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A comparative study of mixing nano particles in the bitumen by dry and wet method

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Abstract

Pavement deterioration owing to rutting, fatigue, and stripping provides substantial issues, needing early rehabilitation to avoid accidents and delays. Given the high costs of pavement repair and reconstruction, the use of additives to extend pavement life emerges as an economically viable approach. While previous initiatives have used admixtures such as crumb rubber, cement, and geosynthetics to improve asphalt binder qualities, this research focuses on improving stripping, rutting, fatigue resistance, and viscosity by incorporating carbon nanotubes (CNTs). Methanol was used as a solvent in the present research to ensure uniform dispersion of CNTs, resolving a recurring issue. Mixing was ensured effectively by using a high-shear mixer that functioned for 40–45 minutes at 300–4800 rpm. To figure out how CNTs affected the performance of asphalt binder, various ratios of 0.3%, 0.6%, 0.9%, and 1.2% were investigated. The use of carbon black nanoparticles (CBNPs), graphene nanoparticles (GNPs), and multiwalled carbon nanotubes (MWCNTs) as bitumen modifiers shows potential for improving the quality of asphalt binder. MWCNTs excellent tensile strength and heat resistance make them ideal for transportation engineering applications. However, challenges exist in CNT preparation, economic implications, and attaining homogeneous dispersion in bitumen. The investigation involves the creation of nine modified bitumen samples utilizing both wet and dry mixing procedures. The findings demonstrate that GNPs have a significant potential to improve bitumen stiffness properties. Furthermore, a higher percentage of nanocomposite resulted in reduced penetration, softening point, and ductility values, enhancing bitumen stiffness and resistance to rutting. Despite promising results, challenges regarding CNT preparation, cost-effectiveness, and uniform dispersion in bitumen indicate the need for additional research and development in this area.

Keywords: Pavement deterioration; Carbon nanotubes (CNTs); Asphalt binder modification; Bitumen stiffness; Nanocomposite dispersion

1. Introduction

Civil engineering research focuses on cement-based materials modified with nanoparticles and polymer fusions, with less attention given to bituminous materials. Asphalt binder is crucial for waterproofing in structures, and nanoscale modifications can improve performance. Nearly 70% of asphalt concrete is used in road construction, and nanotechnology is being introduced to meet 21st-century demands and prevent excessive pavement maintenance. The addition of CBNPs, GNPs, and MWCNTs to bitumen improves its characteristics, leading to new research areas and improved asphaltic performance.

Bitumen, a dark cementing substance, is commonly found in asphalt, mineral waxes, and tar. It is produced using non-renewable energy sources and contains complex hydrocarbons. Refined bitumen is used in road and airport pavements for adhesive, waterproofing, and mineral aggregate binder. It has physical properties such as adhesion, water resistance, viscosity, stiffness, hardness, and specific gravity. It behaves as a fluid at high temperatures and a brittle solid at low temperatures. Whereas Asphalt is a mix of fillers, binders, and aggregates used in constructing and maintaining

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roadways. It consists of 90-95% aggregate and sand, and 5-10% asphalt or bitumen when blended. Asphalt pavements are less flexible when mixed colder, allowing it to adapt to changing weather conditions and resist water. It is also known as bitumen. Furthermore, Bitumen is a mix of around 300 to 2000 chemical constituents, with an average of 500 to 700. It mainly consists of high condensed polycyclic aromatic hydrocarbons, including asphaltenes, resinous components, non-polar aromatics, and saturated compounds. Its chemical composition is primarily composed of carbon, hydrogen, sulfur, oxygen, and nitrogen.

Bitumen is a material with various properties, including its softening point, ductility, penetration, flash and fire point, adhesive capacity, resistance to water, hardness, viscosity, and flow. The softening point is the temperature at which a steel ball falls through bitumen, while ductility determines the extent of bitumen stretch. Penetration tests measure the depth a standard needle will penetrate vertically in five seconds while the bitumen sample is kept at 25°C. Flash and fire tests measure the vapor produced near the surface of the substance when heated to flammable or combustible temperatures. Bitumen's adhesive capacity depends on the type of surface, and its resistance to water can be affected by the presence of inorganic salt. Hardness can be assessed through penetration tests, with typical results for hard coating asphalt being 10, roofing asphalt 15-40, and water-proofing bitumen reaching 100 or more. Viscosity and flow are crucial when bitumen is processed and applied at high and moderate temperatures. When the bitumen deteriorates or loses its favorable characteristics, it becomes hard, affecting its flow and adhesive characteristics. The softening temperature and coefficient of thermal expansion increase as the bitumen's properties change. Attack Oil Refinery Limited (ARL) provided the bitumen for this project, which is penetration grade 60/70.

Nanotechnology is revolutionizing pavement efficiency by creating engineered materials that optimize resource utilization, create ductile, flexible, permeable, or impermeable concrete structures, and construct environmental-resistant concrete and asphalt mixtures. Future applications may reduce maintenance costs, prolong pavement life, and improve construction efficiency. Nanoparticles (NPs) have changed their physical and chemical properties, making them increasingly useful in daily life and replacing limited engineering materials. Carbon black nanoparticles, nano platelets, carbon nano tubes, and multi-walled carbon nanotubes are examples of NPs that offer improved mechanical qualities, resistance properties, and are ideal for airplanes, spaceships, and bridges.

This investigation delves into the efficacy of nanoparticles in enhancing asphalt properties, reviewing scholarly works concerning nanomaterials such as Nano-titanium dioxide, Nano-carbon nanotubes, and Nanosilica. It underscores the considerable influence of nanoparticles on binder attributes, emphasizing their expansive surface area and distinctive qualities like high sensitivity to temperature, ductility, and tensile strength [1]. Examining the application of nanomaterials in nano-scale modified asphalt, the study scrutinizes their rheological behavior, engineering outcomes, and characteristics. It stresses the significance of considering parameters such as binder morphology, dimensions, and mixing temperatures for optimal modification [2]. The investigation evaluates the impact of inorganic nanoparticles on bitumen binder characteristics. Through the combination of graphite, carbon black, and powdered calcium carbonate, modified binders were formulated. Findings indicate that nanoparticles enhance elasticity under low temperatures but reduce crack resistance at elevated temperatures [3]. The study investigates the efficacy of mechanical stirring in producing nano-pavement materials with CNTs modifiers, augmenting performance metrics such as anti-rutting properties, elasticity, and heat stability [4].

Nanomaterials, particularly CNTs, prove effective as modifiers for asphalt binders, enhancing stiffness and rutting resistance. Test methodologies encompass penetration grade, softening point, ductility, and viscosity assessments. The effectiveness of CNTs is influenced by their properties and mixing duration, with dry mixing posing greater challenges [5]. In an experimentation involving the mixing of CNTs with bitumen at varying concentrations (0.1%, 0.5%, 1%), the modified bitumen exhibits commendable performance in penetration tests, notwithstanding aging resulting from high temperature mixing [6].

The research demonstrates the efficacy of nanoparticle-modified epoxy asphalt in enhancing pavement performance. The utilization of CNTs in epoxy asphalt pavement binders (CNTsEAPB) results in reduced freeze-thaw splitting intensity and enhanced dynamic stability, credited to the superior attributes of carbon nanotubes and the potent synergistic interaction between CNTs and epoxy resins [7]. Comparative analysis on the effects of nanoparticles on bitumen at elevated temperatures reveals that the incorporation of Nano clay with conventional bitumen, single-wall carbon nanotubes, and other additives enhances the high-temperature capabilities of bituminous binders, as evidenced by stress creep tests, oscillatory shear loading tests, and viscosity assessments [8].

Investigation into pavement performance employing graphene Nano platelets (GNPs) indicates an extended pavement lifespan, improved resistance to rutting, increased stiffness, binding efficacy, and enhanced skid resistance. However, penetration values decrease with escalating GNP content, and the softening point exhibits a 19% increase with 4% GNPs, albeit at the expense of decreased ductility [9].

2. Methodology

The technique for all laboratory experiments undertaken in the project is detailed in this chapter. Each step of running tests is accurately and thoroughly detailed in order to remove any confusion and misunderstanding for the reader.

2.1. Materials selection

Following is the apparatus used in this project.

- Jugs
- Solvent (Methanol)
- Digital Stopwatch
- Digital Thermometer
- Stirrer
- Graphene Nano Particles (GNPs)
- Multi Walled Carbon Nano Tubes (MWCNTs)
- Carbon Black Nano Particles CBNPs
- Fire extinguisher.
- Sonication Apparatus
- Ductility Apparatus
- Flash and Fire Apparatus
- Penetration Apparatus
- Softening Point Apparatus

2.1.1. Bitumen

Attock Oil Refinery Limited is the source of bitumen that is most commonly available in Pakistan (ARL). The bitumen used in this project was of 60/70 penetration and purchased from Attock Refinery Limited (ARL).

Four samples having MWCNTs, CBNPs and GNPs of different percentages were taken while methanol was used as a carrier solvent in bitumen.

2.1.2. Carbon black Nanoparticles (CBNPs), GNPs and MWCNTS

Four percentages that are 0.3, 0.6, 0.9, and 1.2 of each nanoparticle were used for the research.

MWCNTs having an outer diameter of 10–12 nm, an inner diameter of 30–50 nm, an average length of 0.5-2 m, a density of 2.1 g/cm3, a specific surface area of 60 m2/g, and a purity of 97%. The MWCNTs were imported from the USA, where they were made using the chemical vapor deposition method.

2.1.3. Solvent Selection

The study used methanol as a solvent for sample preparations, as it was easier to remove from bitumen in a shorter time. The FTIR analysis showed no change in bitumen's molecular structure, unlike virgin samples. Methanol was chosen for wet mixing to ensure proper dispersion of nanoparticles, but caution and safety precautions were also taken.

Methanol, also known as ethyl alcohol, is a colorless, volatile, and pleasant-smelling chemical produced by distilling wood and combining carbon monoxide gas and hydrogen. Its high volatility allows it to travel short distances before flashing back to an ignition source.

2.1.4. Sample preparation

The two sample mixing techniques were applied for mixing and sample preparation. Both dry and wet mixing were utilized to prepare the samples. Different steps must be taken when blending wet and dry. An earlier study found that moist mixing causes the nanoparticles in bitumen to disperse uniformly.

2.1.5. Virgin sample preparation

600 g pure bitumen from the container was taken for the controlled sample. Following that, the virgin sample was heated until it became fluid. The ASTM standards were used to perform softening point, penetration, ductility, flash and fire point tests.

2.1.6. Mixer selection

The most crucial stage in creating a modified asphalt binder with carbon nanomaterials is uniformly dispersing the nanoparticles in the binder. This ensures the highest homologous recombination level between the nanoparticles and asphalt substrates, affecting the binder's efficiency. Researchers have developed various blending procedures, including mechanical, high-shear, and ultrasonic mixing, to achieve this.

2.1.7. Modified sample preparation

This study used three percentages (0.3, 0.6, 0.9) of MWCNTs, two percentages (0.3,0.6) for GNPS and four percentages (0.3, 0.6, 0.9,1.2) of CBNPS using methanol as a carrier solvent for wet mixing process and same percentages for the dry process.

2.1.8. Bitumen Modified with Nano Particles

The four testing samples were produced by adopting the wet mixing practice and the same were produced by the dry mixing procedure.

2.2. Healing Time

Healing is a crucial process in materials that allows them to repair damage automatically and autonomously. This work focuses on the nonautonomous self-healing mechanism in materials. When binders are mixed in a high-shear mixer, they cause damage, affecting the penetration grade, softening point, and ductility. Testing after mixing may not yield exact results, as readings may differ significantly from actual values. The mixture requires time to recover, with an empirical formula stating 25 hours. In this study, the additives blended with bitumen were allowed to heal for 25 hours at room temperature. After 25 hours, the modified bitumen healed at room temperature. All test samples were prepared according to ASTMC testing standards.

2.3. Strategy of sampling

At first, we filled the 8 jugs with 420 g bitumen in each. Nanoparticles were weighted according to their respective ratios and transferred to 8 plastic bottles with care. We used to prepare two samples a day and on the next day we performed all tests on those samples. We could not have exceeded that limit because we had limited numbers of molds and apparatus. We also needed a healing time of 25 hours so sampling and testing of the same sample in day was not possible. While methods of sample preparations and testing procedures are being discussed below.

2.4. Sample preparation

2.4.1. Wet Method

Bitumen binder with 0.3% CBNPs

A sample of 420 g bitumen and 0.3% CBNPs was sonicated with 240ml of methanol, using ice to maintain the temperature of 12 °C. Carbon black nanoparticles were added to the methanol solution, which was held in the sonicator for 20 minutes to ensure proper dispersion and stability. The temperature was maintained at this temperature to reduce evaporation. A uniformly blended black color solution was created. The solution was then mixed with bitumen using a high-shear mixer, running at a speed of 300 rpm for the first 5 minutes, then at 4800 rpm for the remaining 20-25 minutes. The temperature rose rapidly until it reached 160 °C, which was maintained for the final 10 minutes. The solvent was added to the bitumen at 160 °C to prevent solvent evaporation. The sample was then stored for a 25-hour healing period.

Bitumen binder with the 0.6% CBNPs

This sample included 0.6% CBNPs. The bitumen was similarly 420 g, and the methanol was 220 ml. Methanol was put into a beaker for sonication, and 0.6% (4.2 g) CBNPs were added to this solvent. By following the same strategy as stated for the 1st sample, we mixed the sample. After preparing the modified bitumen sample, we allowed it to heal for 25 hours at room temperature.

Bitumen binder with the 0.9% CBNPs

CBNPs were present in 0.9% of this sample. Similarly, the bitumen was 420 g and the methanol was 200 ml. Methanol was sonicated in a beaker, and 0.9% (4.2 g) CBNPs were added to this solvent. We mixed the sample using the same approach as described for the first sample. We allowed the modified bitumen sample to heal for 25 hours at room temperature after preparing it.

Bitumen binder with the 1.2% CBNPs

This sample was likewise prepared using the same method. CBNPs and 200 mL methanol. Methanol was put into the beaker for sonication with an addition of 1.2 % of CBNPs. The sonication was carried out in accordance with the standard and procedure described for the first sample.

Following sonication, the solution was blended with bitumen with a high shear mixer. The mixing by the shear mixer is the same as for other samples. After the homogeneous dispersion of the Carbon black nanoparticles in bitumen, the sample was permitted to heal at ambient temperature for 25 hours.

All other samples of GNPs and MWCNTs were prepared following the same methodology as discussed above.

2.4.2. Dry Method

In this method Nano Particles were simply put into the molten bitumen with their respective percentages and mixed at slow rate 300 rpm for first 10 minutes. Then the temperature was then raised up to 180^{0}C (B. Golestani at el.,2012) and maintained for next 20-25minutes and mixed at high rate of shear mixing at 4800 rpm. Then mix for low rpm for next 10 minutes.

All other samples were prepared by following the same procedure.

2.5. Test Module

The following tests were carried out on modified bitumen samples (containing MWCNTs, GNPs and CBNPs).

2.5.1. Penetration of bitumen

The process involves melting and cooling a sample, then measuring its penetration using a penetrometer. Melt bitumen, both virgin and modified, into molds and divide it among three containers. Cool in room temperature air for 1 to 1.5 hours, then place in a 25 °C water bath for 1 to 1.5 hours. Set the penetrometer marker to zero, and gently touch the sample surface. Measure the distance penetrated in tenths of millimeters, taking at least three readings on the surface.

2.5.2. Softening point of bitumen

Melted bitumen (both virgin and modified) filled two horizontal brass rings. Allow them to cool for 30 minutes at room temperature. After that, set the rings and ball assembly in a beaker of 5 °C water for 15 minutes. Finally, heat the beaker at a rate of 5 °C per minute and record the temperature at which the ball falls and contacts the base of the ring ball assembly.

2.5.3. Ductility of bitumen

The ductility test measures the cohesion and flexibility of bitumen, a pavement construction binder that forms ductile thin films around particles. If the binder material isn't ductile enough, it will crack and expose the pavement surface. The test measures the distance a typical briquette can stretch before breaking. Bitumen is melted into molds and placed in a water bath at 25 degrees Celsius for 85-90 minutes. The test is conducted at 12°C and a pull rate of 5cm per minute.

2.5.4. Flash and fire point Reference

When bitumen is heated, it begins to boil, and the hydrocarbons begin to evaporate. The minimal temperature at which vapors become flash at a spot is referred to as the flash point, whereas the minimum temperature at which these vapors catch fire is referred to as the fire point. Samples were placed at 25 degrees Celsius for half an hour before being placed in a flash and fire apparatus, which automatically provided us with flash and fire values in a written form.

3. Results and discussions

The study investigated the impact of incorporating Carbon Black Nano Particles (CBNPs), Multi Walled Carbon Nano Tubes (MWCNTs), and Graphene Nano Particles (GNPs) on the properties of asphalt binder using both dry and wet mixing methods.

- The study reveals that the addition of CBNPs and GNPs significantly increases the penetration values of asphalt binder modified with MWCNTs, despite variations in mixing methods.
- The softening point of asphalt binder, influenced by CBNPs and MWCNT content, varies with CNT content, indicating its suitability for various environmental conditions.
- Higher percentages of MWCNTs, CBNPs, and GNPs in both mixing methods increased ductility values, indicating an enhancement in bitumen binder performance.
- The bitumen binder's flash and fire point increased with higher MWCNTs, CBNPs, and GNPs due to thermal conductivity and minute size, reducing fire risk.
- Nanomaterials like MWCNTs, CBNPs, and GNPs can improve asphalt binders' properties, but optimal dosage and mixing methods are crucial for long-term durability and environmental impact.

3.1. Observations and Results

3.1.1. Pure Bitumen

Table 1 Testing Results of Pure Bitumen

Pure Bitumen					
Particle	**Percentage**	**Penetration (Avg)**	**Softening Point (0C)**	**Flash & Fire Point (0C)**	**Ductility (cm)**
0	0	70	48.25	274,322	150

3.1.2. Wet Process/Method

Table 2 Testing Results of Modified Bitumen (Wet Method)

Wet Method					
Particle	Percentage	Penetration (Avg)	Softening Point (^{0}C)	Flash & Fire Point (^{0}C)	Ductility (cm)
CBNPs	0.3	36	48.5	282,328	21
	0.6	56	48	290,320	29
	0.9	61	47	294,320	25
	1.2	55	51.5	290,326	14
MWCNTs	0.3	66	49	288,318	22
	0.6	50	50	292,320	16
	0.9	61	52	294,320	26
GNPs	0.3	47	53.5	282,328	18
	0.6	51	51.5	288,326	22

3.1.3. Dry Process/Method

Table 3 Testing Results of Modified Bitumen (Dry Method)

Dry Method					
Particle	**Percentage**	**Penetration (Avg)**	**Softening Point (^{0}C)**	**Flash & Fire Point (^{0}C)**	**Ductility (cm)**
CBNPs	0.3	47	52.5	290,322	11
	0.6	53	52	290,324	13
	0.9	52	51.5	290,334	19
	1.2	45	53	291,336	21
MWCNTs	0.3	36	55	290,316	9
	0.6	49	53	286,326	11
	0.9	44	54.5	286,320	8
GNPs	0.3	33	54.5	286,314	6
	0.6	33	55	280,316	7

4. Conclusion

The study reveals that incorporating Multi Walled Carbon Nano Tubes (MWCNTs) into bitumen binder can improve composite characteristics compared to unmodified binder. The addition of a higher proportion of MWCNTs in the wet method reduces the softening point and increases ductility values, while the dry method remains unchanged. Graphene Nano Particles (GNPs) enhance the penetration value of the asphalt binder while lowering its softening point, while Carbon Black Nano Particles (CBNPs) increase the softening point, leading to variations in penetration and ductility values. The study also suggests that the enhanced thermal stability of the modified binder can contribute to pavement resistance to greater surface temperatures, highlighting the potential of nanomaterials like GNPs, CBNPs, and MWCNTs in improving asphalt pavement thermal performance. The findings suggest that nanomaterials in bitumen binder can enhance pavement durability and performance, but further research is needed to optimize dosage levels, mixing methods, and long-term performance assessments.

Recommendations

The study suggests several recommendations to improve the effectiveness of nanomaterial-modified bitumen in pavement engineering. It suggests optimizing mixing methods, focusing on refining wet mixing techniques to achieve uniform distribution and enhance mechanical properties. The modified bitumen is suitable for extreme weather conditions, preventing cracking and enhancing pavement durability. The optimal healing period is recommended for 24 hours after high shear mixing to stabilize the modified binder structure. Future studies should explore different bitumen sources and grades, such as National Oil Refineries, Byco Oil Refineries, and Parco Oil Refineries, to broaden the applicability and versatility of nanomaterial-modified bitumen. The study recommends varying the percentages of Carbon Nano Tubes (CNTs) to assess their impact on the modified bitumen's properties. Prioritizing safety precautions during handling and application is crucial, including the use of personal protective equipment (PPE) and proper ventilation. These recommendations aim to enhance the applicability of nanomaterial-modified bitumen in pavement engineering.

Compliance with ethical standards

Disclosure of conflict of interest; NONE

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