A Study on the Release of Nanoparticles to the Environment from Nano-Enabled Asphalt by Weathering Experiment

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\textbf{Abstract.} Researches in the field of nanotechnology is continuously gaining a lot of interest due to its wide range of applications. This study focused on the incorporation of halloysite nanotubes (HNT’s) on asphalt and on the investigation of the release of the said nanoparticles from the asphalt to the environment through accelerated weathering experiment. Two (2) samples were prepared: asphalt with HNT (A1) and asphalt only (A2). SEM-EDX results showed that A1 initially had nanoparticles on the surface which can be attributed to the added HNT. SEM images further showed the changes on the surface morphologies of A1 and A2 after accelerated weathering experiment. These changes can be further correlated to the intercalation and exfoliation reactions that happened on the surface of asphalt during UV irradiation. Release studies revealed that Al and Si nanoparticles were being released on the surface due to the layer by layer degradation of the asphalt matrix. Hence, continuous exposure of asphalt could result to further degradation of asphalt, leading to the surfacing and release of more nanoparticles.

1. Introduction

In the recent years, nanotechnology has been continuously regarded as a promising field of research due to its numerous industrial applications. Nanotechnology deals with particles having dimensions ranging from 1 nm to 100 nm, which offers a large potential in enhancing the properties of materials [1]. Nanoscale materials incorporated on polymers forming nanocomposites possess excellent physical and chemical properties which include high stress/strain resistance, increased compressive strength, weathering protection, and improved thermal and electrical properties [2,3]. Due to impending applications of nanoscale materials, this gave rise to engineered nanoparticles (ENP’s) which are purposely designed and engineered to meet the desired material properties for specific applications [3].
Among the materials being modified by employing ENP’s, pavement materials are given interest by researchers. Studies in the field of pavement materials tend to focus on utilizing nanomaterials to modify asphalt [4]. Commonly used as a binder to several applications such as corrosion protection, waterproofing and resistance against moisture, asphalt is a black organic material made up of complex hydrocarbons with diverse molecular weights [2]. Being widely utilized in the pavement industry, asphalts are required to be resistant to different environmental and weathering conditions, creep, fatigue, as well as to heavy thermal and traffic loads. Hence, cost-effective modification of asphalt is needed. Numerous ENP’s serve as reinforcements or additives to asphalt in order to enhance its properties and performance [5,6]. ENP’s incorporated to asphalt include nanoclay, carbon nanoparticles, carbon nanotubes, carbon nanofibers, subnano-sized hydrated lime, nano-phosphorus and nano-SiO$_2$ [6,7]. Although incorporation of ENP’s on asphalt can enhance its properties, their stability and compatibility must be considered; otherwise, the asphalt will be damaged prematurely due to aging [2]. For this reason, ENP’s that are incorporated in the asphalt matrix could be released, which can pose potential health and environmental hazards.

Most studies tend to investigate the effects of adding ENP’s on asphalt and analyze the corresponding increase in its properties. In addition, researches on the potential hazards of asphalts were about occupational safety during asphalt processing, and asphalt particles are only in the form of dust or fumes. Very few studies focus on the release of nanoparticles from asphalt when exposed to extreme weathering conditions.

The main goal of this study was to quantify the release of the nanoparticles from asphalt by performing an accelerated weathering experiment. Specifically, the objectives of this study were as follows: a.) to produce a nano-enabled asphalt by incorporating halloysite nanotubes (HNT’s); b.) to subject the nano-enabled asphalt (A1) and regular asphalt (A2) to accelerated weathering conditions; c.) to characterize and observe changes in the surface morphologies of A1 and A2 after accelerated weathering using scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX); and lastly, d.) to quantify and observe the trend of the release of nanoparticles, specifically HNT’s, from A1 and A2 in the form of aluminum (Al) and silicon (Si) using inductively coupled plasma – optical emission spectrometry (ICP-OES).

This undertaking could serve as a fundamental study in developing standards for the potential health and environmental hazards brought about by the release of nanomaterials from asphalt when used in pavement applications.

The release of Al and Si (potentially from HNT added) were the only point of detection for the release of nanoparticles from asphalt. This was correlated to the changes in the surface morphologies of A1 and A2, as seen from the SEM images.

2. Methodology

HNT (Sigma-Aldrich), 2.0 wt. %, was added to asphalt (Shelby, Bayer AG) and mixed mechanically for 1 hour to produce the nano-enabled asphalt (A1). An asphalt without HNT (A2) was also used as reference. Fiber cement panels (155 mm × 70 mm, l × w) were prepared and coated on one side using A1 and A2 (3.80 g of paint/mm$^2$ of panel), and the other side of the panels were coated with wax. The painted panels were then subjected to accelerated weathering machine (Suga Test Instruments Co. Ltd.) for nine (9) weeks using a UV lamp with 388 nm wavelength and irradiance of 24 W/m$^2$. Exposure conditions were based on the established weathering standards for bituminous materials (ASTM D4799). In the duration of the accelerated weathering test, weekly collections of leachates were done. In this process, panels were pulled out of the weathering machine and deionized water was sprayed (with 150 mm distance) on the surface of the asphalt-coated panels. The resulting leachates were then collected. Afterwards, the leachates were digested using aqua regia. Approximately 10 mL of the digested leachates for each type of asphalt per week were then submitted to ICP-OES (Prodigy7, Teledyne Leeman Labs) testing to determine the concentration of Al and Si that can be correlated to the released nanoparticles, specifically from HNT’s added. Furthermore, the coated panels (using A1 and A2) before
and after weathering were subjected to SEM with EDX (Helios NanoLab 600i) to characterize the surface morphologies.

3. Results and Discussion

3.1. Surface morphology characterization

Scanning electron microscopy with energy dispersive x-ray (SEM-EDX). The surface morphologies of the A1 and A2 were analyzed based on the SEM images obtained, as well as the elemental composition through EDX (Figure 1). The surface morphology of A1 shows agglomeration of particles on the surface, which can be potentially HNT nanoparticles. For A2, the image obtained could be due to the uneven application of the asphalt onto the substrate. HNT contains Al and Si elements, and since it was incorporated on A1, EDX results showed the detection of the said elements. For A2, Al and Si were also detected; hence, the asphalt itself already contains Al and Si. In this regard, for the release analysis, Al and Si could be from HNT and asphalt.

![Figure 1. Results for the SEM-EDX analysis of A1 and A2.](image)

For the comparison of the surface of A1 and A2 before and after weathering, their SEM images were presented on Figure 2. It can be observed that for both A1 and A2, changes in the surface morphologies were evident. There was the rearrangement of molecules on the top layer of the surfaces due to UV irradiation and water condensation inside the weathering chamber. Theoretically, considering the weathering process, the microstructures that can be observed for A1 and A2 after weathering were due to the oxidation and polymerization that happened on the surface molecules [8]. Moreover, based on the SEM image of A1 after weathering, it can be said that there was the intercalation and exfoliation reaction between HNT nanoparticles and hydrocarbon chains of the asphalt. In addition, even though A1 underwent weathering and although some HNT nanoparticles in the form Al and Si nanoparticles were released, most particles were still embedded on the surface of A1. This was due to the enhanced property of asphalt with HNT against high-temperature conditions [4]. Unlike in P2 (without HNT), formation
of particles due to the oxidation and polymerization reactions brought about by weathering can be observed.

![Figure 2. SEM images of A1 and A2 before and after weathering.]

3.2. Release of nanoparticles from paint
A1 and A2 were subjected to accelerated weathering, and release of nanoparticles was expected. As can be seen on the plot in Figure 3 and Figure 4 for the release of Al and Si, respectively, there was no significant trend that can be observed. This was probably due to uneven distribution of the nanoparticles in the asphalt matrix, particularly due to the intercalation and exfoliation reactions. An evident observation for both A1 and A2 was the sudden decrease in the release after 5 weeks. This can be correlated to the degradation of asphalt by layer. The nanoparticles on the first exposed layer of the asphalt were released up to week 5. After the degradation of first layer, nanoparticles on the second layer appeared on the surface, then released due to continuous weathering.

![Figure 3. Release of Aluminum (Al) from A1 and A2 during weathering.]

**Figure 2.** SEM images of A1 and A2 before and after weathering.

**Figure 3.** Release of Aluminum (Al) from A1 and A2 during weathering.
4. Conclusion
After performing the experiment, the objectives of the study were successfully satisfied. Weathering of the A1 and A2 were performed considering the necessary standard to be used. SEM-EDX showed the surface morphologies of A1 and A2, and their respective elemental compositions. Furthermore, the SEM images evidently show that there were changes in surface morphologies of A1 and A2, which can be correlated to the oxidation and polymerization reactions producing microstructures on the surface. In addition, intercalation and exfoliation reactions between the nanoparticles and asphalt matrix potentially happened. The release of Al and Si nanoparticles (potentially from HNT nanoparticles) were also investigated. The degradation of asphalt was observed to happen on a by layer basis, so as the release of nanoparticles.

References
[1] Yang J and Tighe S 2013 A Review of Advances of Nanotechnology in Asphalt Mixtures Procedia - Soc. Behav. Sci. 96 1269–76
[2] Fang C, Yu R, Liu S and Li Y 2013 Nanomaterials applied in asphalt modification: A review J. Mater. Sci. Technol. 29 589–94
[3] Mohajerani A, Burnett L, Smith J V., Kurmus H, Milas J, Arulrajah A, Horpibulsuk S and Kadir A A 2019 Nanoparticles in construction materials and other applications, and implications of nanoparticle use Materials (Basel). 12 1–25
[4] Ezzat H, El-Badawy S, Gabr A, Zaki E S I and Breakah T 2016 Evaluation of Asphalt Binders Modified with Nanoclay and Nanosilica Procedia Eng. 143 1260–7
[5] Nejad F M, Tanzadeh R, Tanzadeh J and Hamedi G H 2016 Investigating the effect of nanoparticles on the rutting behaviour of hot-mix asphalt Int. J. Pavement Eng. 17 353–62
[6] Yao H and You Z 2016 Effectiveness of Micro-and Nanomaterials in Asphalt Mixtures through Dynamic Modulus and Rutting Tests J. Nanomater. 2016
[7] Faruk A N M, Chen D H, Mushota C, Muya M and Walubita L F 2014 Application of Nano-Technology in Pavement Engineering: A Literature Review 9–16
[8] Menapace I, Yiming W and Masad E 2017 Chemical analysis of surface and bulk of asphalt binders aged with accelerated weathering tester and standard aging methods Fuel 202 366–79