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1 **Understanding interfacial interaction characteristics of asphalt nanocomposites**
2 **reinforced with diamond nanothread and carbon nanotube**

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11
12 **Abstract**

13 Diamond nanothreads (DNT) and carbon nanotubes (CNT) have emerged as
14 promising reinforcement materials for asphalt. However, the interfacial properties
15 between DNT/CNT and asphalt remain poorly understood, hindering the advancement
16 of DNT/CNT-modified asphalt nanocomposites. In this study, the pullout tests are
17 conducted on asphalt nanocomposites reinforced with DNT, nitrogen-doped diamond
18 nanothread (NDNT), and CNT, to analyze the pullout performance and reinforcing
19 mechanisms across various temperature ranges. The findings reveal that CNT
20 modified asphalt nanocomposites exhibit superior pullout performance compared to

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those reinforced with DNT, primarily due to π - π stacking interactions that facilitate the wrapping of asphalt molecules around the CNT surfaces. Among the DNT variants, the DNT2 modified asphalt nanocomposite demonstrates the highest pullout performance, attributed to its helical structure that enhances mechanical interlocking within the asphalt matrix. Notably, NDNT shows the highest binding energy relative to both DNTs and CNTs, stemming from interactions between hydroxyl groups on asphaltene-phenol and nitrogen atoms on NDNT, leading to the formation of O-H $\cdots$ N hydrogen bonds. Density functional theory (DFT) calculations indicate that nitrogen doping modifies the electronic structure of NDNT, resulting in localized negative charges that enhance its overall electronegativity.

Keywords: Asphalt; Interfacial properties; Diamond nanothread; Carbon nanotube; DFT calculations.

1 Introduction

1.1 Background

While asphalt pavements offer advantages such as smooth and quiet surfaces, rapid construction, and simplified maintenance, their widespread application is constrained by the inherent thermomechanical properties of asphalt¹. The thermomechanical properties of asphalt refer to how its mechanical behavior changes in response to temperature variations^{2,3}. Poor thermomechanical properties lead to temperature-induced distress and fatigue cracking under loads and environmental impacts, necessitating frequent and costly maintenance that strains infrastructure



1 budgets and disrupts traffic. Therefore, it is imperative to improve the
2 thermomechanical properties of asphalt through innovative material modification
3 strategies to enhance the long-term durability of asphalt pavement.

4 **1.2 Literature review**

5 Various modification methods have been developed over the past few decades to
6 enhance the thermomechanical properties of asphalt ⁴. Early approaches primarily
7 focused on incorporating polymers, such as styrene-butadiene-styrene (SBS) and crumb
8 rubber (CRM), to improve asphalt's performance ⁵. SBS enhances high-temperature
9 performance and deformation resistance, while CRM improves low-temperature
10 performance and reduces noise pollution ⁶. However, polymer modifiers are
11 vulnerable to environmental factors like heat, oxygen, and UV radiation, which can
12 compromise the long-term performance of modified asphalt composites. Additionally,
13 fiber reinforcement—utilizing cellulose fibers, mineral fibers, and synthetic fibers—
14 can significantly enhance tensile strength and fatigue resistance by creating a
15 reinforcing network within the asphalt ^{7,8}. However, fibers often tend to accumulate
16 and clump during the mixing process, resulting in uneven distribution and compromised
17 performance of the final composite material. Despite these limitations of traditional
18 modification methods, the introduction of nanomaterials offers a promising alternative.
19 The unique physical and chemical properties of nanomaterials provide significant
20 advantages in enhancing the performance of asphalt, making them an attractive option
21 for future research and application ⁹. Nanomaterials, particularly carbon-based



1 materials such as carbon nanotubes (CNTs) and graphene, as well as inorganic materials
2 like nano-clay, nano-silica, and nano-TiO₂, exhibit exceptional mechanical properties,
3 high specific surface areas, and excellent thermal stability. These characteristics
4 enable these specific nanomaterials to significantly enhance the thermomechanical
5 properties of asphalt. It has been demonstrated that the incorporation of CNTs,
6 graphene, and other nanomaterials can lead to improvements in the stiffness,
7 deformation resistance, fatigue cracking resistance, and self-healing properties of
8 asphalt ¹⁰⁻¹². The significant surface area of nanomaterials facilitates strong
9 adsorption and interaction with asphalt molecules, leading to the formation of
10 homogeneous and stable nanocomposite structures ¹³. Moreover, the enhanced
11 interaction facilitates the load transfer and stress distribution within the asphalt,
12 resulting in increased toughness against deformation and cracking.

13 Diamond nanothread (DNT) becomes a particularly intriguing option due to its
14 predicted exceptional tensile strength, stiffness, and unique surface chemistry ¹⁴. With
15 remarkable mechanical properties, DNT possesses Young's modulus of 850 GPa and
16 bending rigidity of 5.38×10^{-28} N/m². DNTs exhibit a significantly higher torsional
17 elastic limit (almost three times greater) and interfacial load transfer (more than double)
18 compared to CNTs ¹⁵. They also have a low thermal expansion coefficient and
19 remarkable thermal stability, demonstrating negligible thermal deformation and
20 degradation during temperature fluctuations ¹⁶. Their thermal conductivity can reach
21 up to 2000 W/m·K, which facilitates an even distribution of pavement temperature.



1 This, in turn, helps to minimize thermal stress concentrations and lowers the risk of
2 cold cracking of asphalt. Furthermore, the hydrogenated surfaces facilitate covalent
3 bonding between DNTs and matrix, allowing for their functionalization without
4 introducing any defect in the backbone structure, making them especially suitable as
5 modifiers for nanocomposites^{17,18}. In particular, nitrogen-doped diamond nanothread
6 (NDNT) enhances the interfacial interactions due to its unique surface properties, which
7 improve adhesion with the asphalt matrix. The surface chemistry of DNT, NDNT,
8 and CNT is fundamentally different, leading to variations in interfacial adhesion.
9 Enhanced interfacial adhesion is vital for preventing debonding and ensuring effective
10 stress transfer throughout the modified material. The complexity of asphalt molecules
11 has hindered a thorough understanding of how DNT, NDNT, and CNT reinforce the
12 interfacial properties of asphalt nanocomposites. While previous studies have
13 primarily concentrated on the individual effects of CNTs on asphalt properties, our
14 research uniquely explores the interfacial load transfer capabilities and shear resistance
15 of both DNT and CNT modified asphalt for the first time. To the best of the authors'
16 knowledge, few studies have clarified the reinforcing mechanisms of DNT, NDNT, and
17 CNT within the asphalt matrix at the atomistic level. The unveiled mechanisms are
18 crucial for understanding the unique interactions between the reinforcements and
19 asphalt, which can aid in predicting and optimizing the performance of DNT modified
20 asphalt nanocomposites.



1.3 Research motivation

Experimentally investigating DNT/CNT reinforced asphalt at the nanoscale is difficult due to the challenges in manipulating and observing nanoscale interactions in the laboratory. Molecular dynamics (MD) simulations provide a powerful and advantageous alternative^{19, 20}. MD simulations are widely employed to investigate the interfacial behaviors and mechanical properties of DNT/CNT modified materials due to the atomistic resolution and ability to capture molecular interactions. MD simulations have been utilized to study the interfacial contact behaviors between CNTs and asphalt binders, revealing that the addition of multi-walled CNTs can significantly enhance the adhesion ability of asphalt on aggregate surfaces, particularly for alkaline aggregates²¹. The effects of DNT on the glass transition temperature of poly(methyl methacrylate) (PMMA) composites are investigated by MD simulations, demonstrating the exceptionally high glass transition temperatures and low densities of DNT modified PMMA composites²². Besides, MD simulations and DFT calculations are combined to explore the frictional performance of DNT modified polymer composites, underscoring that DNT significantly enhances the frictional resistance of polymer composites by the improved interfacial interactions²³. Furthermore, MD simulation overcomes the experimental limitations by enabling the direct visualization and quantification of interactions at the atomistic level, providing atomistic insight into the reinforcement mechanisms between asphalt and DNT/CNT²⁴⁻³¹. While asphalt consists of complex and diverse components, MD simulation can effectively manage



this complexity and offer insights into the interactions between DNT/CNT and asphalt molecules^{32, 33}. Asphalt properties, including aging, fatigue cracking, and moisture resistance, have been detailly investigated by MD simulations, and the availability and validity of MD can be demonstrated^{6, 34, 35}. Additionally, MD simulations have demonstrated the ability to assess the mechanical strength, thermal conductivity, and interfacial adhesion of DNT/CNT nanomaterials^{36, 37}. Compared to the high costs and time investments associated with nanoscale experiments, MD offers a more cost-effective and efficient approach to explore a broader range of parameters and predict the performance of DNT modified asphalt, thus accelerating the development of optimized asphalt nanocomposites.

1.4 Research objective

The objective of this study is to investigate the shear resistance of DNT/CNT modified asphalt nanocomposites, comparing the reinforcing mechanisms between DNT and CNT in asphalt nanocomposites at the first time. Pullout tests are employed to assess the interfacial load transfer capabilities between asphalt and DNT/CNT, while DFT calculations are applied to examine the interfacial binding and electrostatic properties. Results show that the uneven hydrogenated surface of DNT creates geometric restrictions with asphalt matrix, facilitating the mechanical interlocking and reducing the mobility of asphalt along the longitudinal direction of DNT, thereby enhancing load transfer. Hydrogen bonding increases the shear resistance of NDNT by constraining molecular motion of asphalt molecules within the matrix. The



binding energy between NDNT and asphalt molecules is higher than that of other DNTs due to the polarized nitrogen-doping surface. In contrast, CNT modified asphalt nanocomposites exhibit higher resistance to shear deformation and increased rigidity than DNTs. The π - π stacking interactions are crucial, allowing asphalt molecules to wrap around CNT surfaces, which improves adhesion and load transfer. The delocalized π -electrons of CNT enhance adhesion with aromatic rings in asphalt. By assessing the effectiveness of DNTs and CNTs in asphalt nanocomposites, this study uncovers new strategies for developing more efficient nanomaterials for asphalt reinforcement, which can significantly enhance the durability and lifespan of asphalt pavement.

2 Model and methodology

2.1 Atomistic model

The 12-molecule model representing AAA-1 asphalt from the Strategic Highway Research Program (SHRP) asphalt systems is employed in this study, which has been widely adopted in asphalt research³⁸. Four components, including asphaltene, polar aromatics, naphthene aromatics, and saturates, are identified in this model, as shown in Figure 1(a). Each component consists of several representative molecules, which are determined by the Hansen solubility parameters and mass fractions of the corresponding elements and components in asphalt³⁹. Three molecular structures, namely asphaltene-phenol, asphaltene-pyrrole, and asphaltene-thiophene, are chosen to represent asphaltene molecules, as they more accurately reflect the true asphaltenes and



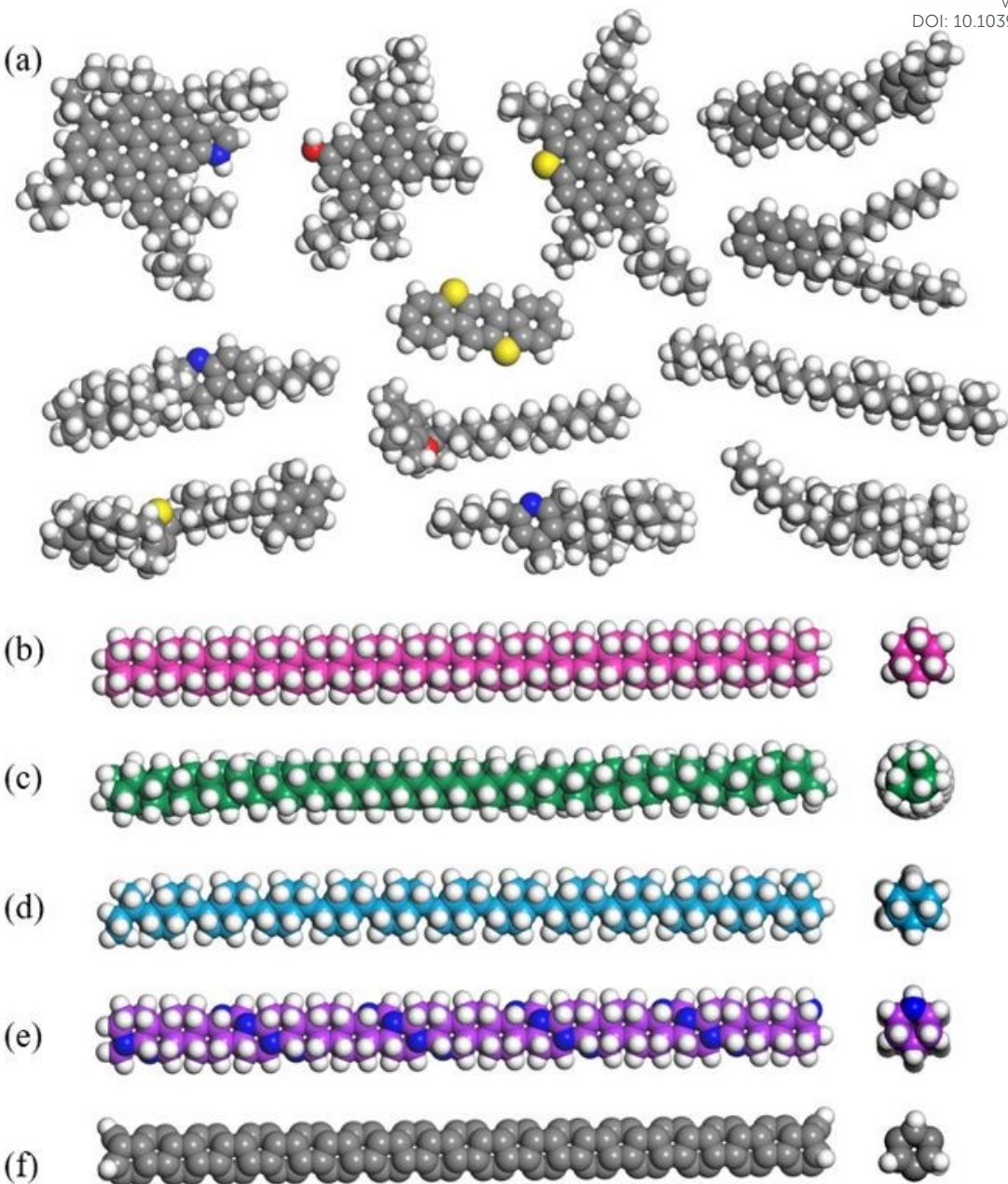
1 mitigate the “pentane effect”⁴⁰. The polar aromatics are represented by five different
2 molecules from the sedimentary rock samples of geochemistry literature, including
3 quinolinohopane, thioisorenieratane, benzobisbenzothiophene, pyridinohopane, and
4 trimethylbenzeneoxane⁴¹. Two naphthene aromatic molecules are identified in this
5 model as perhydrophenanthrene-naphthalene (PHPN) and dioctyl-cyclohexane-
6 naphthalene (DOCHN), possessing the average distribution of aromatic, naphthenic
7 and paraffinic carbons of crude oils. Finally, hopane and squalene are selected as the
8 saturate components of asphalt, aligning with the direct separation and quantitative
9 analysis of n- and iso-alkanes in neat SHRP asphalts. Hopane is typically found in
10 crude oils, while squalene is derived from both plant and animal sources and is also
11 present in petroleum⁴². The molecular formula and fractions of different asphalt
12 components are presented in Table 1. The mass ratios of four components in the
13 asphalt model are calculated and shown in Figure 2, which is in good accordance with
14 the asphalt from the experimental measurement³⁹. The molecular mass ratios help
15 determine the balance between the reinforcing capabilities of the nanomaterials and the
16 viscosity of the asphalt, which is essential for ensuring optimal dispersion and
17 interaction within the nanocomposite. The number of each type of molecule used in
18 our model asphalts was carefully adjusted to align with experimental data on asphalt
19 speciation and atomic composition from SHRP asphalts³⁹. This approach ensures that
20 our model accurately represents the complex composition of real-world asphalt, which
21 typically contains a balance of various sizes and atom types, including carbon,



1 hydrogen, nitrogen, sulfur, and oxygen⁴³. Various stable DNT topologies have been
2 found by the first-principle calculations, which can be synthesized and characterized
3 using experimental methods⁴⁴. Three typical DNTs with the same aspect ratios are
4 selected and identified as DNT1, DNT2, and DNT3 in this study, as shown in Figure
5 1(b)-(e). These DNTs exhibit sp^3 hybridization and are present in their lowest energy
6 states. DNT1 is derived from a hydrogenated carbon nanotube with a chirality of (3,
7 0), known for its stability and favorable electronic properties. DNT2 features a coiled
8 structure, providing insights into how curvature affects mechanical properties and
9 interactions with surrounding materials. DNT3 adopts a zigzag configuration,
10 allowing us to explore the effects of this topology on the overall performance and
11 compatibility with asphalt. Each of these structures exhibits sp^3 hybridization and is
12 present in its lowest energy state, making them suitable candidates for our
13 investigations. Besides, NDNT is proposed to investigate the influence of
14 heteroatoms on DNTs interacting with asphalt. NDNT is constructed by substituting
15 the carbon atoms on certain locations of the nanothread backbone by nitrogen atoms,
16 and the nitrogen ratio of NDNT model is 16.7% to ensure adequate dopants⁴⁵.
17 Furthermore, a molecular structure of CNT with a chirality of (3, 0) is also constructed
18 to compare with the DNT and NDNT structures with the same aspect ratio. The same
19 length and aspect ratios of DNT, NDNT, and CNT are chosen to ensure a fair
20 comparison in the pullout test.

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Figure 1 Atomistic configurations of (a) 12-molecule asphalt model. Front views and side views of (b) DNT1, (c) DNT2, (d) DNT3, (e) NDNT, and (f) CNT with chirality of (3, 0). (The dark blue atoms on NDNT refer to the doped nitrogen atoms).



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Table 1 Molecular formula and ratios of asphalt components.

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Component	Molecular type	Molecular formula	Number	Molecular mass (g/mol)	Mass ratio (%)
Asphaltene	Asphaltene-phenol	C ₄₂ H ₅₄ O	12	574.9	5.3
	Asphaltene-pyrrole	C ₆₆ H ₈₁ N	8	888.4	5.5
	Asphaltene-thiophene	C ₅₁ H ₆₂ S	12	707.1	6.5
	Quinolinhopane	C ₄₀ H ₅₉ N	16	553.9	6.8
	Thioisorenieratane	C ₄₀ H ₆₀ S	16	573.0	7.0
Polar aromatics	Benzobisbenzothiophene	C ₁₈ H ₁₀ S ₂	60	290.4	13.4
	Pyridinohopane	C ₃₆ H ₅₇ N	16	503.9	6.2
	Trimethylbenzeneoxane	C ₂₉ H ₅₀ O	20	414.7	6.4
Naphthene	PHPN	C ₃₅ H ₄₄	44	464.7	15.7
aromatics	DOCHN	C ₃₀ H ₄₆	52	406.7	16.2
Saturate	Hopane	C ₃₀ H ₆₂	16	482.9	5.9
	Squalane	C ₃₅ H ₆₂	16	422.8	5.2



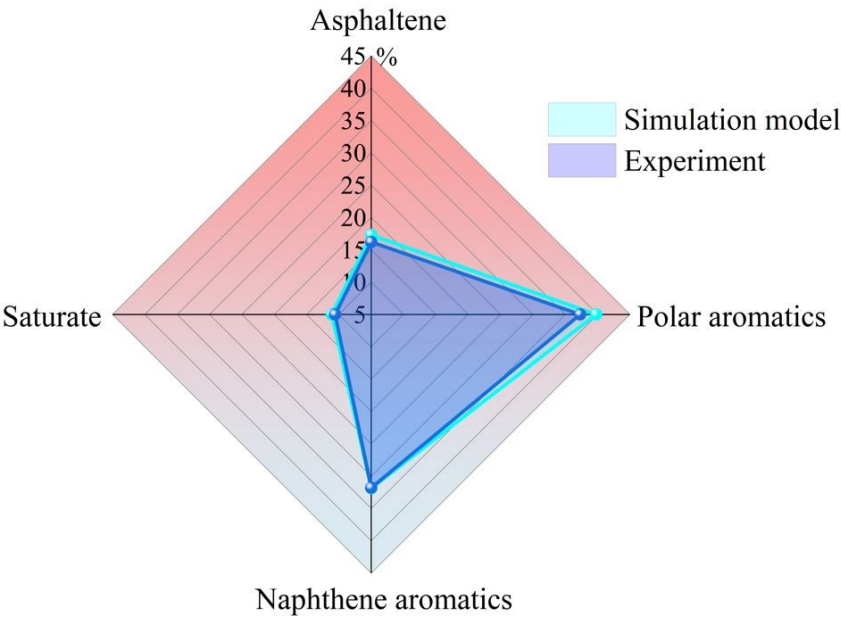


Figure 2 Mass ratios of four asphalt components between model and experiment.

2.2 Forcefield

In this study, we applied the Consistent Valence Forcefield (CVFF) for the MD simulations due to its broad applicability and proven effectiveness in accurately modeling molecular interactions in asphalt and CNT based nanomaterials. Although CVFF might have limitations in modeling highly specific hydrogen bonding or other nuanced interactions compared to COMPASS or PCFF forcefield, it is capable of reliably calculating essential physical and mechanical properties of asphalt, including density, cohesive energy density, and diffusion coefficient, which are crucial for understanding the behavior of asphalt in various applications^{46, 47}. Furthermore, CVFF has been successfully employed to investigate the mechanical properties of CNTs and DNTs, capturing their unique bonding characteristics and structural behaviors^{48, 49}. Additionally, CVFF is well-suited for MD simulations because it

effectively treats both bonded and non-bonded interactions, ensuring that our simulations accurately reflect the dynamic behaviors of nanocomposites⁵⁰. The functional expression of CVFF is presented as:

$$E_{total} = \sum_b K_b (b - b_0)^2 + \sum_\theta K_\theta (\theta - \theta_0)^2 + \sum_\phi K_\phi [1 + s \cos(n\phi)] + \sum_\chi K_\chi [1 - \cos(2\chi)] \\ + \sum_{nonbond} \left\{ \epsilon_{ij} \left[\left(\frac{r_{ij}^o}{r_{ij}} \right)^{12} - \left(\frac{r_{ij}^o}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\epsilon_0 r_{ij}} \right\} \quad (1)$$

Here, the energy terms are composed of the bonded interaction terms and the non-bond interaction terms. The bonded interaction terms involve bond interactions, bond angle interactions, torsional angle interactions, and out-of-plane angle interactions. The non-bond interaction terms involve the van der Waals interactions and the electrostatic interactions. The van der Waals interactions are represented by the LJ-12-6 function, while the electrostatic interactions are described by the Coulombic function.

2.3 Simulation method

The adopted asphalt model and forcefield are validated by computing the key properties, including density, viscosity, and glass transition temperature (T_g). The density values are obtained from the simulation results after a 1-ns NPT simulation at 300 K and 101 kPa, once the asphalt system reaches full equilibrium. Green-Kubo method⁵¹ is a precise and effective way to determine the shear viscosity of the asphalt system, and the formula is shown below:

$$\eta = \frac{V}{\kappa_B T} \int_0^\infty \langle P_{\alpha\beta}^S(0) P_{\alpha\beta}^S(t) \rangle dt \quad (2)$$



1 where η refers to the viscosity of asphalt, κ_B refers to the Boltzmann constant, V and
 2 T are the volume and temperature of the system, respectively. $P_{\alpha\beta}^S(0)$ and $P_{\alpha\beta}^S(t)$
 3 are the instantaneous values of the off-diagonal stress tensor components $\alpha\beta$ at the
 4 initial time and at a specific time of t , respectively. The glass transition temperature
 5 represents the motion characteristics of polymeric materials, specifically referring to
 6 the mobility of molecular chains⁵². The glass transition temperature of the asphalt
 7 system is determined using a stepwise cooling approach within molecular dynamics
 8 simulations. Initially, the system is equilibrated at 420K for 1 ns under NPT
 9 conditions (1 fs timestep, Nose-Hoover thermostat/barostat). The temperature is then
 10 lowered in 20K decrements to 100K. Each cooling step involves a 150-ps NPT
 11 simulation, comprising a 50-ps cooling phase and a 100-ps equilibration period. The
 12 specific volume values at each temperature are averaged and recorded. Three
 13 independent simulations are performed to ensure statistical accuracy.

14 The pullout test is conducted to investigate the shear resistance and interfacial
 15 interactions between asphalt and DNTs, as depicted in Figure 3. Before the pullout
 16 process, both DNT and CNT structures undergo a thorough equilibration procedure,
 17 including initial optimization using a 500-ps NPT ensemble at 300K and 101kPa,
 18 followed by the application of nonperiodic boundary conditions along the length
 19 direction with a 120Å vacuum gap. A further 200-ps NVT ensemble at 300K is
 20 applied for additional relaxation, simulating realistic conditions during the interaction
 21 of DNT/CNT with asphalt. The dragged end of the reinforcement is considered rigid,



1 while the remaining atoms are flexible. The pullout simulation is conducted by
 2 applying a constant velocity of 5×10^{-4} Å/fs to one end of the reinforcement within an
 3 NVT ensemble, while the lateral edges of the 10 Å thick asphalt are kept fixed. The
 4 pullout velocity is chosen based on the previous pullout speed of CNT from the asphalt
 5 matrix, which can lead to reasonable results⁵³. The pullout simulation results are
 6 averaged across multiple independent configurations to minimize the random error.

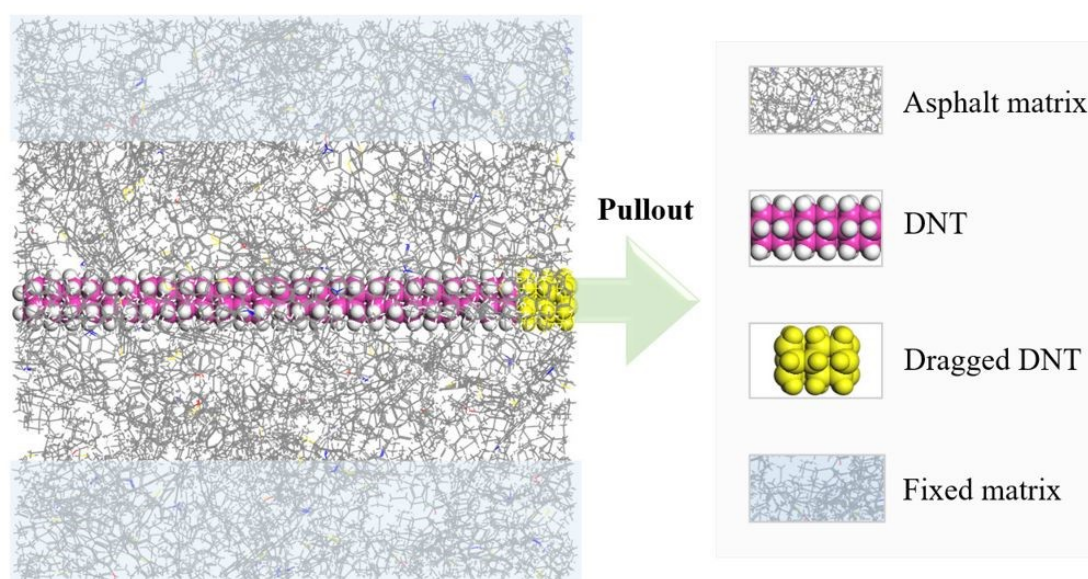


Figure 3 Diagram of DNT pulled out from asphalt matrix.

10 The binding energy and molecular electrostatic potential are computed to
 11 investigate the interaction difference between asphalt components and reinforcements.
 12 The molecular electrostatic potentials between asphalt and reinforcements are
 13 accurately computed using density functional theory(DFT). For these calculations,
 14 the generalized gradient-corrected functionals of Perdew-Burke-Ernzerhof(PBE) are
 15 applied to assess the electronic properties. The atomic orbital basis set is defined



1 using double numerical plus d-functions, with a global orbital cutoff radius set at 3.3
 2 Å. Geometry optimization and DFT calculations are performed using the DMol3
 3 module in Materials Studio, with an energy convergence tolerance of 0.001Ha, a
 4 maximal force of 0.02Ha/Å, and a maximal displacement of 0.001Å. Incorporating
 5 dispersion corrections would increase both the complexity and computation time of our
 6 DFT calculations; therefore, they are not included to maintain computational efficiency
 7 ⁵⁴. Additionally, since asphalt and reinforcement materials primarily rely on polar and
 8 electrostatic interactions rather than dispersion forces, the necessity for dispersion
 9 corrections is less critical ⁵⁵. The formula of binding energy(E_{Bind}) is presented as:

$$10 \quad E_{\text{Bind}} = E_{\text{Asphalt-reinforcement}} - E_{\text{Asphalt}} - E_{\text{Reinforcement}} \quad (3)$$

11 Where $E_{\text{Asphalt-reinforcement}}$ refers to the total energy of the asphalt and reinforcement
 12 system, E_{Asphalt} and $E_{\text{Reinforcement}}$ refer to the energy of the isolated asphalt and the
 13 isolated reinforcement, respectively.

14 The scheme of atomistic modeling and methodology is shown in Figure 4.



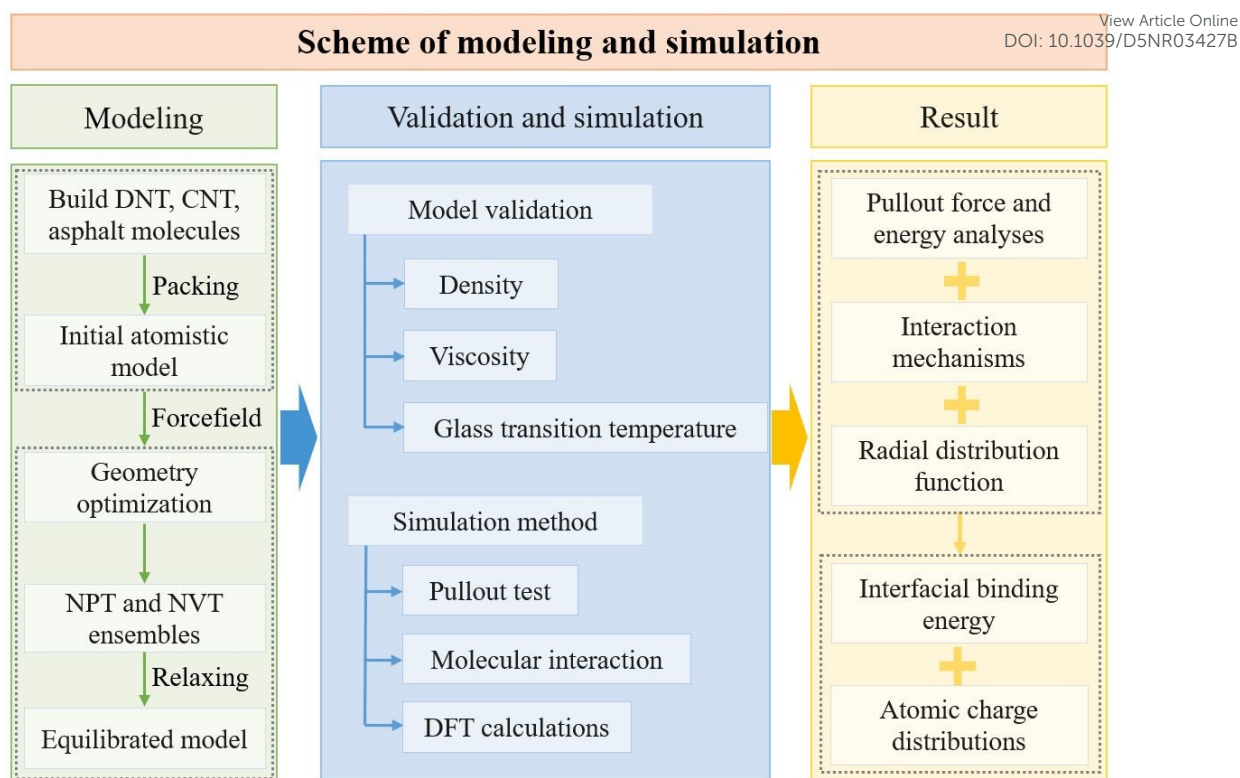


Figure 4 Scheme of atomistic modeling and simulation.

3 Results and Discussion

3.1 Model validation

The calculated density values of DNT1, DNT2, DNT3, NDNT, and CNT modified asphalt nanocomposites are all 1.01 g/cm³. The density value of pure asphalt is 1.02 g/cm³, showing a 2% deviation from the experimental value of approximately 1.0 g/cm³^{39, 56}. The density values of DNT/CNT modified asphalt nanocomposites are slightly lower than that of pure asphalt, indicating the lightweight feature of DNT/CNT modified nanocomposites. The viscosity of pure asphalt, DNT1 modified asphalt nanocomposite, DNT2 modified asphalt nanocomposite, DNT3 modified asphalt nanocomposite, NDNT modified asphalt nanocomposite, and CNT modified asphalt



nanocomposite are 1.46 cP, 1.79 cP, 1.72 cP, 1.53 cP, 2.09 cP, and 2.15 cP, respectively.

The calculated viscosity is 1.46 cP, which deviates by about 3% from the viscosity result of 1.5 cP for the AAA-1 asphalt system ⁵⁷. It is found that DNT/CNT reinforcements can significantly increase the viscosity of asphalt, attributing to the increased interactions between DNT/CNT and asphalt matrix. The calculated T_g values of pure asphalt, DNT1 modified asphalt nanocomposite, DNT2 modified asphalt nanocomposite, DNT3 modified asphalt nanocomposite, NDNT modified asphalt nanocomposite, and CNT modified asphalt nanocomposite are 246K, 254K, 251K, 260K, 275K, and 255K, respectively. The calculated T_g value is 246 K, with a deviation of approximately 1% from the experimental T_g of 248.56 K for the AAA-1 asphalt system ⁵². Compared to pure asphalt, the improved T_g values of DNT/CNT modified asphalt nanocomposites indicate the enhanced thermal stability and better deformation resistance to temperature fluctuations. Notably, NDNT modified asphalt nanocomposite has higher viscosity and T_g values than other DNTs. It is reckoned that nitrogen dopants of DNT structures play a positive role in the overall network strength and stability of DNT modified asphalt nanocomposites.



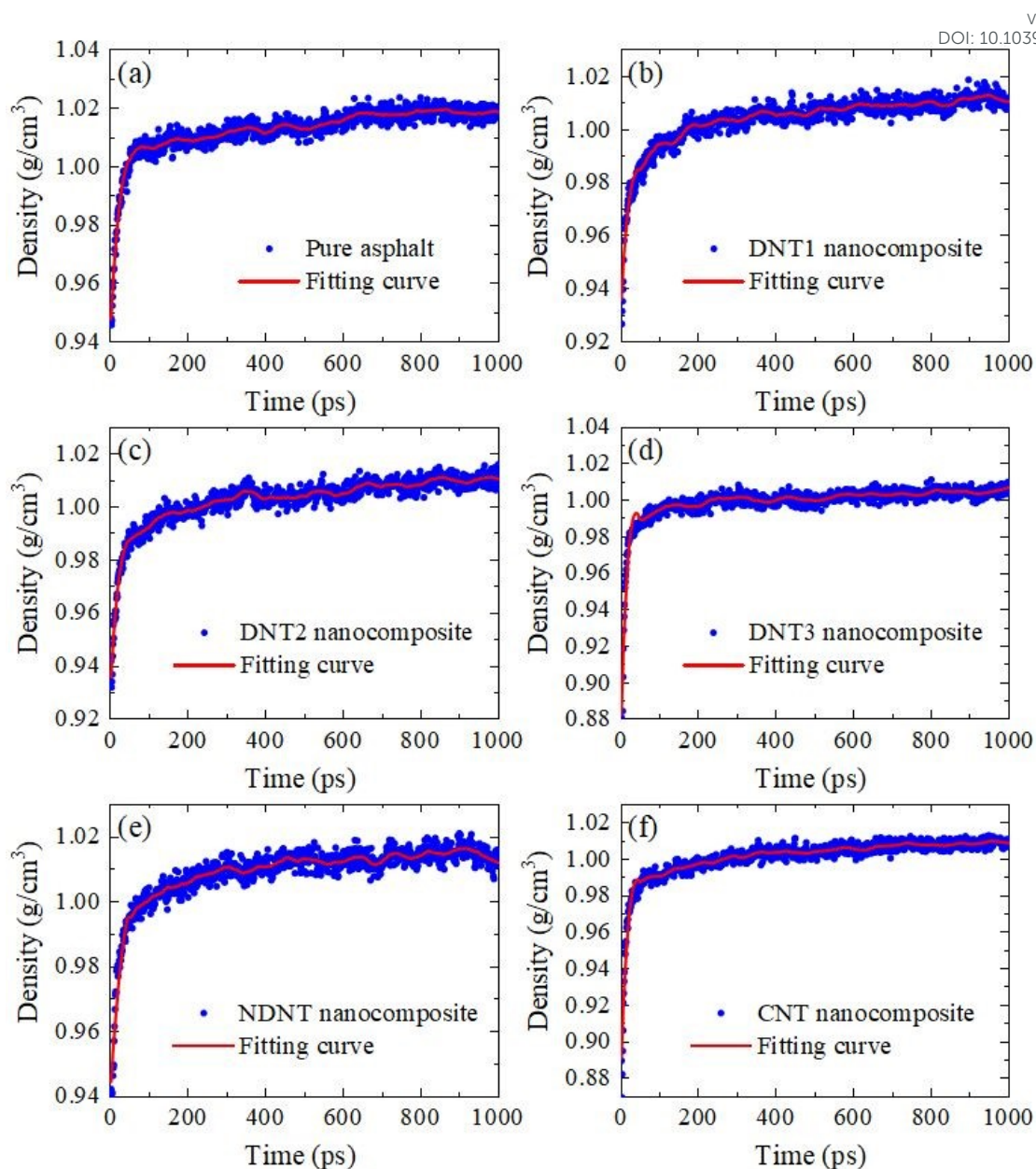


Figure 5 Density values of (a) pure asphalt, (b) DNT1 modified asphalt nanocomposite, (c) DNT2 modified asphalt nanocomposite, (d) DNT3 modified asphalt nanocomposite, (e) NDNT modified asphalt nanocomposite, (f) CNT modified asphalt nanocomposite during the equilibrium process.



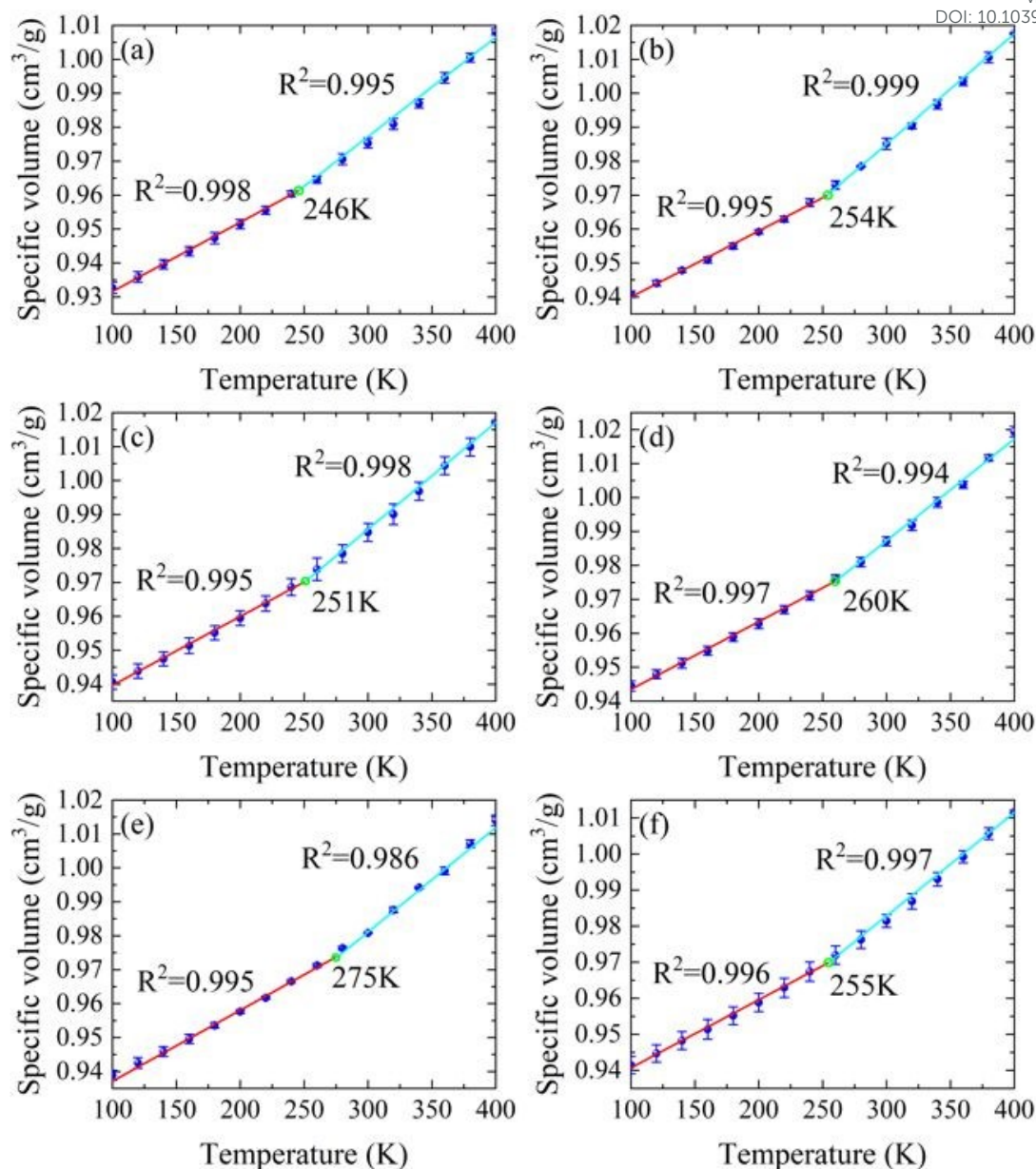


Figure 6 Specific volume values of (a) pure asphalt, (b) DNT1 modified asphalt nanocomposite, (c) DNT2 modified asphalt nanocomposite, (d) DNT3 modified asphalt nanocomposite, (e) NDNT modified asphalt nanocomposite, and (f) CNT modified asphalt nanocomposite vary under different temperature ranges. The T_g values of DNT/CNT modified asphalt nanocomposites are relatively higher than those of pure asphalt, indicating the higher deformation resistance to temperature changes.



3.2 Pullout test

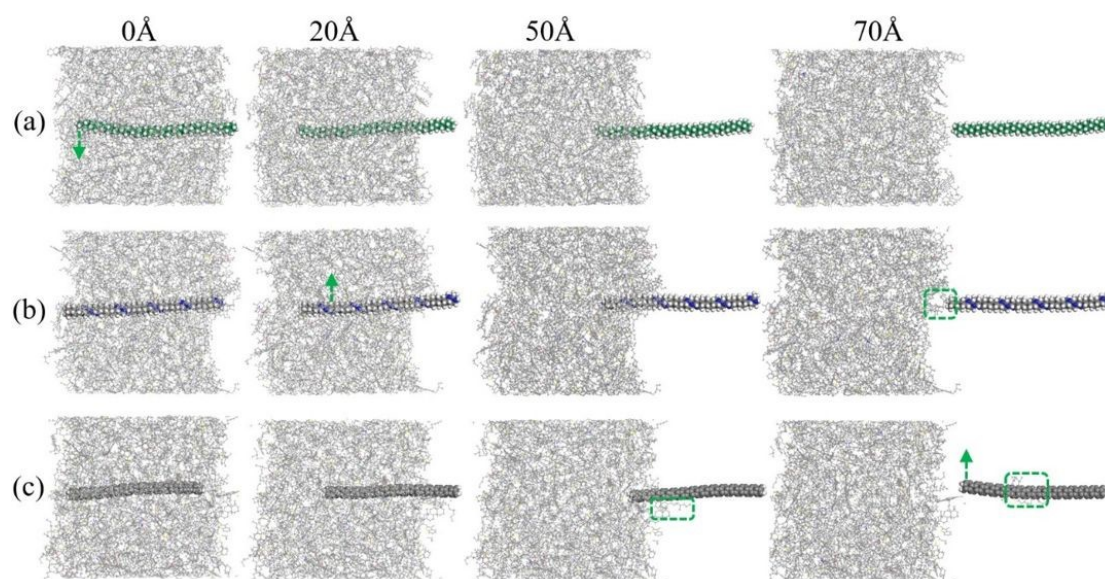


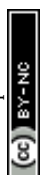
Figure 7 Snapshots of (a) DNT2, (b) NDNT, and (c) CNT pulled out from asphalt matrix.

The pullout tests are carried out to investigate the load transferring capability between DNT/CNT and asphalt matrix. The snapshots of DNT2, NDNT, and CNT pulled out from asphalt matrixes are depicted in Figure 7(a)-(c). It can be observed that the deformation occurs continuously perpendicular to the axial direction of DNT/CNT during the pullout process, while no noticeable deformation can be observed along the axial direction. All DNT/CNT structures with this aspect ratio exhibit high axial stiffness and significantly lower lateral stiffness, which makes them effective at transferring loads in the axial direction while being weaker laterally. During the pullout process, no asphalt molecules are extracted by the DNT, although a few asphalt chains bridge the interface between the NDNT and asphalt. In contrast, there is significantly more interaction between asphalt and CNT. Several asphalt molecules



1 adhere to the CNT surface before complete pullout, and some are transported away
2 once the CNT is fully extracted. These close interactions highlight the strong
3 interfacial bonds and load-transfer capabilities between asphalt and CNT.

4 To quantitatively investigate the influence of different topological structures on
5 the reinforcing capability, the pullout force values of DNT/CNT during the pullout
6 process are calculated and depicted in Figure 8. The pullout displacement of
7 DNT/CNT is recorded within $60\text{\AA}$, since the DNT/CNT is completely pulled out
8 beyond $60\text{\AA}$. It can be observed that the pullout force of DNT/CNT increases rapidly
9 at the initial stage and then fluctuates around a constant value. The root mean square
10 (RMS) values of pullout force are extracted to quantitatively assess the pullout
11 performance of DNT/CNT. The RMS values of pullout force for DNT1, DNT2,
12 DNT3, NDNT, and CNT are 0.507nN , 0.514nN , 0.486nN , 0.511nN , and 0.575nN ,
13 respectively. It demonstrates that CNT modified asphalt nanocomposite possesses the
14 highest pullout force among all the nanotubes, which echoes the findings that CNT has
15 stronger interfacial interactions. The pullout force of DNT2 modified asphalt
16 nanocomposite is the highest among the DNTs. The improved pullout performance
17 of DNT2 is attributed to its helical structure, which enhances mechanical interlocking
18 within the asphalt matrix and minimizes relative movement between the asphalt and
19 DNT2. The pullout force of NDNT is comparable to that of DNT2, whereas DNT3
20 exhibits the lowest pullout force among all the DNT variants. Additionally, NDNT
21 shows significantly higher pullout performance than DNT1, suggesting that the



nitrogen-doping atoms can enhance the interfacial interactions between the asphalt and the nanotubes.

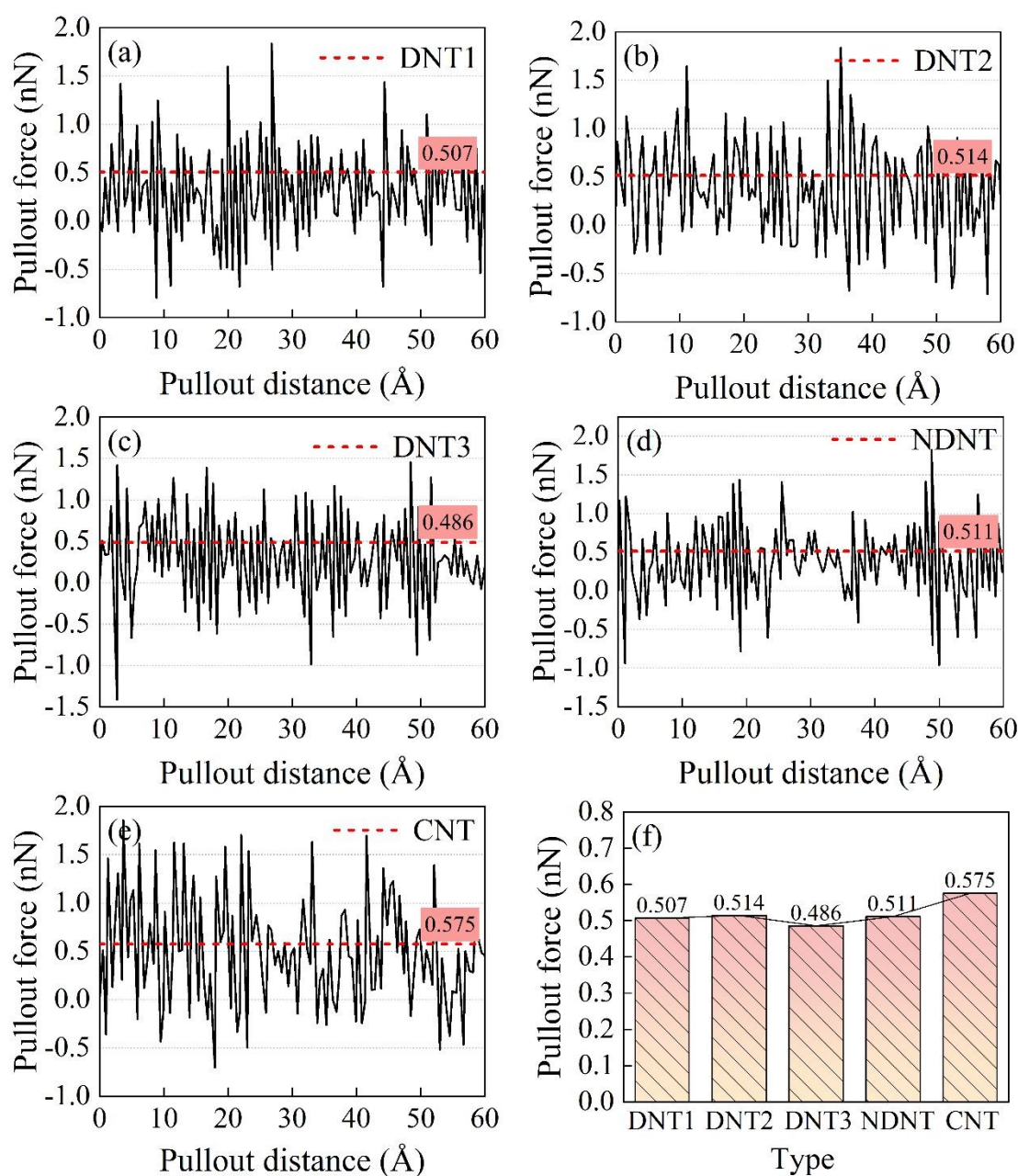


Figure 8 Pullout force changes with the pullout distance during the pullout process. (The red line indicates the RMS values of the data set).

The pullout energy curves of DNTs, NDNT, and CNT during the pullout process



are presented in Figure 9. The pullout energy of DNT/CNT steadily increases up to 60 Å, ultimately reaching its peak value, which refers to the complete extraction from the asphalt matrix. The pullout energy of CNT is the highest, approximately 1.5 times greater than that of DNT2 and DNT3. The increased pullout energy reveals that the CNT modified asphalt nanocomposite exhibits greater resistance to shear deformation, contributing to its overall rigidity. The pullout energy of DNT2 is the highest among the DNT reinforcements, which aligns with its significantly greater pullout force discussed in the previous section. Meanwhile, the pullout energy of NDNT is slightly lower than that of DNT2, but still surpasses that of DNT1 and DNT3. DNT3, with its zigzag structure, exhibits the lowest pullout energy and load-transfer capacity within the asphalt matrix. Notably, the pullout energy of DNT3 is higher than that of DNT1 up to 47 Å, but falls below that of DNT1 beyond this distance. As demonstrated in Figure 8, the pullout force of DNT3 decreases more rapidly when the pullout distance exceeds 47 Å, resulting in the lower pullout energy.



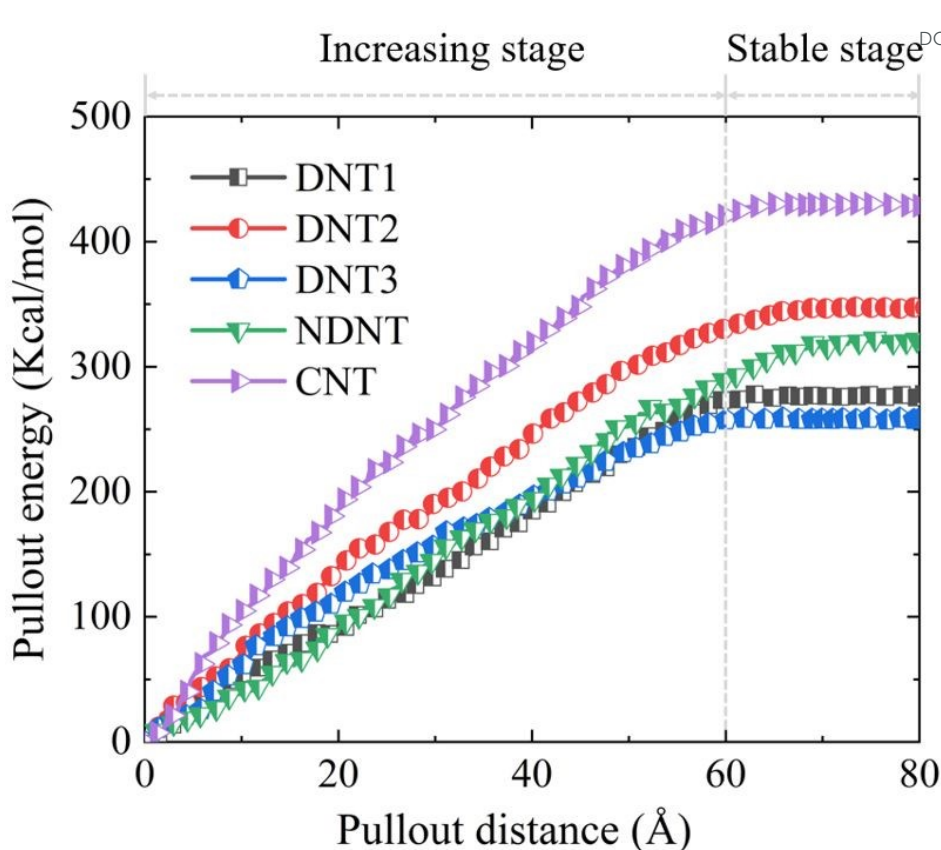
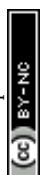


Figure 9 Pullout energy fluctuates with displacement during the pullout process.

The molecular interaction details at DNT and asphalt interfaces are demonstrated in Figure 10(a). It can be observed that the hydrogen atoms on the hydrogenated DNT surface can mechanically interlock with the asphalt atoms at the interface, which contributes to the shear resistance during the pullout process. A schematic representation of the interlocking effect between DNT and asphalt is depicted in Figure 10(b). The uneven hydrogenated surface of DNT creates geometric constraints within the asphalt matrix, facilitating the mechanical interlocking interactions. This interaction reduces the mobility of asphalt along the longitudinal direction of the reinforcement, thereby enhancing mechanical interlocking and improving load transfer



1 capabilities between the DNT and the asphalt matrix. The H-bond interaction
2 between NDNT and asphaltene is presented in Figure 10(c). It shows that the
3 hydroxyl group on asphaltene-phenol can interact with the nitrogen atoms on NDNT to
4 generate the O-H $\cdots$ N H-bond. The H-bond interaction contributes to the enhanced
5 shear resistance of NDNT by increasing the motion constraints within the asphalt
6 matrix, in contrast to DNTs without the nitrogen dopant. The π - π stacking interactions
7 between CNT and naphthene aromatic molecule(DOCHN) are presented in Figure
8 10(d). The π - π stacking interactions are crucial for enhancing the shear resistance of
9 asphalt, facilitating the wrapping of asphalt molecules around the surface of CNTs. It
10 is found that the ratios of aromatic carbon can constitute up to 40% of the total carbon
11 content of asphalt, primarily derived from components including asphaltenes, polar
12 aromatics, and naphthene aromatics ³⁹. These molecules can generate a significant
13 number of π - π stacking interactions around CNTs, thereby enhancing the overall load
14 transfer capabilities of CNTs during the deformation and pullout process.



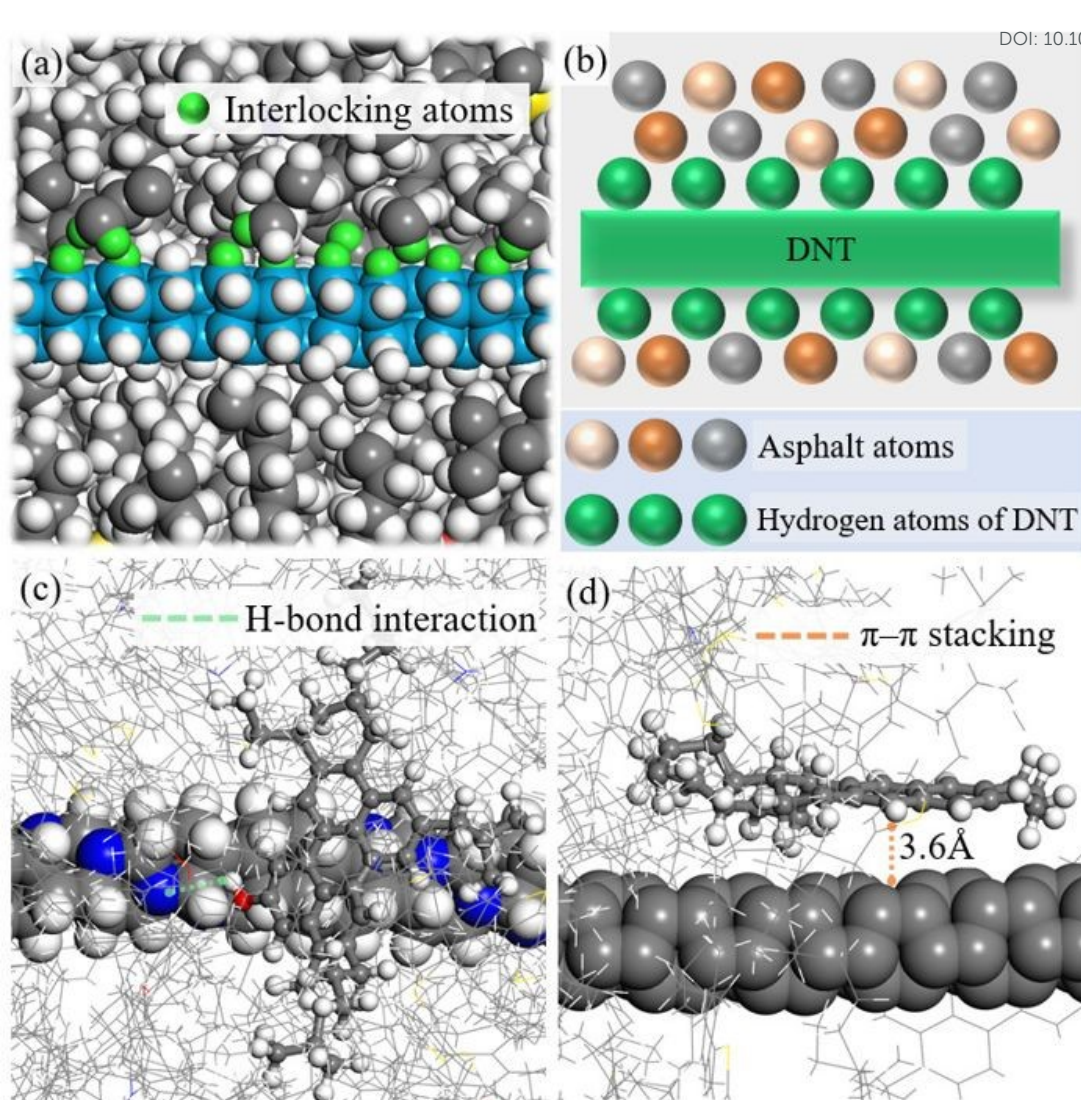
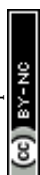


Figure 10 Molecular details between (a) DNT and asphalt interface; (b) Schematic illustration of interlocking effect at DNT-asphalt interface; (c) H-bond interaction between NDNT and asphaltene molecule; (d) π - π stacking interactions between CNT and naphthene aromatic molecule.

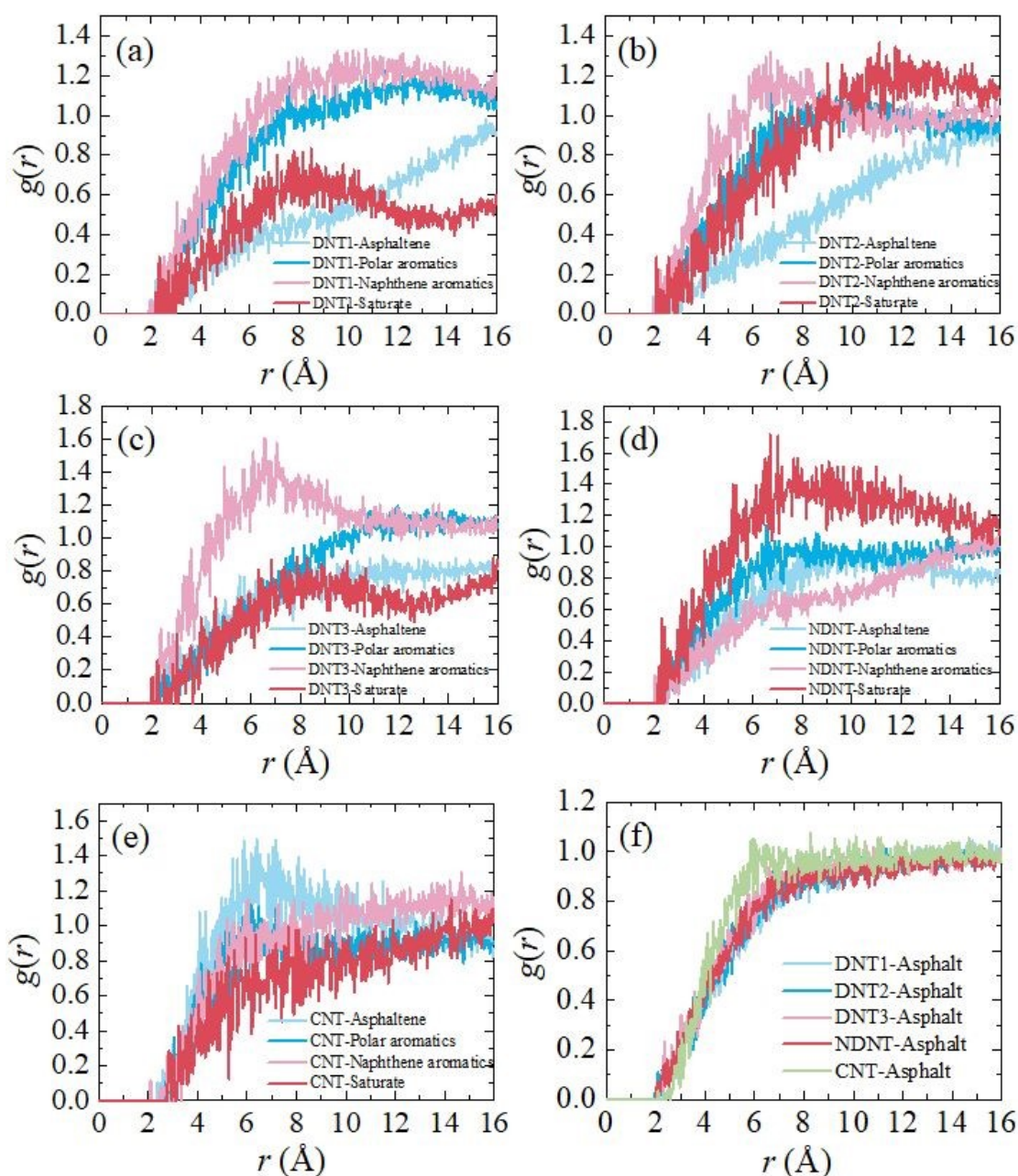
The radial distribution function (RDF) curves between DNT/CNT and asphalt components are depicted in Figure 11(a)-(c). It is noticeable that the $g(r)$ values for naphthene aromatics and DNTs peak within 8 Å, indicating stronger interactions



1 between the two. The molecular chains of naphthene aromatic molecules, including
 2 DOCHN, can interact with the DNT surface through mechanical interlocking, leading
 3 to enhanced interactions. The $g(r)$ curves between NDNT and asphalt molecules are
 4 depicted in Figure 11(d). It is found that the $g(r)$ values between saturate and NDNT
 5 are higher than those of polar aromatics, asphaltene, and naphthene aromatics,
 6 respectively. The chain-like structures of saturates can mechanically intertwine with
 7 NDNT and enhance their interactions. Additionally, the nitrogen atoms on NDNT can
 8 engage in hydrogen bonding with the heteroatoms of asphaltenes and polar aromatics,
 9 further enhancing these interactions. As illustrated in Figure 11(e), the $g(r)$ values
 10 between saturates and CNT are comparatively lower than those for other asphalt
 11 components. This suggests that CNT interacts more closely with asphaltenes, polar
 12 aromatics, and naphthene aromatics, while exhibiting fewer active interactions with
 13 saturate molecules. This discrepancy arises from CNT's enhanced interactions with
 14 aromatic carbons through π - π stacking, which is a feature absent in saturate molecules.
 15 The RDF curves between DNT/CNT and asphalt are shown in Figure 11(f). It
 16 demonstrates that DNTs and NDNT exhibit higher $g(r)$ values than CNT within $3.6\text{\AA}$,
 17 while showing lower values beyond this threshold. This divergence stems from the
 18 distinct surface morphological characteristics between DNTs and CNT. The
 19 hydrogenated surface of DNT engages more intimately with asphalt molecules through
 20 mechanical interlocking, whereas π - π stacking interactions between CNT and asphalt
 21 start to prevail at approximately $3.6\text{\AA}$. Notably, the $g(r)$ values between CNT and



- 1 asphalt are higher than those for DNTs and NDNT from 3.6 Å to 16 Å, suggesting
- 2 stronger interactions between asphalt and CNT within this distance.



- 3
- 4 Figure 11 RDF curves between asphalt components and (a) DNT1, (b) DNT2, (c) DNT3,
- 5 (d) NDNT, and (e) CNT after the full equilibrium. (f) RDF curves between DNT/CNT
- 6 and asphalt molecules after the full equilibrium.

7



3.3 DFT calculation

Binding energy provides a quantitative measure of the interfacial interactions between asphalt and reinforcements⁵⁸. The binding energy values between different asphalt components and DNT/CNT are presented in Figure 12. It shows that the binding energy values between polar components and DNT/CNT are relatively higher than those between nonpolar asphalt components and DNT/CNT. This indicates that the heteroatoms in the polar components of asphalt are essential for improving interfacial interactions with DNT/CNT. Among all asphalt components, the binding energy between asphaltene and DNT/CNT is the highest, primarily due to the larger molecular volume of asphaltene and the presence of heteroatoms. The binding energy values for DNT2 and DNT3 are the lowest among all components, with DNT2 showing an interaction of 13.7 Kcal/mol with saturates and DNT3 exhibiting 13.8 Kcal/mol with naphthene aromatics. NDNT achieves the highest binding energy with asphalt components, except for polar aromatics, where its value is slightly lower than that of CNT. The binding energy between NDNT and asphaltene is 55.8 Kcal/mol, comparatively higher than the 49.9 Kcal/mol observed for CNT and much greater than the 40 Kcal/mol for DNT1, 34.5 Kcal/mol for DNT2, and 35.7 Kcal/mol for DNT3. This increased binding energy is attributed to the presence of polarized nitrogen atoms in NDNT, which enhances the interfacial interactions between NDNT and asphalt molecules. The binding energy between CNT and asphalt is slightly lower than that of NDNT but significantly higher than that of DNTs. As previously mentioned, the



aromatic rings in asphalt molecules can interact with CNT and adhere to its surface through π - π stacking interactions, thereby enhancing interfacial interactions. Additionally, it has been observed that the binding energy values between DNT1 and asphalt molecules are the highest among the DNTs. DNT2 and DNT3 exhibit significantly lower binding energy compared to others, indicating weaker interactions between asphalt molecules and DNT2/DNT3. The reduced binding energy at the DNT-asphalt interface can be ascribed to the hydrogen passivation of the DNT surface.

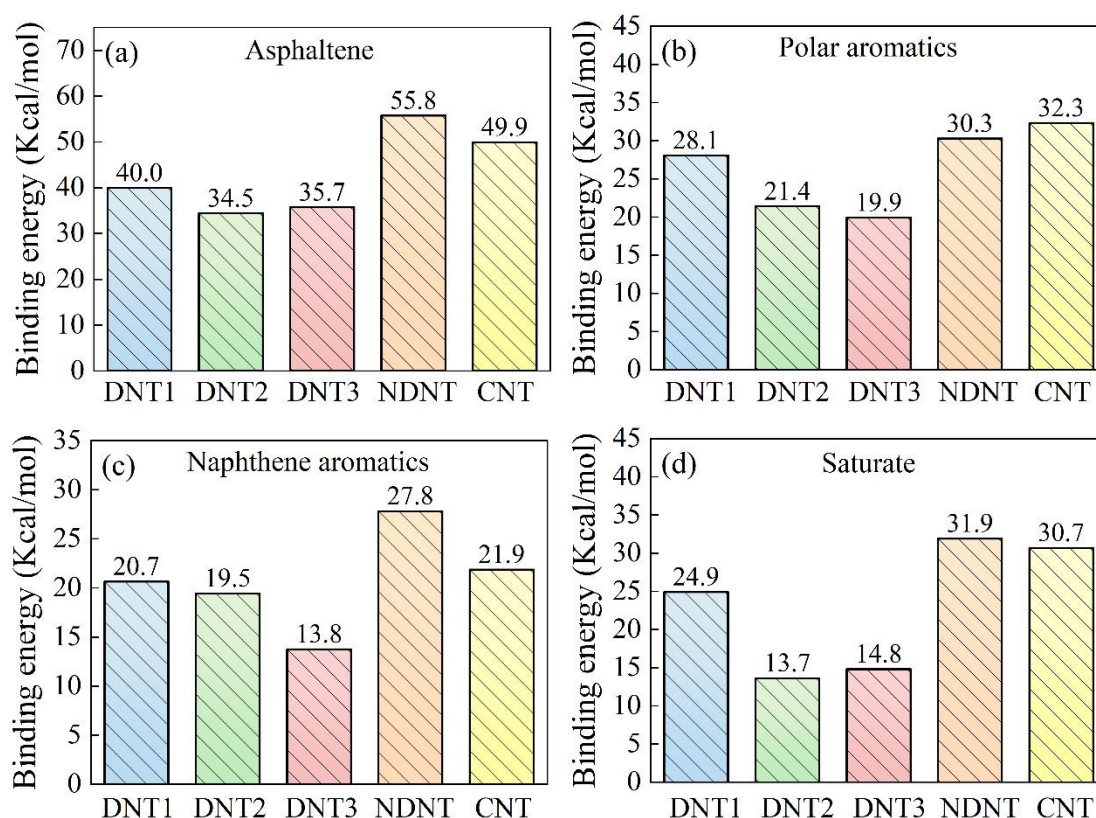


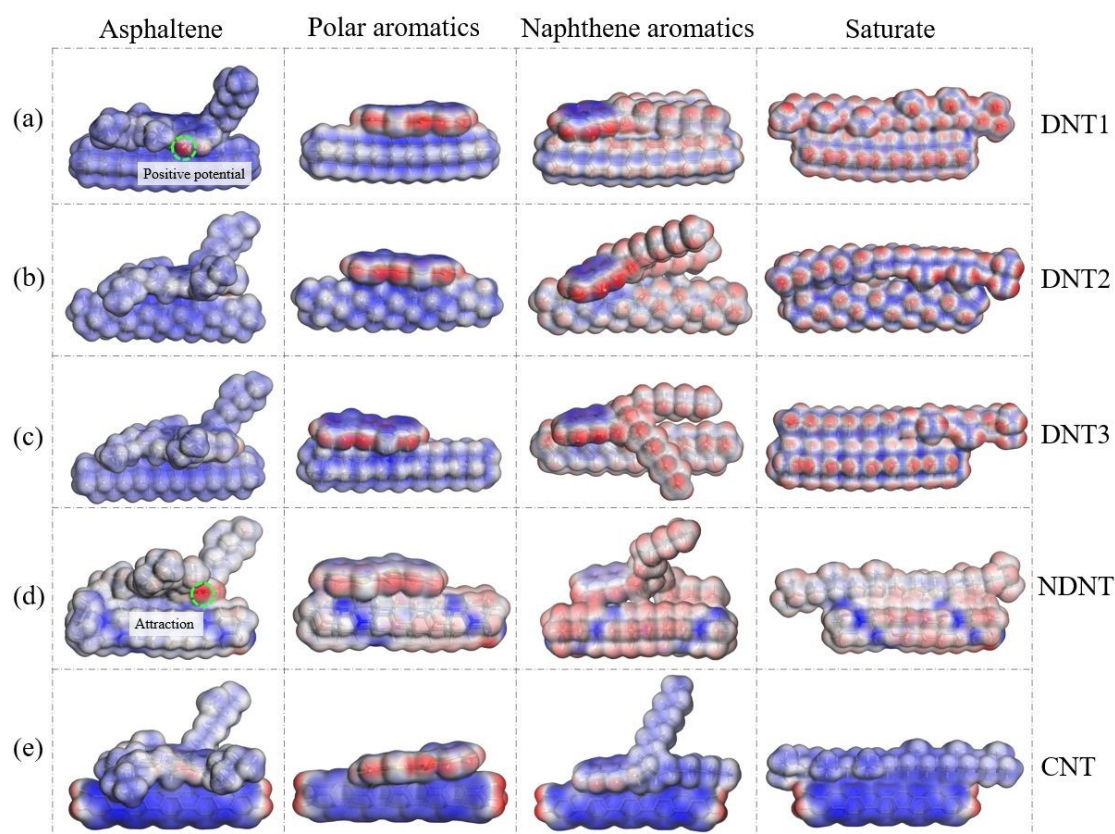
Figure 12 Binding energy between (a) asphaltene and DNT/CNT, (b) polar aromatics and DNT/CNT, (c) naphthene aromatics and DNT/CNT, (d) saturate and DNT/CNT. The binding energy between NDNT and asphalt components is relatively higher than that of other DNTs, which is attributed to the polarized nitrogen-doped surface.



1
2 The atomic charge distributions between asphalt and DNT/CNT are demonstrated
3 through molecular electrostatic potential maps, which can provide detailed insights into
4 the mechanisms underlying interfacial interactions. The molecular electrostatic
5 potentials between DNT/CNT and asphalt molecules are calculated and depicted in
6 Figure 13. The positive potential is denoted by the red color on the molecules, while
7 the negative potential is represented by the blue color. As shown in Figure 13(a)-(c),
8 DNTs exhibit the positive potential on the hydrogen atoms and the negative potential
9 on the carbon atoms of the backbone, generating a relatively rough electrostatic
10 potential map. The rough electrostatic potential of DNTs helps to create potential
11 energy wells that trap the aliphatic chains of asphalt molecules, making it energetically
12 unfavorable for them to move along the axis of DNTs. The interactions between
13 DNTs and asphalt molecules are mainly governed by a combination of van der Waals
14 forces, electrostatic attractions, and mechanical interlocking. In contrast to DNT, the
15 presence of nitrogen dopants can alter the electronic structure of NDNT, as shown in
16 Figure 13(d). This leads to the creation of localized negative charges, enhancing the
17 overall electronegativity. It can be observed that the nitrogen atoms of NDNT exhibit
18 strong negative potentials, while the hydrogen atom connected to the nitrogen atom on
19 asphaltene exhibits strong positive potentials. The interactions between NDNT and
20 asphaltene can be significantly enhanced by the attraction between the electropositive
21 regions of asphaltene and the electronegative domain of NDNT. The strong



1 electrostatic attraction contributes to the bonding and adhesion between NDNT and
 2 asphaltene, enhancing the overall stability and compatibility. As presented in Figure
 3 13(e), there are electronegative domains on the CNT surface but electropositive
 4 domains on the ends of the hydrogen atoms on CNTs. The electrostatic potential on
 5 CNT surface is comparatively smooth, since the delocalized π -electrons in the CNT
 6 structure result in a more even distribution of electron density along the surface. The
 7 delocalized π -electrons in CNTs can engage in π - π stacking interactions with the
 8 aromatic rings in asphalt molecules, leading to stronger adhesion and load transfer
 9 capability.



11 Figure 13 Molecular electrostatic potentials between asphalt components and (a) DNT1,
 12 (b) DNT2, (c) DNT3, (d) NDNT, and (f) CNT through DFT calculation.



4 Conclusion and discussion

4.1 Conclusion

The shear resistance and interfacial properties of asphalt nanocomposites reinforced with DNTs and CNTs are investigated through MD simulations, focusing on interfacial interactions during the pullout process. The findings reveal that NDNT modified asphalt nanocomposites exhibit the higher viscosity and T_g values compared to other DNTs, while CNT modified composites demonstrate the greater pullout force than those reinforced with DNTs. This improvement in shear resistance is primarily due to π - π stacking interactions that facilitate the wrapping of asphalt molecules around CNT surfaces. This improvement in shear resistance is crucial for pavement applications, as it enhances the material's ability to withstand mechanical stresses and reduce deformation over time. Among the DNTs, DNT2 modified asphalt nanocomposites show the highest pullout performance, attributed to DNT2's helical structure, which promotes the mechanical interlocking and reduces the relative movement within the asphalt matrix. Additionally, the hydrogenated surface of DNT enhances interactions with asphalt molecules, and the formation of O-H $\cdots$ N hydrogen bonds between hydroxyl groups on asphaltene-phenol and nitrogen atoms on NDNT further increases the shear resistance. While the binding energy between CNT and asphalt is slightly lower than that of NDNT, it remains significantly higher than that of DNTs. DFT calculations indicate that nitrogen doping modifies the electronic



1 structure of NDNT, resulting in localized negative charges that enhance
2 electronegativity, while delocalized π -electrons in CNTs improve adhesion and load
3 transfer capabilities. These findings suggest that incorporating NDNTs and CNTs
4 into asphalt mixtures can lead to more sustainable and resilient pavement materials with
5 improved long-term durability. Overall, this study underscores the considerable
6 potential of DNTs, NDNTs, and CNTs in developing sustainable and resilient asphalt
7 nanocomposites for the pavement industry. Importantly, our research extends beyond
8 pavement applications, offering broader implications for materials science and
9 nanotechnology. By clarifying the interfacial interactions and mechanisms at play,
10 our work paves the way for further exploration of nanomaterials in various composite
11 systems, promoting interdisciplinary research and collaboration.

12 By investigating the shear resistance and interfacial properties of asphalt
13 nanocomposites reinforced with DNTs and CNT through molecular dynamics
14 simulations, we explore fundamental interactions that enhance the performance of
15 asphalt material. The unique properties of DNTs, such as their helical structure and
16 hydrogenated surfaces, significantly improve mechanical interlocking and interfacial
17 interactions with asphalt, which are critical for developing sustainable and resilient
18 materials. Additionally, our findings on the electronic structure modifications due to
19 nitrogen doping in NDNTs further contribute to understanding how nanomaterials can
20 optimize the performance of composite systems. By examining these differences at
21 the atomistic level, our study not only clarifies the unique roles of DNTs and CNTs but



also contributes new insights into optimizing asphalt nanocomposites for improved durability and performance. This emphasis on comparative analysis and the exploration of new reinforcement mechanisms represents a significant advancement over prior works, paving the way for more effective applications of nanomaterials and other nanocomposite materials across various applications, including lightweight structural materials, energy storage systems, and advanced coatings. Our work not only addresses the immediate challenges in asphalt technology but also opens avenues for interdisciplinary research that could benefit a wide range of applications.

4.2 Discussion

While MD simulations are effective for investigating the interfacial interactions of various materials, they inherently operate on a time scale ranging from nanoseconds to microseconds. This limitation restricts the ability to observe the long-term behaviors of asphalt nanocomposites, including aging and fatigue processes. Consequently, although we have revealed the improvements of DNT/CNT in shear resistance and interfacial properties, these enhancements may not accurately reflect the performance of asphalt materials over extended periods in real-world conditions. To address these limitations, future research could include complementary approaches, such as experimental studies that monitor the long-term performance of DNT/CNT modified asphalt nanocomposites under realistic conditions. Additionally, employing multi-scale modeling techniques that bridge the gap between molecular dynamics and continuum mechanics could provide valuable insights into the macroscopic behavior of



these materials over longer time scales.

The effectiveness of nanomaterials in enhancing asphalt properties relies heavily on the interfacial interactions between the nanomaterials and the asphalt matrix. In a homogeneous distribution, each nanomaterial can interact uniformly with asphalt molecules, promoting effective load transfer and increased shear resistance. However, in a heterogeneous arrangement, some regions may experience stronger interactions while others may not benefit from the reinforcement, leading to inconsistent performance. This variability in distribution can arise from factors such as mixing techniques and processing conditions, which may not be fully controlled in practical applications. In the MD simulations, we assume a homogeneous distribution of nanomaterials within the asphalt matrix. Consequently, the mechanical properties of the asphalt nanocomposite between the simulations and experiments may exhibit discrepancies. Therefore, future studies should explore the effects of different nanomaterial distributions to provide a more comprehensive understanding of their impact on asphalt performance.

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Data availability

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The raw simulation data, input files for the LAMMPS simulations ¹, and analysis scripts used to generate the findings reported in this study are not publicly deposited in a repository due to their large size and specialized formatting, but are available from the corresponding author, Dr. Xuefeng LIU (xfliu6-c@my.cityu.edu.hk), upon reasonable request. The CVFF force field parameters used in this study are derived from previously published and cited works ^{2,3}, while the LAMMPS software package ⁴ employed for the simulations is publicly available. Additionally, all other relevant data and methodological details necessary for understanding and reproducing the conclusions of this manuscript are provided within the article.

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