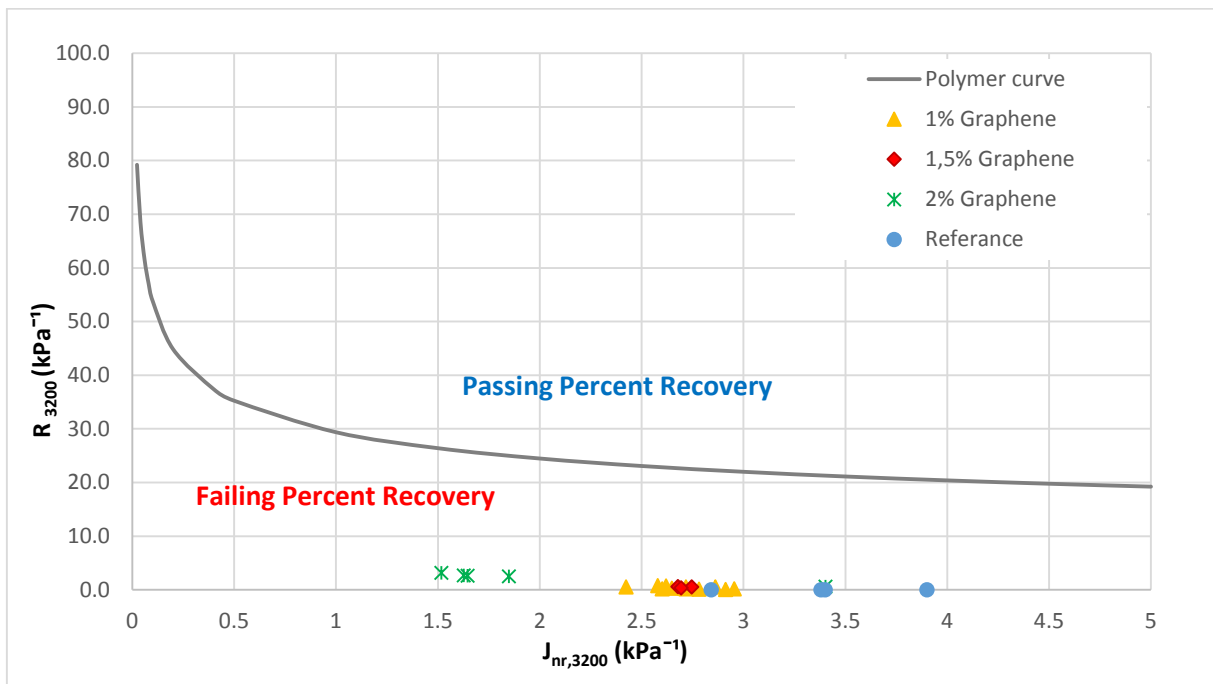


Figure 14: Polymer modification curve, in terms of polymer modified binders.



### 5.3 Bending Beam Rheometer

The *BBR* test results for creep stiffness measured after 60 seconds loading time are shown in Figure 15 and Figure 16. Note that due to lack of *PAV* aged material only one sample per temperature was tested.

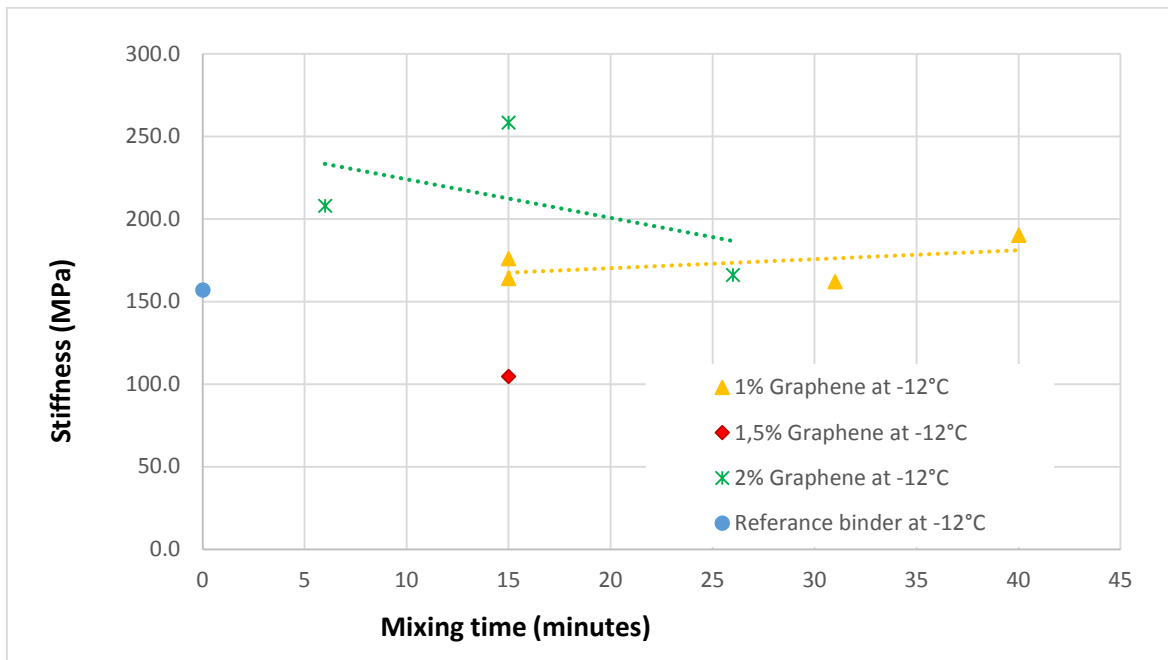


Figure 15: BBR results for PAV-aged binder at -12°C, Stiffness (MPa)

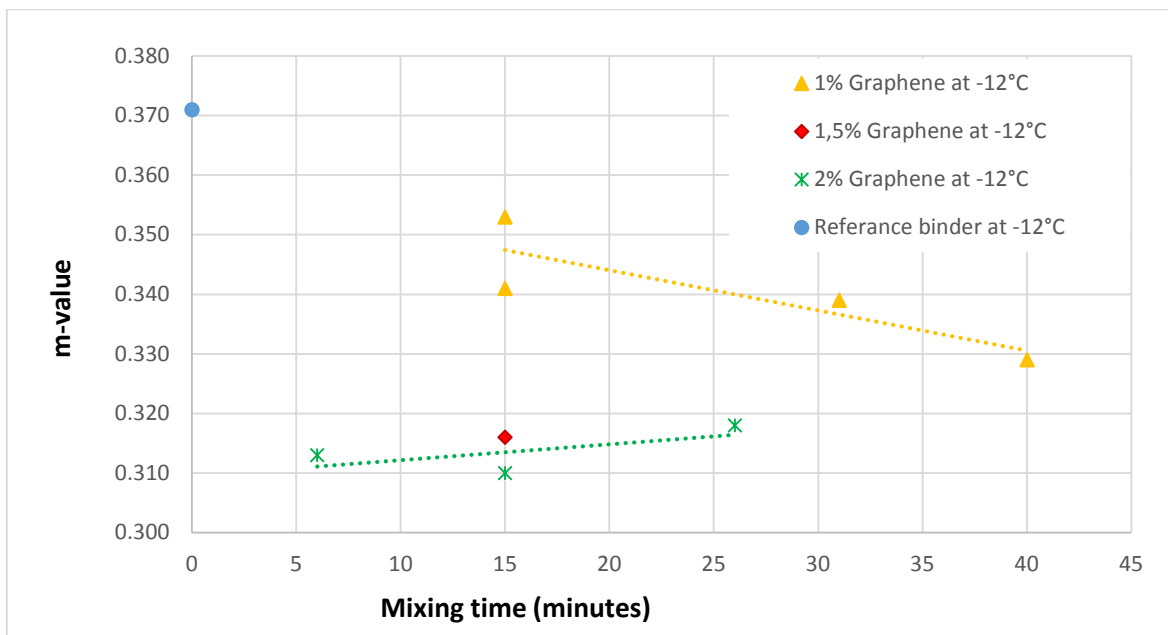


Figure 16: BBR results for PAV-aged binder at -12°C, m-value

## 6. Discussion

This study presents a first step towards the use of graphene as additive to bitumen. Mixing time, percentage of graphene added to bitumen and type of fresh binder were chosen depending on the laboratory experience with other types of additives, bitumen and adjustments during the laboratory work. There is no available standard or recommendation about the use of graphene as additive to bitumen, or guidelines for use in bitumen given from producer of graphene.

Unaged reference binder was mixed in period of 15 minutes on what is marked as LS-low speed (150rpm) and NS-normal speed (300rpm) to isolate mixing effect. Results shown in Figure 8 marked with brown and dark blue points shows mixing effect on original binder, where the results obtained after mixing on lower speed gives denser data points than mixing on higher speed. As expected, 6 minutes mixing time gave large gaps between data points while longer mixing time for graphene gives more concentrated data point of  $G^*/\sin(\delta)$  and  $G^*\sin(\delta)$ , it seems that after the samples mixed for 15 minutes achieved the maximum values. Graphene mix with 2% after 6 minutes had visible lumps traces on *DSR* samples. Lumps occurred also when mixed graphene 1% after 20 minutes without stopping. Test results after *DSR* presented in Figure 8 are from picked samples without visible lump traces. It is not clear why have lumps occurred on 1% mix after 20 minutes mixing on 150 rpm and on the other mix after 15 min same rpm, possible reason could be in difference type and amount of hand mixing after mixing with IKA mixer. Mixing speed has varied depending of percentage of graphene.

Results after *RTFOT* aging shows that  $G^*\sin(\delta)$  increases by adding more graphene. All *DSR* samples were without any visible lump traces. Results after *RTFOT* are shown at 64°C for better comparison, although groups with 2% graphene after 15 and 26 minutes mixing had passed 70 °C. Drop in  $G^*\sin(\delta)$  for group of 2% from 15 to 26 minutes mixing is possibly a sign of inhomogeneity in mixture, one can only conclude that difference in  $G^*\sin(\delta)$  is caused by variation in graphene content between sample groups (2% 15 minutes and 2% 26 minutes).

Test results on *DSR* after *PAV* shows “randomness” or variation of graphene effect on all graphene groups. Large gap in  $G^* \sin(\delta)$  are also noticeable when compared to reference binder probably sign that effect of graphene nanoplatelets is not spread homogenously.

Reduction in *Jnr* and increase in elastic recovery after *MSCRT* when compared to reference binder is significant as shown in Figure 122 and Figure 133, however when results plotted on polymer modification curve one can better notice modification degree when compared to polymer modified binders, Figure 144.

*BBR* results are presented with great insecurity since only one sample was tested per temperature. Minimum passing temperature is interpolated between the last passing temperature and the failing temperature. The m-value seems to decrease with increasing graphene content while the stiffness is very scattered with short mixing time compared to longer mixing periods. It is not clear to which extent is utilized effect of graphene in binder or what is optimum or maximum for use in bitumen besides what is maximum for mixing equipment. Properties of Graphene nanoplatelets compared with other graphene types in Table 1 shows that Graphene nanoplatelets have much higher tensile strength and about half density than Graphene Oxide used as additive to cement. E-modulus is unknown for graphene nanoplatelets while GOs e-modulus is between 23-42 GPa. We know from literature that by measuring  $G^*$  it is possible to calculate E-modulus given that;

$$G = \frac{E}{2(1 + \mu)}$$

Where  $\mu$  is Poisson's ratio of bitumen who is assumed 0,5 (40), E-module can be calculated by using following formula  $E=3 \cdot G$  (Table 5).

E-module for RTFOT aged binder		
Binder	Mixing time (min)	Average E-module (MPa)
Reference	0	7,2
Graphene 1% LS	15	10,2
Graphene 1%	15	13,7
Graphene 1%	30	12,6
Graphene 1%	40	11,9
Graphene 1,5%	15	10,2
Graphene 2%	15	25,0
Graphene 2%	26	16,2

Table 5: E-module after RTFOT ageing

From Table 5 it seems that the effect of graphene on the E-modul varies between 3 to 17,9 MPa depending of percentage and mixing time.

While dispersing and mixing method to cement is much more optimized and chemical reaction is more predictable (41), when graphene nanoplatelets mixed with binder and are observed under optical microscope, illuminated by spotlight, no visible structure that connects graphene particles is observed in all three used percentages, as shown in Figure 17 .

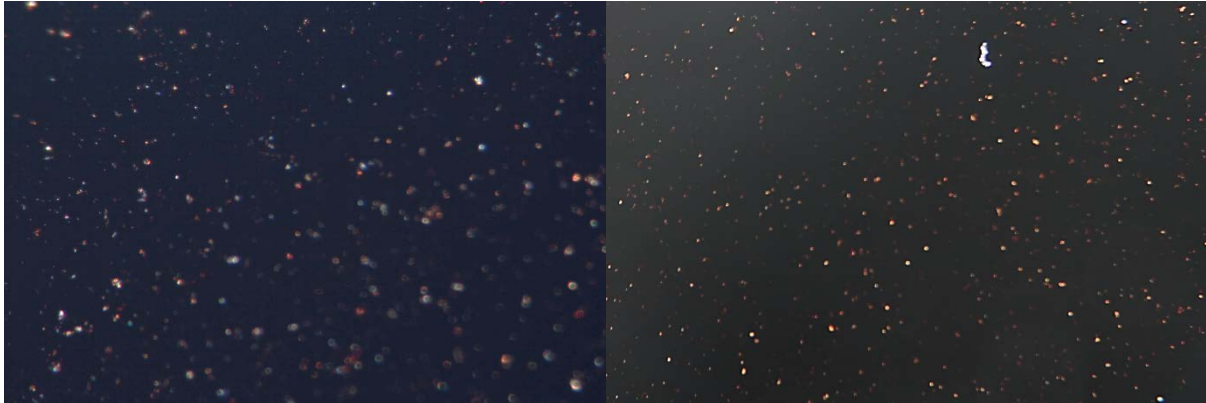


Figure 17: Microscope pictures of graphene nanoplatelets mixed in binder

Samples without graphene are also observed under microscope with and without spotlight and no glowing points but only black background where noticed. It is unclear what kind of links has graphene made when mixed in binder. It is reasonable to assume that no continuous graphene sheet has formed through all binder. Inhomogeneity is measured by variation in  $G^*/\sin\delta$  and  $G^*\sin\delta$  between samples of the same percentage content and mixing time. As in within group after 6 min mixing time with 2% of the graphene had higher  $G^*/\sin\delta$  then after 15 and 26 minutes. This measurement points out that the graphene percentage in samples after 6 minutes mixing time is higher than in 15 and 26 minutes. From this, I assume that the graphene percentage was not the same in all samples.

## 7. Conclusion

This study investigated the effect of graphene on the behavior of bitumen. Although difficulties have been encountered during the preparation of the specimens due to inhomogeneities within the compound the following conclusion can be drawn:

- Mix with 2% of graphene is *PG* rated one class higher than the reference binder.
- Dispersion and mixing time affects  $G^*/\sin(\delta)$  for unaged and *RTFOT*-aged binder as well as  $G^*\sin(\delta)$  for *PAV* aged binder. Graphene modified binder is stiffer than reference 70/100 but the effect can vary as seen from Figure 8 to Figure 11 between groups and between samples inside the same group.
- Increase in elastic recovery is noticeable from Figure 122 and Figure 133 as well as reduction in non-recoverable creep compliance but still under what is defined passing percent recovery for polymer binders, Figure 14. Large gap between data points is sign that the effect of graphene is not uniform.
- Low temperature properties of graphene modified binder stays the same as reference binder after uncomplete *PG*-grading. Interpolated failing temperature suggest that graphene modified binder is stiffer than reference binder in some degree depending of graphene content.
- Graphene modified binder has increased E-module depending of percentage and mixing time.
- Conventional mixing of graphene with binder gives large gap between data points. These unstable results are sign that graphene mix is not homogenous and therefore not optimal solution when it comes to use of graphene as additive.

## **8. Future work**

Taking in to account my experiences from working with graphene as additive in asphalt binder the following conclusions for future work can be drawn:

- Investigate possibility of other graphene products for use in asphalt engineering based on properties as E-module, tensile strength and surface area.
- Optimize mixing process by using dispersers and surfactant and to reduce gap in data points.
- Investigate possibility of blending graphene in softer binder over longer time to insure that graphene is evenly spread.

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