GRAPHENE NANO-PLATELET (GNP) REINFORCED ASPHALT BINDERS AND MIXTURES

Mihai Octavian Marasteanu[1, a], Jia-Liang Le[1, b], Mugurel Ioan Turos[1, c]

[1] *Department of Civil, Environmental, and Geo- Engineering, University of Minnesota, Minneapolis, United States*

[a] maras002@umn.edu
[b] jle@umn.edu
[c] turos001@umn.edu

Digital Object Identifier (DOI): dx.doi.org/10.14311/EE.2016.104

ABSTRACT

Researchers at the University of Minnesota have developed a graphene nano-platelets reinforced asphalt binder that has superior mechanical properties over pavement service temperatures, compared to existing binder formulations. The costs of these materials are comparable to polymer modified binders that are considered as best performers in pavement construction. Examples will be presented to show that for some formulations, asphalt binder strength at low temperatures doubled compared to the original binder, and fracture energy increases significantly for asphalt mixtures.

It was also found that the addition of graphene nano-platelets significantly reduces the compaction effort required to prepare asphalt mixtures. For some formulations, the reduction in compaction effort is more than half of the original mixtures. Results will be presented for mixture test samples prepared using traditional mixture preparation, as well as mixture test samples prepared from loose mix. The effect on rutting behavior is also discussed

Keywords: Asphalt, Compaction, Complex Modulus, Fracture-toughness, Low-Temperature

GRAPHENE NANO-PLATELET (GNP) REINFORCED ASPHALT BINDERS AND MIXTURES

Mihai Marasteanu
Professor
Email: maras002@umn.edu

Jia-Liang Le
Assistant Professor
Email: jle@umn.edu

Mugurel Turos
Scientist
Email turos001@umn.edu

Department of Civil, Environmental, and Geo- Engineering
University of Minnesota
Minneapolis, MN 55455
USA

ABSTRACT

Researchers at the University of Minnesota have developed a graphene nano-platelets reinforced asphalt binder that has superior mechanical properties over pavement service temperatures, compared to existing binder formulations. The costs of these materials are comparable to polymer modified binders that are considered as best performers in pavement construction. Examples will be presented to show that for some formulations, asphalt binder strength at low temperatures doubled compared to the original binder, and fracture energy increases significantly for asphalt mixtures. It was also found that the addition of graphene nano-platelets significantly reduces the compaction effort required to prepare asphalt mixtures. For some formulations, the reduction in compaction effort is more than half of the original mixtures. Results will be presented for mixture test samples prepared using traditional mixture preparation, as well as mixture test samples prepared from loose mix. The effect on rutting behavior is also discussed

KEY WORDS: Asphalt, Compaction, Complex Modulus, Fracture Toughness, Low Temperature

1. INTRODUCTION

In the past decade, significant efforts have been devoted to improving the performance of asphalt pavements. A major part of these efforts was focused on the development of new asphalt-based pavement materials with better performance and increased durability. Recently, there has been an emerging interest in applying nanotechnology to asphalt pavement materials [1, 2] and a number of attempts were made to incorporate carbon nanotubes (CNTs) into the asphalt binders and mixtures. It was found that the dispersion of CNTs in asphalt binders represents a major challenge [2], and the very high material cost make the application of CNTs in asphalt pavements prohibitive.

In this study, the application of Graphene Nanoplatelets (GNPs) to asphalt binders and mixtures is investigated. The GNP is made from exfoliated graphene, which has been shown to possess superior mechanical and electron transport properties [3-6]. The aspect ratio of GNP is significantly lower than that of CNT, which makes dispersion easier. In addition, the cost of GNP is comparable to some common polymer modifiers such as styrene butadiene styrene (SBS), which makes it a very attractive candidate for asphalt paving applications.

2. EXPERIMENTAL WORK

The experimental work consisted of testing performed on asphalt binders over a wide range of temperatures and on testing performed on asphalt mixtures at low temperatures. Different types of GNP materials were used in the experiments: MICRO750 (M750): a graphene nano-flake powder with minimum 96.22% carbon and an average surface area of 12 m^2/g; MICRO850 (M850): a graphene nano-flake material with 99.54% carbon and an average surface area of 12m^2/g; and 4827: a surface enhanced synthetic graphite material with 99.66% carbon and 0.34% ash and an average surface area of 250 m^2/g.

2.1. Asphalt binder testing

Binder testing was done following the Superpave Performance Grade (PG) Specifications that are detailed in a number of AASHTO specifications and are based on rheological measurements using a Dynamic Shear Rheometer (DSR) used to obtain complex modulus and phase angle of viscoelastic materials, a Bending Beam Rheometer (BBR) used to obtain the creep stiffness and the slope of the creep stiffness curve called m-value, and strength tests performed at low temperatures. In this investigation, a modified BBR instrument called BBR Pro, which has a proportional valve that

offers a complex control of the pressure in the air bearing system and a 44 N load cell, was used to perform strength tests under constant loading rate until failure. The procedure is explained in detail elsewhere [7].
Preliminary experiments were performed on a plain PG 58-28 asphalt binder in unaged condition and focused on low temperature properties. The GNP samples were carefully added to the hot asphalt binder and then mixed with a glass rod until a homogeneous mix was observed. An initial proportion of 6% by weight was used. No problems related to potential clustering of the graphene platelets were detected. BBR creep stiffness results, obtained at -24°C on two replicates, are shown in the Figure 1.

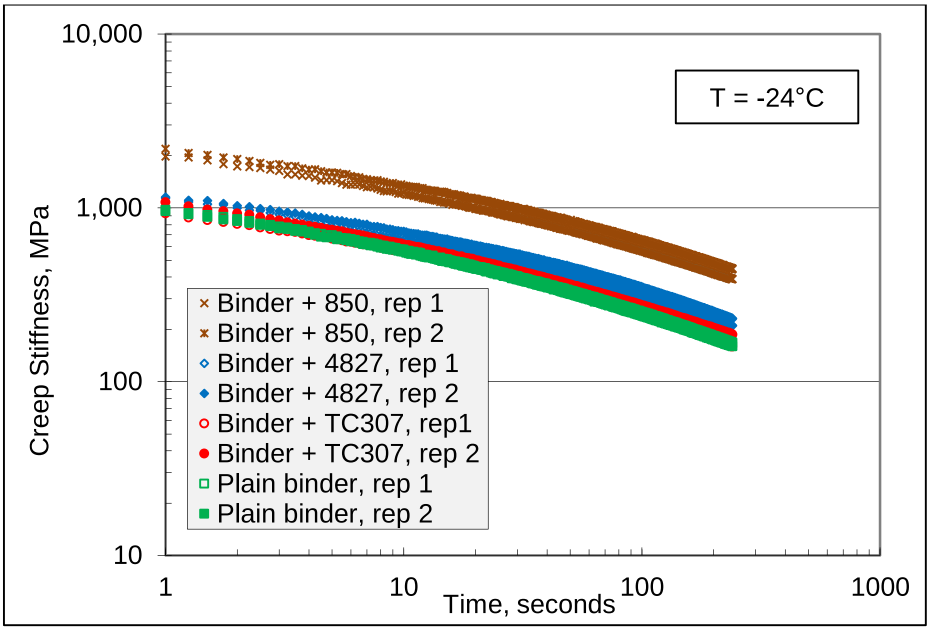

Figure 1. Preliminary BBR results for unaged binder PG58-28

It can be observed that the addition of the graphene type 850 significantly increases the creep stiffness of the asphalt binder; the stiffness more than doubles compared to the plain asphalt binder. Smaller changes are observed for the other types of graphene. At the same time, the slopes of the curves do not change, which indicates that the "m-values" do not change and that the relaxation properties are not affected by the significant increase in stiffness.
Bending Beam Rheometer strength tests were also performed on the binder beams at the same temperature of -24°C. The stress strain curves and the strength results for the two replicates tested are presented in Figures 2 and 3.

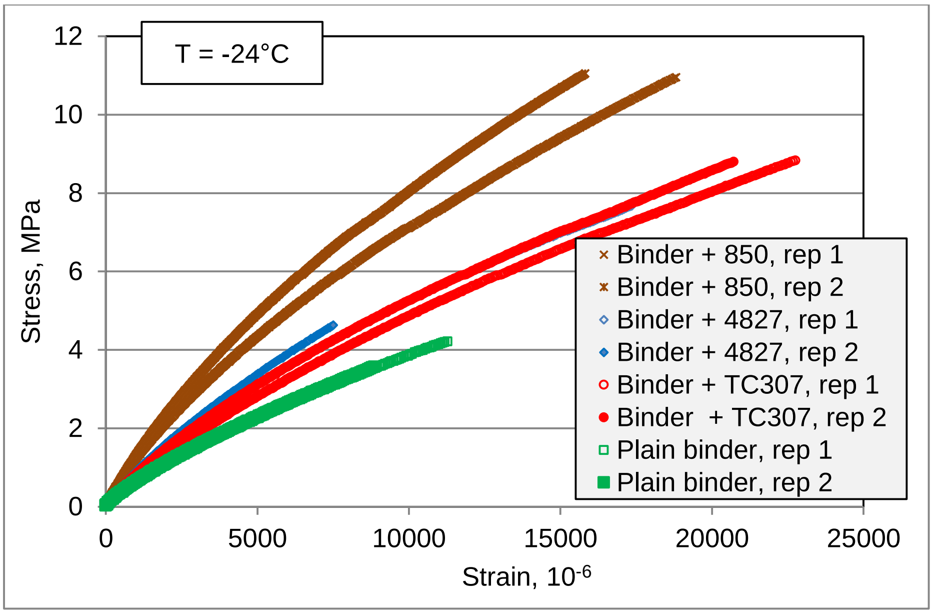

Figure 2. Preliminary BBR stress-strain results for unaged binder PG58-28

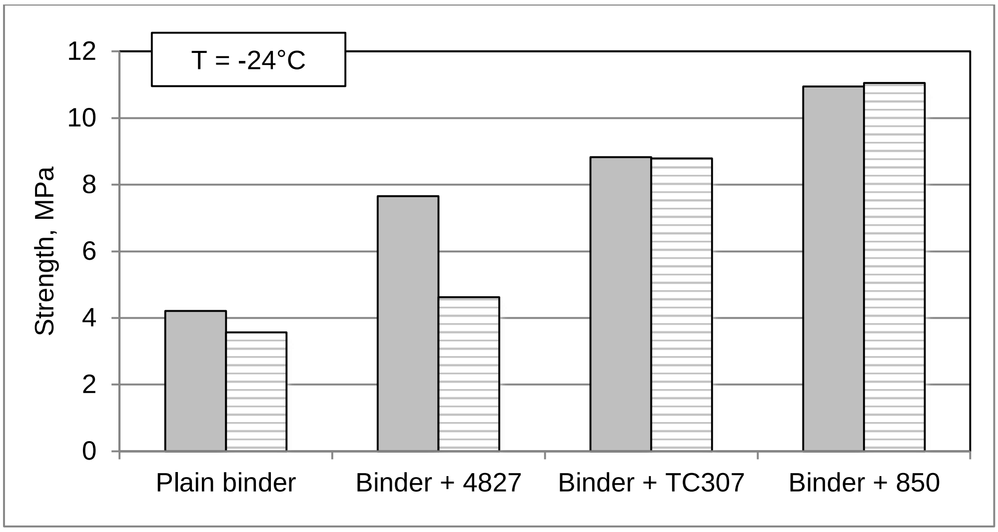

Figure 3. Preliminary BBR strength results for unaged binder PG58-28

It can be observed that the addition of the three types of graphene has a significant impact on the strength properties of the binder. In particular, the addition of type "850" leads to a threefold increase in strength, from 3.9MPa to 11.5MPa. At the same time, a twofold increase in failure strain, from 1% to almost 2%, is also observed that indicates that the strain tolerance of the material also improves.

Similar testing was performed on a plain PG 52-34 binder and a SBS-modified PG 64-34 binder in PAV condition. The GNP was added to the liquid asphalt binders in two amounts: 3% and 6% by weight. Similar to the preliminary results, the most significant improvement is observed in the strength properties of the binders at low temperature, in particular for the unmodified binder. It was observed that, on the average, the addition of 3% of 750 increases strength 1.8 times, addition of 3% 850 increases strength 2.5 times, and addition of 3% 850 increases strength 2.3 times. These are very significant changes not observed with any other additives used in binder modification. Improvements were also observed when similar amounts of GNP were added to the polymer modified binder that already has good strength properties. On the average the increase in strength was approximately 20%. It is important to note that the increase in strain at failure were similar to the increases in strength, a clear indication that the strain tolerance of the GNP reinforced binders are significantly improved.

Rheological tests were also performed using the Dynamic Shear Rheometer (DSR) and master curves of the norm of the complex modulus and of the phase angle were generated. Examples are presented in figures 4 and 5.

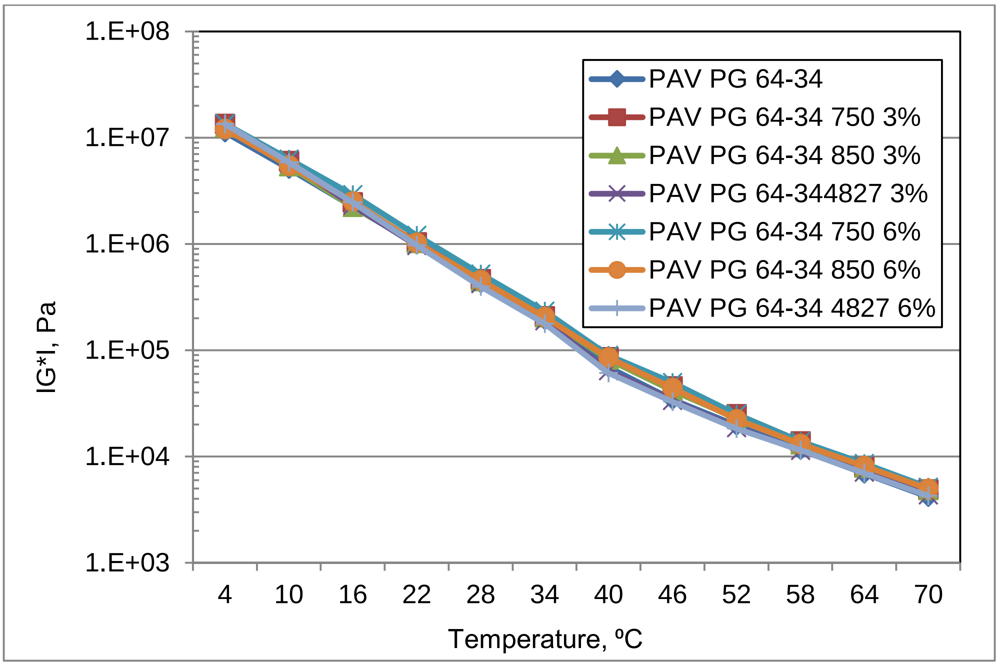

Figure 4. |G*(10rad/s)| temperature master curves for modified binder PG64-34 in PAV condition

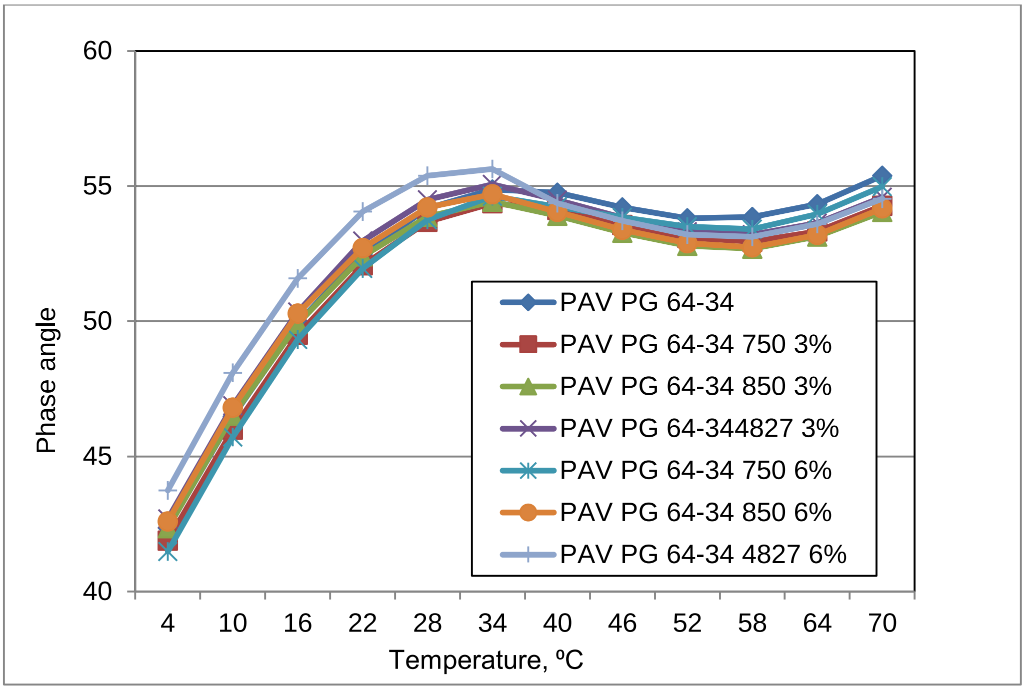

Figure 5. Phase angle at 10rad/s temperature master curves for modified binder PG64-34 in PAV condition

No significant changes are observed in the two material parameters at high and intermediate service temperatures when 3% or 6% GNP by weight is added to the asphalt binders investigated.

Based on the experimental investigation, it can be concluded that the addition of 3 to 6% GNP significantly improves the strength properties and strain tolerance of asphalt binders at low temperatures. At the same time, the relaxation properties at these low temperatures are not negatively affected. No significant changes were observed in the intermediate and high service temperature properties of asphalt binders when GNP was added.

2.2. Asphalt mixture testing

A Superpave mix design for a 12.5 mm nominal maximum aggregate size mixture was used to prepare mixture samples. The experimental work consisted in Semi-Circular Bending (SCB) fracture tests performed according to AASHTO TP-105 [8]. The fracture energy measured by the SCB test is a material property that directly represents the fracture resistance under mode-I loading (tensile fracture). Table 1 summarizes the calculated fracture energy and apparent fracture toughness of different GNP-modified asphalt mixtures.

Table 1. Fracture energy and apparent fracture toughness of GNP-modified asphalt mixtures

Binder	GNP, % by weight	GNP type	Fracture energy	Fracture toughness
			G_f, KJ/m^2	K_{1C}, MPa•m$^{0.5}$
64-34	0		0.495	0.880
64-34	3	M850	0.614	0.948
64-34	6	M850	0.995	1.000
64-34	3	4827	0.643	0.920
64-34	6	4827	0.601	1.008
52-34	0		0.556	0.829
52-34	3	M850	0.480	0.752
52-34	6	M850	0.460	0.785
52-34	3	4827	0.614	0.897
52-34	6	4827	0.418	0.807

It is observed that for all polymer-modified binder asphalt mixtures the addition of GNP leads to a considerable increase (about 28%) in fracture energy. For example, addition of M850 with 6% by weight of binders gives rise to almost 100% increase in fracture energy. For unmodified binder asphalt mixtures, the results are mixed.

2.3 Compaction study

An investigation was performed to determine if the addition of GNP influences the laboratory compaction properties of asphalt mixtures. In the first part, we investigated the effect of adding graphene to the binder used to prepare asphalt mixtures. In the second part we investigated the effect of adding graphene directly to an already prepared asphalt mixture (loose mix). The results are presented below.

A PG 58-28 plain binder was used to prepare a Superpave mix with 12.5 mm nominal maximum aggregate size and 5.5% binder content (by weight). Two types of graphene, Micro 850 and 4827, were mixed by hand with the binder. For the asphalt mixture sample size used in the study, 297 grams corresponds to 5.5% binder content. The following blends were made:

- Blend A represents the original mix design requirement with 5.5% binder and no GNP
- In blend B, 18g of binder are replaced with 18g of 850 (6% of binder weight) to keep the binder-graphene blend to 5.5% (of the total mixture weight) proportion.
- For blend C, 84g of 850 was added to the 297g of binders. This represents a 1:1 volume ratio between the binder and the graphene, which is equivalent to 28% of binder weight.
- Blend D represents 297g of binder plus 23g of 4827, which represents 8% of binder weight.

The compaction curves for one cylinder compacted to 5% air voids, for each type of blend, are presented in Figure 6.

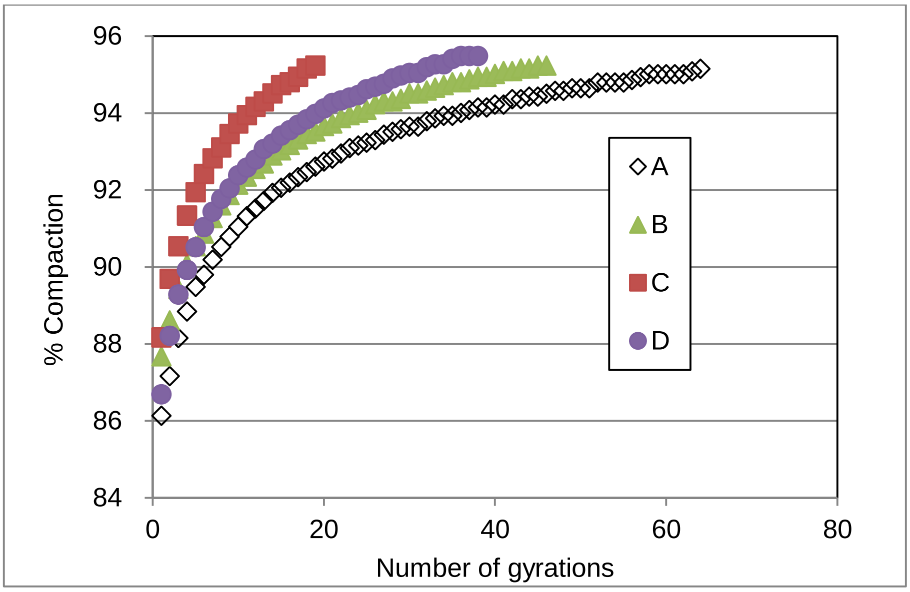

Figure 6. Compaction curves for mixtures prepared with asphalt binders with and without graphene

It can be observed that the addition of graphene decreases the number of gyrations required to compact the mixture to 5% air voids (95% compaction). The most significant effect was obtained when adding 28% (by weight of binder) of the 850 graphene. A smaller reduction was obtained when only 6% was added.

For the loose mix experiment, materials from a previous project were used in this experimental work. The binder used to produce the mixture was a plain PG 58-28 and the mix design was different than the one used to prepare mixtures shown in Figure 6. The loose mix has been stored in sealed buckets at constant room temperature since 2010. The buckets containing loose mix were heated in the oven at 145°C for two hours. After heating, four pans were filled with 7.1 kg of loose mix. The loose mix from the first pan, the control sample, was poured in the mixer bowl without any additional material. After 6 minutes of mixing, 7.020 kg were poured back into the pan sitting on the scale, and then kept in the oven for another two hours at 135°C. The loose mix from the other three pans was blended with three different types of GNP: Micro 850, Micro 750 an 4827. A 7 kg compacted cylinder contains 5.5% binder, (0.385 kg). The amount of graphene added was 8% of asphalt binder weight. The graphene particles were added gradually, during a two minutes period, to the mixing bowl, which already contained the loose mix. The mixing process took 6 minutes in total. In a similar way, 7.020 kg were poured back into the pan sitting on the scale, and then kept in the oven for another two hours at 135°C for conditioning. After two hours, four cylinders were compacted at 5% air voids using a gyratory compactor and following the current AASHTO procedure. The compaction curves are presented in Figure 7.

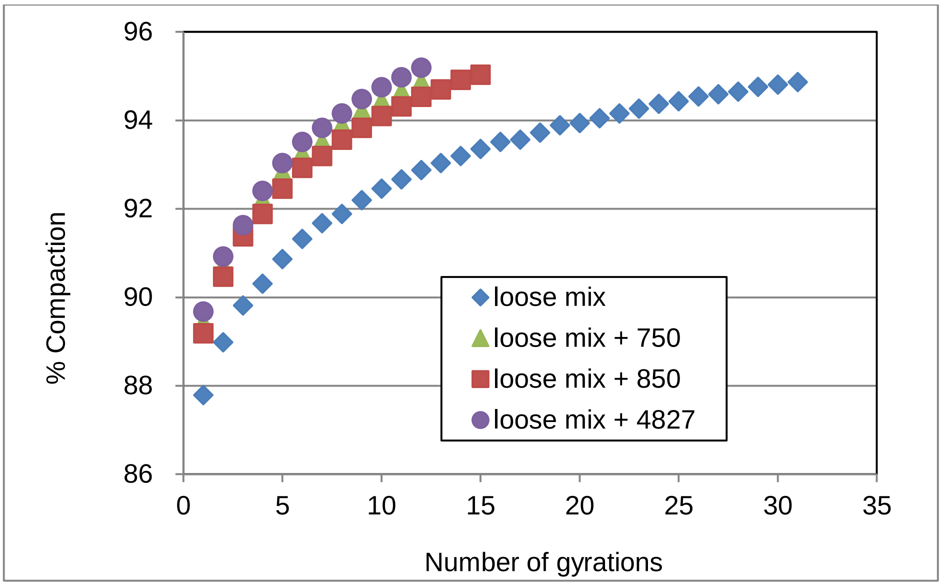

Figure 7. Compaction curves for loose mix with and without graphene

After the first gyration, a 2% air void reduction is already noticed in the samples with graphene versus the control sample. The 5% air void target was reached after 12 to 15 gyrations for the graphene coated mix, and after 31 gyrations for the control mix. This represents a significant reduction in the compaction effort. Although loose mix is not representative of field construction conditions, the results can be an indication of improved compaction properties for mixtures that contain high RAP or RAS contents and, therefore, deserve further investigation.

2.4 APA rut testing

A series of mixture testing was performed at high temperature, to investigate if the addition of GNP makes the asphalt mixtures more prone to rutting. This testing was done to address concerns that the "lubricant" effect that is responsible for the reduction in compaction effort at conventional compaction temperatures (130°C to 140°C) can remain significant even at summer service temperatures. The results obtained with an APA rut testing device, showed that the addition of graphene improves the rutting resistance. An example is shown below for an asphalt mixture prepared with and without graphene and compacted at 130°C to 7% air voids. The test was conducted at 58°C.

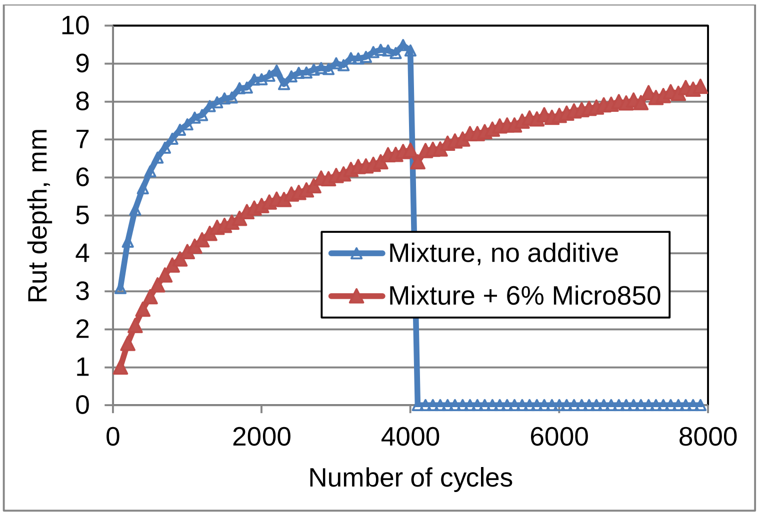

Figure 7. APA results for mixture with and without graphene

CONCLUSIONS

Based on the results of this investigation, the following conclusions can me drawn:

- GNP can be easily incorporated into asphalt binders, and due to its relatively low aspect ratio no potential clustering is observed during the mixing.
- The addition of GNP into both polymer-modified and unmodified asphalt binders does not significantly affect the complex shear modulus and phase angle at intermediate and high service temperatures.

- Compared to conventional polymer-modified and unmodified asphalt binders, the addition of GNP can moderately increase the creep stiffness of the binder but does not affect the "*m*" value, and therefore, does not affect the relaxation properties at low temperature
- The GNP-modified asphalt binders have superior flexural strength at low temperatures compared to the conventional asphalt binders. For both polymer-modified and unmodified asphalt binders, a moderate addition of GNP, i.e. 3% to 6% by weight of the binder, can lead to about 130% increase in flexural strength.
- The addition of GNP increases SCB fracture energy of asphalt mixtures at low temperatures. Compared to the increase in flexural strength of GNP-modified asphalt binders, this increase is less pronounced.
- The addition of GNP can effectively reduce the compaction effort of asphalt mixtures, without negatively affecting the rutting performance of the mixtures.

These experimental results indicate that the GNPs could be used as an effective means for improving the resilience and durability of asphalt pavements. The authors hope that this study will stimulate further research efforts on investigating the physical mechanisms that are responsible for the observed improvements of the properties of the GNP-modified asphalt binders and mixtures. Additional research is also needed, before implementing the use of these materials into construction practice, to address potential health and safety concerns related to graphene handling and storage and stability of the modified binders.

ACKNOWLEDGMENTS

The support provided by NCHRP-IDEA 173 is greatly acknowledged. The results and opinions presented do not necessarily reflect those of the sponsoring agencies. The authors would also like to acknowledge the Minnesota Department of Transportation for providing the materials used in this study.

REFERENCES

1. Steyn, W. J. (2011) "Applications of nanotechnology in road pavement engineering", *Nanotechnology in Civil Infrastructure*, pp 49-83.
2. Shirakawa, T., Tada, A. and Okazaki, N. (2012) "Development of functional carbon nanotubes-asphalt composites", *International Journal of GEOMATE*, 2(1), 161-165.
3. Novoselov, K. S., A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 438, 2005, 197.
4. Zhang, Y., Y. W. Tan, H. L. Stormer, and P. Kim. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature*, 438, 2005, 201.
5. Lee, C., X. Wei, J. W. Kysar, and J. Hone. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321, 2008, 385.
6. Kim, K., W. Regan, B. Geng, B. Aleman, B. M. Kessler, F. Wang, M. F. Crommie, and A. Zettl. High-temperature stability of suspended single-layer graphene. *Phys. Status Solidi*, RRL4, No. 11, 2010, 302-304.
7. Marasteanu, M. O., Cannone Falchetto, A., Turos, M. and Le J-L., "Development of a Simple Test to Determine the Low Temperature Strength of Asphalt Mixtures and Binders", IDEA Program Final Report NCHRP 151, 2012.
8. AASHTO TP105-2013. *Standard Method of Test for Determining the Fracture Energy of Asphalt Mixtures Using the Semicircular Bend Geometry (SCB).* American Association of State Highway and Transportation Officials, 2007.
9. Berman, D., A. Erdemir and A. V. Sumant. Graphene: A new emerging lubricant. *Materials Today*, Vol 17, No. 1, 2014, 31-42.