Morphological and nanomechanical analyses of ground tire rubber-modified asphalts

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Abstract Automobile industries produce more than 5.2 million tons of scrapped tires each year in the United States. Disposal of such a huge amount of waste scrapped tires has become a serious environmental issue. Scopes to use scrapped tires in the form of Ground Tire Rubber (GTR) in pavement industry have been analyzed in recent years. The GTR has potential to improve hot mix asphalt's performance from the view points of stiffness, resilience and shock absorbance properties. On the other hand, in recent years, researchers have attempted to explain performance of asphalt in terms of its nanomechanical characteristics. In this study, the PeakForce Quantitative Nanomechanical Mapping (PFQNMTM) mode of an atomic force microscope has been employed to find basic nanomechanistic properties and the morphology of GTR-modified asphalt binders. A performance grade (PG) binder (PG 64-22) modified with two different grades of GTR (Mesh #30 and Mesh #40) samples have been evaluated in this study. Nanomechanical properties such as adhesion, energy dissipation, deformation, and DMT (Derjaguin, Muller, and Toporov) modulus for the GTR-modified binders have been quantified. Each sample was scanned for three different (5×5 , 10×10 , and 20×20 μm) areas. The PFQNMTM analyses revealed distinct microstructures and grain distributions among tested additive modified binder samples. Two distinct phases, namely Catana and Peri-phase, were observed in GTR-modified samples,

although the DMT moduli were found to be in a close range in these areas. The neat binder showed another phase, named Perpetua, which was missing from the GTR-modified samples. It was observed that modification of asphalt by addition of GTR considerably changes the mechanistic properties of the base binder.

Keywords Asphalt binder · Morphology · Elastic modulus · Ground tire rubber

Introduction

Advanced technology has worked favorably to increase the amount of vehicles in the United States at a constant rate. These vehicles are generating more than 300 million scrap tires each year in the United States (US) [1]. The most common forms of tire disposal are stockpiling, landfilling, and improper dumping, which pose serious environmental hazards as well as health concerns. Accidental fire in stockpile would cause a disaster; trapped rainwater in tires provides a good breeding environment for mosquitos, flies and other insects. Moreover, available land resources are depleting day by day, calling for new sustainable ways to process and dispose ever-growing scrap tires. The U.S. Environmental Protection Agency (EPA), in association with other agencies, has conducted several field trials to find out innovative and sustainable uses of scrapped tires in lieu of stockpiling and landfilling. The main constituent of scrapped tire is mostly in different forms of rubber [2]; its use as Ground Tire Rubber (GTR) as an additive in hot mix asphalt (HMA) in road construction could be a potential area to use scrapped tires in a sustainable way.

To characterize the mechanistic performance of asphalt binders used in HMA, agencies and suppliers in the US

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predominately follow the Superpave binder test protocols and specifications introduced in 1993. The performance grade (PG) system of asphalt binders, introduced as part of the Superpave specifications, provides basic properties of asphalt binders through well-established mix design methods focusing on consistency, macro-scale workability, and strength properties, yet not effective enough in predicting field performance of asphalt pavements [3]. The Superpave specifications do not go well to reflect the internal molecular changes of asphalt after modification with different polymers and non-polymer additives [4]. Physical and chemical changes are expected to occur in asphalts after modified by GTR, which cannot be observed through existing Superpave test procedures. Working principal of an AFM lets investigators determine basic mechanical properties of asphalt binders at micro- and nano-levels; hence, it can play an important role in characterizing GTR-modified asphalts.

An AFM works on the basis of van der Waals forces between different atoms and its tip. Maintaining a fixed amount of attraction force between an AFM tip and material's atoms, it scans the surface of the material from a nano-level distance, proving morphology of atomic resolution order. Measuring the changes in van der Waals forces as well as the force required to cause deformation on the surface of the sample, an AFM can measure different mechanistic properties such as adhesion, modulus of elasticity, hardness, and energy dissipation. Several studies [5–7] have estimated these properties of neat and polymer-modified asphalt binders using different AFM systems. Previous studies related to characterization of asphalt materials at nano- and micro-scale using AFM have been

summarized in Table 1. Nanoindentation, a popular method of an AFM system to test properties of different samples, has been employed by Dourado et al. [5] to quantify stiffness properties and elastic recovery of asphalt binders. These researchers have found that “bee” areas are uniformly distributed over the surface of the binder, which is more elastic relative to the flat matrix. They reported bees' adjacent flat areas to be softer than the flat matrices. Jäger et al. [8] used the same technique to find stiffness behavior in different phases of an asphalt binder. These authors reported that chemical structures of different phases affect mechanical properties, which are greatly influenced by types of additive used in the binder modification processes. Yu et al. [9] used an AFM to measure adhesion forces between the AFM tip and asphalt binder and reported that the “raised areas” in the asphalt binder have higher adhesion values than in the “recessed areas”; the ratio of adhesion values of the former to the latter area on the surface being about two. Some researchers (e.g., [10]) suggested using the Derjaguin, Muller, Toporov (DMT) modulus of asphalt binder for characterization purposes as it considers the adhesion values of the material, while the Young's modulus does not consider the material's adhesion properties. A few other recent studies (e.g., [11, 12]) also estimated the DMT moduli of neat asphalt binders using different AFM systems.

Asphalt binder is a viscoelastic material and has considerable amount of adhesive properties. For this reason, the DMT modulus has been adopted in this study to find out the effect of GTR on the strength properties of asphalt binders. This study is aimed at observing the changes in morphology and important nanomechanistic properties

Table 1 Previous studies on asphalt materials using AFM

Author(s)	Focus	Remarks
Dourado et al. [5]	Elastic recovery and stiffness properties of neat binder by nanoindentation	Stated that “bee structures” are uniformly distributed over entire area Bee areas are more elastic than adjacent flat areas
Jäger et al. [8]	Stiffness behavior in different phases by nanoindentation technique	Mechanical properties in different phases are dependent on chemical structures Additives affect localized mechanical properties
Yu et al. [9]	Adhesion force between AFM tip and asphalt	Adhesion in higher areas is about twice the adhesion in recessed areas
Derjaguin et al. [10]	Effect of adhesion on Young's modulus	Suggested using DMT modulus instead of Young's modulus for adhesive materials
Fischer et al. [11]	Characterizing asphalt using DMT model at different temperatures	Peri-phase is stiffer than the Perpetua Peri-phase is less viscous than the Perpetua DMT is about 200 MPa at 40 °C
Nahar et al. [12]	DMT modulus of asphalt	Elastic behavior of an asphalt binder is related to its adhesive properties
Pfeiffer and Saal [13]	Thermal effect on asphalt at nano-level	Overall morphology of the sample depends largely on temperature history and test temperature

(adhesion, elasticity, dissipation and deformation) of asphalt binders modified with different grades and amounts of GTR.

Experimental setup

The TappingTM mode of an AFM is a popular method to get the morphology of any sample. For mechanistic properties, nanoindentation is the most preferred one among several other modes due to its capability of providing a wide range of outputs. In this method, indentations by sharp tips are performed at selected points of the sample, and force–displacement curves are obtained for further analysis. This technique has been reported to have a few limitations. A few researchers [14, 15] have reported difficulties of the nanoindentation technique to measure quantitative properties of asphalt. In this method, the applied force on the tip is correlated with the deformation of sample (indentation of tip into the sample). The relation between the applied force and indentation depth is called as “force curve”. Allen et al. [14] concluded that improper force on AFM tips to acquire force curves might result in non-representative values; too high force over a period of several seconds might cause penetration of tips into the thin specimen and substrate, and too low force might result in inconsistent outcome. Tarefder et al. [15] also reported difficulties of the nanoindentation technique to characterize asphalt samples because of their adhesive surface. Moreover, researchers often end up performing nanoindentation only at pre-selected places. Asphalt has a very complex chemical combination of hundreds of components, making a non-homogenous surface. Nanoindentation at selected places might not catch the actual scenario for the total asphalt material. Bruker Corporation [11, 16] has introduced a new mode of Quantitative Nanomechanical Mapping (QNMTM), namely PeakForce Quantitative Nanomechanical Mapping (PFQNMTM). The PFQNMTM technique is a combination of the TappingTM and QNMTM modes. It captures the topography of the sample and obtains the force curve simultaneously [11, 12, 16] and

calculates the mechanistic properties at each point of the scan area. The construction processes of a typical force–displacement curve are shown in Fig. 1. The tip force used to cause a very small deformation on the sample surface is recorded along with the amount of deformation (penetration in the sample). The relation between the force on tip and corresponding penetration (force–distance relationship) in the sample can be used to find out different mechanical properties of the sample. The model for DMT modulus is graphically shown in Fig. 1c.

In this study, the PFQNMTM mode has been employed to characterize GTR-modified asphalt samples. A total of three types of samples were mapped for this study. The details of the tested samples are provided in Table 2. Sample 1 is a virgin binder and called as the Control. GTR Mesh #30 and Mesh #40 samples have been blended with the virgin binder, and they are labeled as Sample 2 and Sample 3, respectively. For both of the GTR-modified samples, an amount of 15 % GTR by the weight of the neat binder has been used in this study.

To replicate the field blending process, the GTR was blended with the base binder manually by following a wet blending process developed by the research team and published elsewhere in the literature [17]. In this procedure, the sample was heated up to 163 °C and then stirred for 1 min using a glass rod. Then it was kept in a mechanical oven for another 9 min. A total 6 cycles of stirring and heating was performed over an hour to finish the blending procedure. For preparing AFM test samples, the heat cast approach [18, 19] has been adopted in this study. In this approach, a preheated asphalt sample droplet was placed on a clean glass plate and then heated in the oven at 163 °C for about 15 min. Then the glass plate was allowed to cool down to room temperature. These samples were tested by the AFM system within a week of preparation. While using a Bruker Dimension Icon system, SCANASYST-AIR tips (silicon tips on nitride lever), also manufactured by Bruker, were used to test the binder samples following PFQNMTM mode [20]. Each test was replicated for at least three successful scans. Three different scan areas of 5 × 5, 10 × 10, and 20 × 20 μm were

Fig. 1 **a** PeakForce TappingTM mode working principle, **b** construction of force curve, and **c** analysis of force curve [15]

Table 2 Test samples of this study

Label	Sample description	Source of materials
Sample 1	PG 64-22 (control)	Ergon Asphalt and Emulsions, Inc., Memphis, TN, USA
Sample 2	PG 64-22 + 15 % GTR Mesh #30	GTR from Liberty Tire Recycling, Pittsburgh, PA, USA
Sample 3	PG 64-22 + 15 % GTR Mesh #40	GTR from Liberty Tire Recycling, Pittsburgh, PA, USA

considered. Different scan areas were meant to provide detailed information of the overall morphology of the sample. The smallest scan area was intended for “bee structure” characterization, while the largest area was intended to cover both bee and flat matrices. The machine used NanoScope 9.1 software to scan and save the data. All captured data were processed using the Nanoscope Analysis (Version 1.5) software.

Results and discussion

Previously, researchers have reported at least 3 different areas in the asphalt sample morphology, which are “bee structures”, “adjacent areas of bee”, and “flat matrices”. Loeber et al. [21] named these distinct areas as “Catana” or “Bee-phase”, “Peri-phase”, and “Perpetua-phase”, respectively. Graphical explanations of these phases are given in Fig. 2. The Catana (Bee) phase is the most irregular portion of the binder surface, containing alternate protrusions and intrusions.

The height (or depth) of these structures comes around 50 μm in neat PG 64-22 binder. Peri-phase is the surrounding part of Catana, having small amount of irregularities in surface compared to Catana, while the Perpetua-phase is the flat surface of asphalt. Another phase named “Sal phase” has been reported to be present in some

modified asphalts [21]. The properties of asphalt in Perpetua have been found to be significantly different from Catana or Peri-phase.

Figures 3 and 4 show the relationship between morphology and other characteristics of 3 different sets of samples (Control, Mesh #30 GTR and Mesh #40 GTR-modified asphalt binder). Both of the figures have 3 columns: Column (a) contains scan results for Control sample (PG 64-22), whereas Columns (b) and (c) show the results for GTR Mesh #30 and Mesh #40 blend, respectively. The scan size reported here is of 10 $\mu\text{m} \times 10 \mu\text{m}$. Among 8 available channels in PFQNMTM, data acquired from 5 channels containing height, adhesion, deformation, dissipation and DMT modulus of tested samples have been reported in this study. Figure 3 shows the measurements for height and adhesion, and Fig. 4 contains deformation, dissipation and DMT modulus maps for all samples. The aforementioned mechanistic properties were estimated at the same time of scanning.

Morphology of the sample is given by the “Height” channel. For the Control sample, all three phases were observed in different amounts. Catana-phases were seen to be distributed over the surface and the height of the bee structures ranged up to 74 nm. The morphology of the base binder was changed considerably after addition of GTR. Both of the GTR samples eliminated Perpetua-phase from the scene as can be seen in Fig. 2b, c. GTR-modified samples were observed to have only two phases (e.g., Catana and Peri-phase); the boundary between them was indistinguishable. However, the overall height of the surface irregularity of the modified binders was almost similar to that of the Control. It is also observed that the distribution of Catana and Peri-phases for GTR-modified samples were uniform over the surface of the sample. The adhesion force between the AFM tip and the sample surface is provided in the second row of Fig. 3. Adhesion values for the Control sample have been seen to be largely dependent on the morphology of the surface, whereas Peri-phase has higher adhesion values than Perpetua or Catana-phase. These findings are in agreement with observations made in a previous study [9].

This study has also found some special traces of different adhesion value in the Perpetua-phase. The flat area of Perpetua has higher adhesion values while those traces of roughness showed very low adhesion value. The

Fig. 2 Different morphological phases of asphalt

Fig. 3 Height and adhesion map for **a** PG 64-22 (Control), **b** 15 % GTR Mesh #30 blended with PG 64-22, and **c** 15 % GTR Mesh #40 blended with PG 64-22

maximum adhesion value for the Control sample was found to be around 9 nN, which was decreased for GTR Mesh #30 blend to 8 nN while increased to 12 nN in the case of GTR Mesh #40 blend. Fineness of the additive or blending efficiency could be the possible reason behind these differences in adhesion values. Finer particle (Mesh #40) is expected to produce a more uniform blend than that of a coarser particle (Mesh #30), hence providing differential adhesion values.

Deformation is a relative measure of any material's hardness. The deformation map (Fig. 4) of any sample stands for the depth of penetration caused at the scanning position for a fixed force on the AFM tip. A higher value of deformation indicates lower stiffness of the sample. From Fig. 4a through c, it is seen that the addition of GTR stiffened the sample to some extent. The increase in hardness for Mesh #40 GTR-modified asphalt is significantly higher than that of Mesh #30 GTR.

Dissipation or energy dissipation for any sample is an indirect measure of elastic behavior of the material. Dissipation is calculated by measuring the hysteresis between extending and retracting curves in the "force curve"; a large value indicates highly non-elastic behavior of the sample. The trend of dissipation energy is directly related to the adhesion force, which can be seen in Fig. 4. Fischer et al. [11] reported a similar relationship between adhesion

and dissipation values. The Mesh #40 GTR sample produced the maximum value of dissipation energy among the three tested samples.

The DMT modulus (Fig. 4c) of the tested samples was also following the trend of morphology. This trend can be seen clearly from the DMT modulus map of the Control sample. The Catana and the Peri-phase of the Control sample have similar magnitude of moduli, which are lower than that of the Perpetua-phase. The maximum value of DMT modulus for the neat binder is 90 MPa, and it increases up to 280 MPa for Mesh #30 GTR-blended sample and 200 MPa for Mesh #40 GTR-blended sample. Although the map for Mesh #30 GTR sample shows several peak (maximum and minimum) values, the other GTR-modified sample (Mesh #40) exhibits almost similar values on the surface. Finally, it can be summarized that GTR affects the DMT modulus of asphalt binder, increasing the maximum value by 200 %.

Conclusion

An AFM has been proved to be a viable machine to characterize nanomechanistic properties of asphalt binder and modified asphalt binder, producing consistent results. The PeakForce Quantitative Nanomechanical Mapping (PFQNMTM) mode was found to be a simple and effective

Fig. 4 Deformation, dissipation, and DMT modulus map for **a** PG 64-22 (Control sample), **b** 15 % GTR Mesh #30 blended with PG 64-22, and **c** 15 % GTR Mesh #40 blended with PG 64-22

technique to obtain the desired nanomechanical data of ground tire rubber (GTR)-modified asphalt binders. The adhesion of the neat binder was found to be linked with the morphology of the sample. The dissipation and deformation values were directly related to the adhesion values of the sample. The GTR additive significantly changed the microstructure and mechanical properties of the base binder. Among three phases seen in the neat binder, Perpetua-phase diminished, and Catana and Peri-phases overlapped each other after modification by GTR. The GTR affected the adhesion, deformation and dissipation properties of the neat binder, but the most affected one was the DMT

modulus. The GTR-blended asphalts showed over 200 % increase in the DMT modulus compared to the base binder. The outcomes of this study are expected to enhance the insight about modified asphalt binders. Further study on this topic can establish meaningful correlation between nano-scale properties of asphalt binder with the macro-scale parameters, which will help in predicting asphalt's field performance.

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