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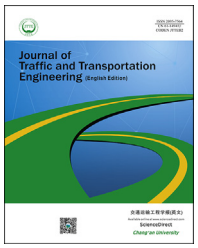

Review Article

Research progress on supramolecular structures of asphalt

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HIGHLIGHTS

- Introduce the supramolecular theory and its application in the asphalt micro-analysis.
- Present a brief review of asphalt supramolecular structures and research results.
- Propose a new view of study on relationship between molecular structure and mechanical properties of asphalt.

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ABSTRACT

The properties of asphalt binder play an essential role in the design life of asphalt pavement. Analysis of asphalt mechanical behaviors based on the chemical structures provides the theoretical basis for the improvement of asphalt performance in service life. Intermolecular interactions have a significant impact on the macroscopic properties of asphalt, a colloidal material, resulting in the parameters characterizing asphalt molecular structures fail to directly connect with mechanical properties of asphalt. This paper introduces the supramolecular theory, presents a brief review of existing supramolecular models and research methods of asphalt, aiming to explore a new methodology for the investigation between asphalt microstructures and macroscopic properties. Results showed the supramolecular theory focuses on the intermolecular interactions, providing more accurate indicators for the investigation on the asphalt supramolecules. Supramolecular analysis of asphalt has proposed feasible methods and established favorable connections with asphalt properties, giving a new view of understanding asphalt microstructure and a new approach to capture mechanical behaviors of asphalt.

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1. Introduction

Due to the excellent road performance, asphalt is widely applied in highway construction serving as a binder to form asphalt mixtures with the aggregates. As one of the major materials in road paving, asphalt has long been subjected to multiple coupling effects, such as sunlight, temperature, humidity and load, putting forward the higher requirements for asphalt properties to improve the quality and service life of the pavement (Tan et al., 2020). The performance of asphalt such as adhesion, self-healing, anti-aging and anti-fatigue properties, have been investigated by various experimental methods, giving rise to rapidly growing studies based on the macroscopic scale (Ding et al., 2022a, b; Jin et al., 2022; Li et al., 2021; Luan et al., 2022; Sun et al., 2022; Zhang et al., 2022).

The micro composition of asphalt is closely related to the macroscopic properties (Barré et al., 2009; Delgadillo et al., 2006; Redelius and Soenen, 2015). It is impossible to make a comprehensive and reasonable explanation for variations on the microstructure and mechanical behaviors of asphalt only by the macro analysis, due to the complicated internal structure of asphalt including element composition, chemical composition, microphase structure and so on (Ren et al., 2020; Tan et al., 2020). Consequently, it is of great significance to evaluate the performance of asphalt at micro scale. Draw on the micro-analysis of asphalt by gel permeation chromatography (Yang et al., 2018b), infrared spectrum (Gundla, 2018; Hung and Fini, 2019), photoelectric microscopy (Wang and Zhao, 2016; Xing et al., 2020; Yang et al., 2018a) and other laboratory tests, existing parameters of molecular structure could not give an accurate characterization to the microstructure of asphalt.

"Supramolecule" is defined as the complex and organized aggregation structure formed through noncovalent interactions by two or more molecules, with definite microstructures and macroscopic properties (Chen et al., 2001), as shown in Fig. 1. A complex structure is built not only by contributions of molecular structure, system composition and self-assembling processes, but additional subtle characteristics exert effects in the whole process (Calandra et al., 2015). Noncovalent interaction is the core concept in the supramolecular research. Single noncovalent interaction is relatively weak compared with the covalent bond interactions, while the cumulative effects of multiple weak interactions could form the strong supramolecular structures.

As a colloidal material, asphalt molecules form the supramolecular structure through intermolecular interactions. In other words, noncovalent interactions play a core role in the construction of a stable asphalt microstructure. Liu et al. (2017) have recently shown that mechanical properties of asphalt are equally relevant to the intermolecular interactions of asphaltene, and supramolecular structure is instructive for the performance investigation of asphalt. Therefore, investigations on chemical structures of asphalt by non-covalent effects based on the supramolecular concept could not only make up for the shortcomings of conventional micro-analysis methods, but also propose a new view of the asphalt molecular structure. Meanwhile, supramolecular structure as a meso-structure could be a linkage between macro-mechanical properties and microstructures of asphalt. Supramolecular theory provides a more powerful context for revealing the relationship between internal structures and compositions as well as macroscopic properties of asphalt materials.

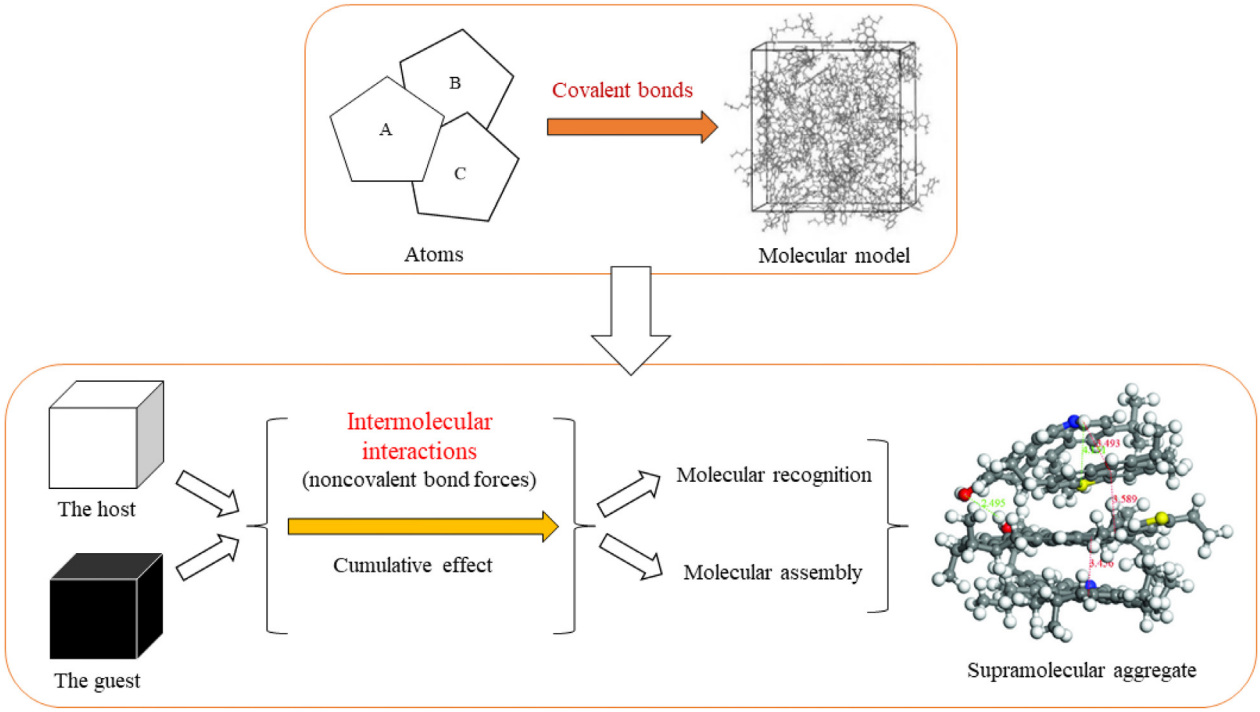

Fig. 1 – Schematic diagram of the formation of supramolecular structure.

The supramolecular theory was introduced in this paper to investigate the essence of asphalt microstructure. Composition and research methods of asphalt supramolecules were briefly reviewed, and the effects of supramolecular structure on the properties of asphalt were evaluated. This paper aims to propose a new method of investigation on the relationship between chemical structures and microscopic properties of asphalt, and provides the reference for asphalt supramolecular system.

2. Composition of supramolecular structure

2.1. *Supramolecular theory*

Supramolecule is the smallest unit after elementary particle, nucleus, atom and molecule. In 1978, French scientist Lehn first proposed a concept of "supramolecular chemistry", leading a qualitative leap in traditional chemical science (Lane, 2002). Supramolecular chemistry focuses on the structure and the function of chemical aggregates build through noncovalent interactions between molecules. As one of the primary research objects in supramolecular chemistry, intermolecular weak interactions such as hydrogen bonding, π-π stacking and van der Waals interaction, could be transformed to strong forces with directionality and selectivity through superposition or coordination, contributing to the construction of thermodynamically stable and ordered supramolecular structures (Pei and Ding, 2019; Sougata et al., 2018). Such supramolecular systems present new properties completely different from original constituent molecules, so that supramolecular polymers with specific structures and functions could be synthesized. Theoretical and experimental investigations on supramolecular system have been widely discussed in the science of chemistry, materials, nanoscience and so on (Yan et al., 2004), showing a great potential for application in road engineering (Cho et al., 2010; Gao et al., 2019).

2.2. *Intermolecular interactions*

Intermolecular interactions are the core components in the supramolecular system. Gray et al. (2011) and Murgich (2002) suggested that there were a variety of interactions between molecules in asphalt, including π-π stacking, hydrogen bonding, acid-base interaction, metal coordination bond, van der Waals force, charge transfer, electrostatic interaction and hydrophobic interaction.

π-π stacking is a weak interaction between molecules of compounds with conjugated structure and is also known as aromatic interaction. π-π stacking interaction is commonly used to describe the van der Waals and induced forces between two parallel aromatic systems, which magnitude and direction are decided by intermolecular distance and angle (Hunter et al., 1990). Miao et al. (2018) observed the oil-water emulsification resulted from the formation of a cage structure through π-π stacking interaction between asphaltene molecules. Ren et al. (2019a) indicated that multiple π-π interactions accelerated asphaltene aggregation.

Hydrogen bonding is such an interaction between the hydrogen atom bonded to a molecule or a fragment and another atom or cluster. Due to the favorable directivity and saturability, hydrogen bonding is of great significance in the stability of supramolecular structure (Kharlampieva et al., 2009). The freedom of the supramolecular polymer chains is affected by the number of hydrogen bonding, giving rise to the variation on the viscosity of the solution (Pei et al., 2020). Wang et al. (2019) indicated the stronger the polarity of groups containing active hydrogen, the more serious the asphaltene aggregation.

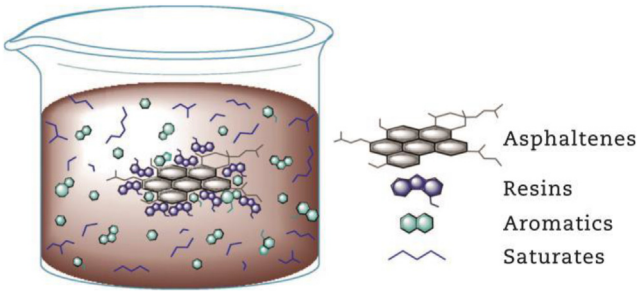

Fig. 2 – Colloidal structure of asphaltene in a dispersing medium of lighter resins, aromatics, and saturates (Mousavi et al., 2016a).

van der Waals force is one of the prevalent inter-molecular interactions, which is equal to the sum of inter-molecular attraction and repulsion. It was reported that the energy of van der Waals in asphalt molecules is lower (da Costa et al., 2012), which played a major role in the adhesion between the asphalt with the aggregates (Xu and Wang, 2016).

The protonic acids such as asphaltene molecules containing carboxylic acid group interact directly with bases to form salts, which is called acid-base interaction and considered to be the strongest driving force for the aggregation of asphaltene molecules by Shattock et al. (2008). Liu et al. (2017) proved that the acid-base interaction and the hydrogen bonding were more relevant to the size of asphaltene supramolecules than other noncovalent interactions.

The nonvalent force resulted from mutual repulsion between groups with hydrophobic structures and water is referred to as hydrophobic interaction. Hydrophobic guest molecules or the hydrophobic groups in molecules spontaneously enter the hydrophobic cavity for aggregation to reduce the energy of the system, thus increasing the stability of the supramolecules and contributing to the formation of micellar structures and aggregated structures (Dill et al., 2005).

Metal coordination bond is mainly reflected in the interaction between the metal and the ligand, which is similar to the covalent bond in terms of strength. Li et al. (2020) found the coordination of the side chains of supramolecular polymer with the multivalent ions promoted the construction of a stable three-dimensional mesh system, inducing an increase in the viscosity of the polymer.

3. Supramolecular structures of asphalt

3.1. *Supramolecular models of asphalt*

Currently, study of supramolecular chemistry for asphalt systems has just begun. Gray et al. (2011) argued that

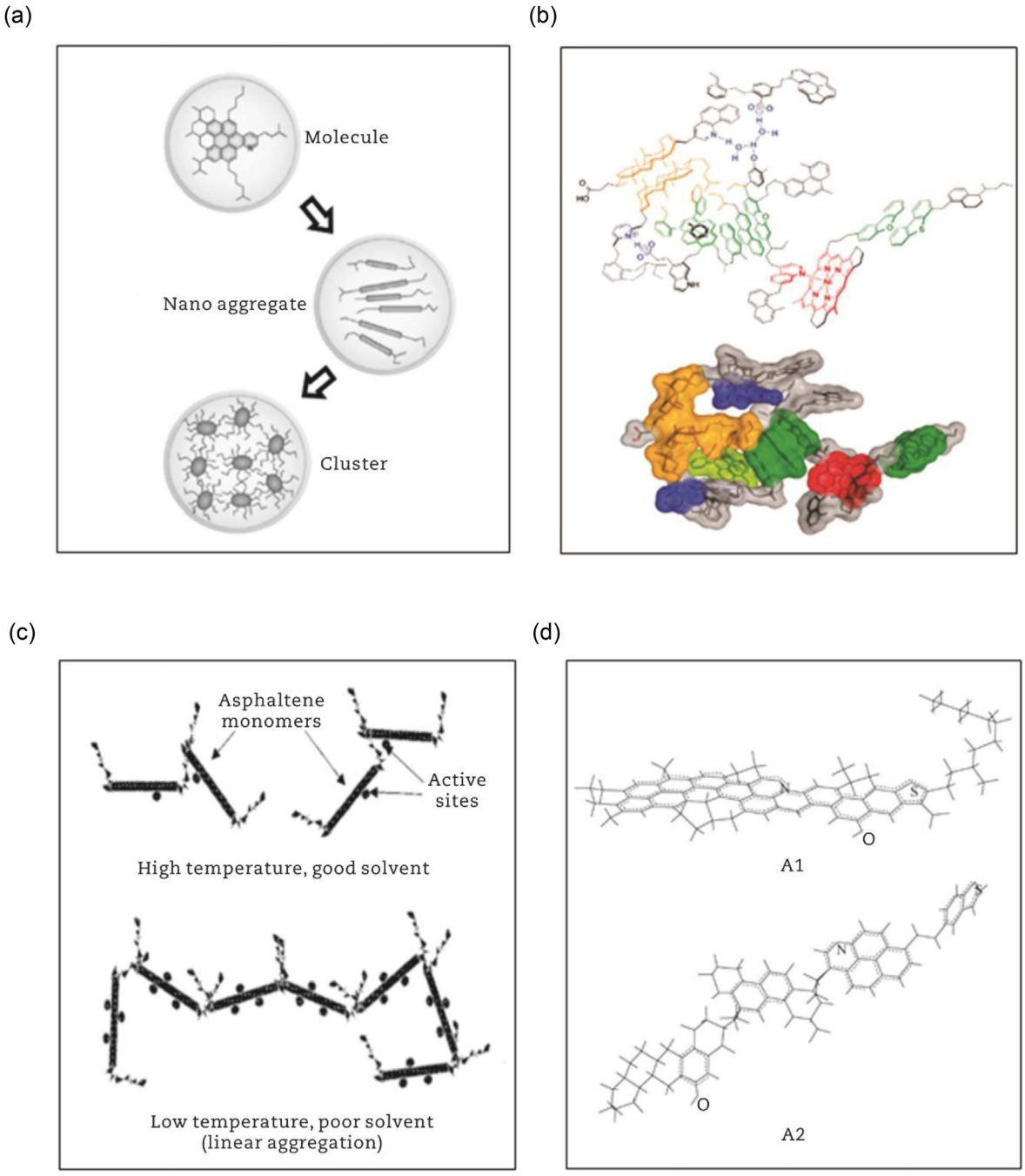

Fig. 3 – Asphaltene aggregation models. (a) Nano-aggregate model (Mullins et al., 2012). (b) Supramolecular assembly model (Gray et al., 2011). (c) Linear polymerization model (Agrawala and Yarranton, 2001). (d) Solubility model (Acevedo et al., 2010).

supramolecular interactions played an imperative role in the construction of chemical structures of petroleum asphalt and proposed a supramolecular self-assembly model based on these interactions, giving rise to the wide attentions.

Studies have shown that asphalt is not a true solution, but a colloidal dispersion system, as shown in Fig. 2 (Mousavi et al., 2016a). This colloidal system regards the asphaltenes as the atomic nucleus, with the resins as the stabilizer adsorbed on the asphaltene surface, surrounded by the light resins, aromatics and saturates as the dispersion mediums. Usually, fractions of saturates, aromatics, resins and asphaltenes, determined by the so-called S.A.R.A. analysis, would affect the supramolecular assembly (Caputo et al., 2020). The resins and aromatics presented positive effects in the activation of the colloidal structure while the alkane components showed the negative impacts (Ren et al., 2013). Researches have shown that the colloidal structure was directly linked to macroscopic properties of asphalt such as the rheology properties (Haghshenas et al., 2022) and the fatigue performance (Santagata et al., 2009). The fatigue resistance would collapse and the endurance of asphalt could not be predicted when the colloidal instability was below a certain

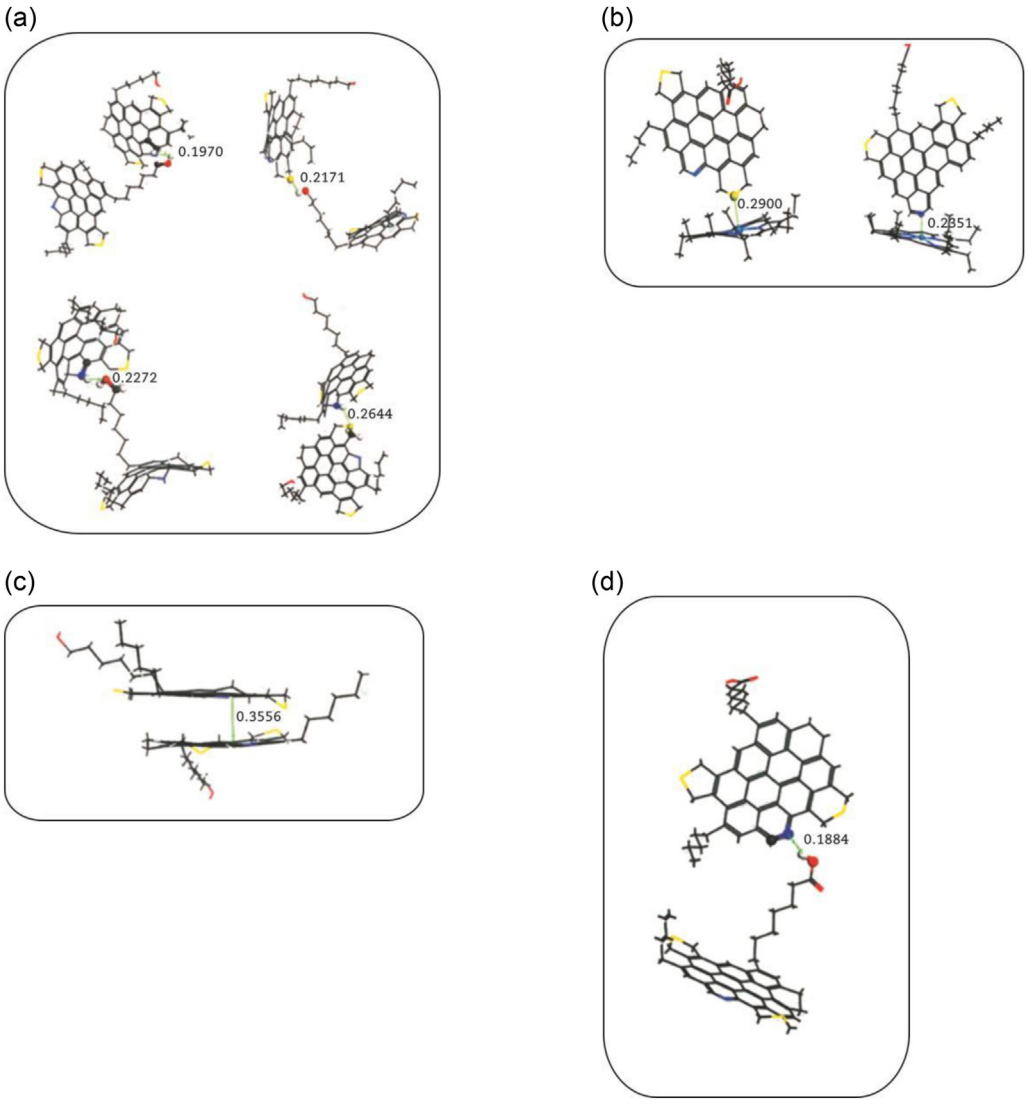

Fig. 4 – Asphaltene aggregates formed by various interactions (Liu et al., 2017). (a) Four types of hydrogen bonding. (b) Axial coordination between nickel porphyrin and asphaltene. (c) π-π interaction. (d) Acid-base interaction.

threshold (Salehfard et al., 2021). There are large aromatic fused rings and heteroatoms such as S, N and O in asphaltene, accounting for the colloidal properties of asphalt. Asphaltene molecules are reoriented, aggregated and associated through the π-π stacking and the hydrogen bonding to form the complicated macromolecular cluster structures called "supramolecular aggregates" (Ren et al., 2013).

The asphaltene aggregate is also a type of supramolecular structure in asphalt. Existing asphaltene aggregation models consist in the nano-aggregate model, the supramolecular assembly model, the linear polymerization model and the solubility model, as shown in Fig. 3. The nano-aggregate model emphasizes the π-π interaction, which is applicable to the most typical and common asphaltene molecular structures. In the supramolecular assembly model, the diversity of asphaltene molecules is taken into account to provide a more comprehensive description of interactions in asphaltene aggregates and the cumulative effect of multiple interaction is emphasized. The linear polymerization model and the solubility model focus on the active sites of asphaltenes and simplify the aggregation behavior. Despite of the respective focuses, above asphaltene aggregation models consider intermolecular interactions as a vital factor in the construction of asphaltene aggregates, the asphaltene molecules with a single structure have not been separated yet, leaving the molecular structure of asphaltene still controversial.

3.2. *Driving force of asphalt supramolecules*

At present, complex molecular structures of asphalt preclude a clear view in the natures of intermolecular interactions, leading to a long-standing controversy about the driving force of asphalt molecular aggregation. There are two main opinions about the driving force of aggregation, a single interaction dominates or multiple interactions cooperate with each other (Zhang et al., 2019). Mostowfi et al. (2009), Betancourt et al. (2009) and Wang et al. (2021) suggested that the main driving

Table 1 – Research on asphalt supramolecular system using experimental methods.

Method	Main opinion	Reference
FTIR	Hydrogen bonding strength of three residual oil asphaltenes followed the descending order of Liaohe asphaltene, Shengli asphaltene, Gudao asphaltene according to the height and area of absorption peaks.	Liu et al. (2010)
	Chemical shifts in the IR spectra indicated the π-π stacking and hydrogen bonding were the main driving forces of asphaltene aggregation.	Zhao et al. (2021)
NMR	A two-dimensional translational diffusion of short hydrocarbon chins around the asphaltene nanoaggregates was observed using NMR dispersion technique.	Vorapalawut et al. (2015)
	Asphaltene aggregation arose from dipolar interaction.	Zielinski et al. (2010)
SAXS	The increase of spacing and size distribution of styrene-b-ethylene-co-butylene-b-styrene (SEBS) microphase indicated the aggregation structure was affected by the interaction between the epoxidized soybean oil and the SEBS.	Zhang et al. (2021b)
	The size of aggregates formed by various asphaltene molecules was larger than that formed by the same asphaltene molecules, suggesting the intermolecular association was stronger than the intramolecular association.	Du et al. (2020)
SANS	The molecular weight and the association size of asphaltene decreased with the temperature, demonstrating that the colloidal structure of asphalt was easy to be destroyed at high temperature.	Ravey et al. (1988)
WAXS	The formation of hierarchical structure through the molecular and supramolecular aggregation could be evaluated by the diagnostic fingerprint used in WAXS profile characterization which was related to the Bragg distance.	Calandra et al. (2020)
Dynamic light scattering	The hydrodynamic radius of asphaltene toluene solution increased with the concentration of asphaltene, which was expected as the increased intermolecular interactions intensified the aggregation of asphaltene.	Liu et al. (2017)
AFM	The grouping and subgrouping of natural solid asphalt could be diagnosed based on the supramolecular structure.	Golubev and Kovaleva (2011)
	The evolution of asphalt microstructures including the "bee-structure" was resulted from the molecular interactions among chemical components in asphalt.	Yu et al. (2015)
TEM	The stacking properties of asphaltene molecules were easily affected by the largest fused aromatic ring system than the poly-aromatic system.	Zhang et al. (2014)
Fluorescence spectroscopy	The conjugation system of asphaltene was composed of 2–3 rings aromatic nucleus which would form complex aggregates through the intermolecular and intramolecular associations.	Donatella et al. (2013)
	The significant difference between asphaltene and solvent promoted the asphaltene aggregation which would be intensified with the temperature and the standing time of asphaltene solution.	Yao (2019)

force of asphaltene aggregates was π-π interaction resulted from the aromatic ring structure. Hydrogen bonding between heteroatomic functional groups was considered to be the main force in the association of asphalt molecules (Rogel et al., 2002; Sun, 1998). The van der Waals force (Xiao et al., 2020), acid-base interaction (Al-Sahhaf et al., 2002; Junior et al., 2006) or polymerization-like reaction (Agrawala and Yarranton, 2001) were also treated as the main factors leading to the asphaltene molecular conjugation. Moreover, it had been demonstrated that asphalt molecular aggregation was contributed to the cumulative effects of π-π stacking and H-bond (da Costa et al., 2012), π-π stacking and van der Waals (Takanohashi et al., 2002), hydrogen bonding and acid-base interactions (Du et al., 2020), or the dipolar interactions with charge transfer interactions (Bian et al., 2013; Li et al., 2007; Miao et al., 2018). Liu et al. (2017) illustrated that the π-π interaction between asphaltene molecules showed highest energy compared with the hydrogen bonding, acid-base interaction and metal coordination, as shown in Fig. 4.

The controversy over the driving force of asphalt molecular association, on the one hand, from the complexity and diversity of asphalt molecular structures. Asphalt molecules, especially the asphaltenes contain a large number of active sites where strong intermolecular interactions generate. The structure and composition of diverse asphaltene molecules are also different. On the other hand, it is impossible for existing separation and characterization techniques to elaborate the real asphalt molecular structures, so the types of interactions between various asphalt molecules are likely to be different. Moreover, the molecular and supra-molecular organization take place at various length-scales with interactions of different hierarchical levels (Calandra et al., 2019). However, studies have focused presently on the commonality of asphalt molecular structure and the intermolecular interactions to make it as accurate as

Table 2 – Research on asphalt supramolecular system using simulation methods.

Method	Main opinion	Reference
MD	The dominant force for asphaltene aggregation was indicated as the π-π stacking or the Van der Waals interaction, and the hydrogen bonding improved the stability of the aggregates.	Bian et al. (2019); Wang et al. (2015, 2021)
	Compounds with aromatic, strong polarity or strong alkalinity as well as high temperature contributed to suppress the association of asphaltene molecules.	Li et al. (2007); Tang et al. (2022)
	The aggregation state of asphalt systems constructed by asphaltene molecules with long alkane branches was more susceptible to the effect of SBS molecules; the mixing of two asphalt with various chemical components resulted in the reduction of the intermolecular distance in the aggregates.	Ding et al. (2015, 2019)
	Intermolecular interactions changed under the tensile strain which was contributed to the increment of the potential energy of asphaltene aggregates.	Ye et al. (2021)
	MD was also used in study on dissociation of asphaltene supramolecular structure. π-Electron reduced for the hydrogenation of asphaltene, contributing to the disaggregation between asphaltene molecules.	Cai et al. (2020)
DPD	The interfacial behavior of asphaltenes was the result of a combination of multiple interactions among which π-π interaction and spatial displacements play the dominant role.	Wu et al. (2021)
	Asphaltene molecules in the bulk oil interacted by the π-π stacking of the aromatic cores.	Ruiz-Morales and Mullins (2015)
	The molecular structure of asphaltene presented a significant impact on the orderliness of the colloidal structure. The micellar structure with high consistency of aromatic systems showed higher orderliness while the one with alkyl side chains showed higher dispersion.	Zhang et al. (2010)
	The viscoelastic interfacial film was formed by the self-assembly of the interfacial active asphaltene through the π-π stacking, hydrogen bonding and other noncovalent interactions.	Ma et al. (2021)
DFT	The stability of asphaltene dimer was depended on the number of aromatic rings and also the heteroatoms existed in the aromatic core and the aliphatic side chains, which may lead to the variations of the electrostatic charge distribution on the van der Waals surface of molecules.	Wang et al. (2017)
	The π-π stacking played a vital role in the formation of the nanoaggregates, depend on the arrangement of π-electron in the poly-aromatic system of asphaltene.	Martin-Martinez et al. (2015)
	The essence of formation of hydrogen bonding in asphalt was due to the superposition of valence orbital electrons of H atoms and heteroatoms.	Ren et al. (2019b)
	The spacing of the water-grafted asphaltene dimer was lower than that of original dimer, showing that water promoted the intermolecular aggregation through hydrogen bonding.	Mousavi et al. (2021)
	The supramolecular structure formed through the hydrogen bonding and the π-π interaction between asphaltene molecules, which surrounded water molecules contributing to the adsorption of asphaltene at the oil-water interface.	Miao et al. (2018)

possible to describe the aggregation behavior of asphalt molecules. The understanding of intermolecular interactions and aggregation driving forces of asphalt still need to be further investigated (Yu et al., 2012).

4. Research methods of asphalt supramolecular structure

With the development of supramolecular chemistry in recent years, investigations of supramolecular systems have received wide attention, giving rise to growing literatures on the intermolecular interactions. Molecular self-assembly, supramolecular compounds and supramolecular aggregation behavior have also been explored in depth. At present, study on asphalt supramolecular systems could be conducted using experiment and simulation methods.

4.1. *Experimental method*

Test methods such as the Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), scattering and microscopy techniques have been used in the investigation of asphalt supramolecular systems, as shown in Table 1. The intermolecular interaction position or the group stretching vibration would be affected by the supramolecular system, showing a series of chemical shifts in the FTIR spectra, so that the supramolecular interactions

could be investigated semi-quantitatively according to the shifts. Chemical environment of atoms changed due to the formation of the supramolecular aggregates, and the variations are equally presented as chemical shifts in the NMR spectra. Scattering techniques such as the small angel X-ray scattering (SAXS), small angel neutron scattering (SANS) and wide angel X-ray scattering (WAXS) are the primary tools to investigate the variations on the size and shape of supramolecular aggregates. The atomic force microscopy (AFM), electron microscope and other microscopy approaches could be conducted to capture the variation characteristics on the micro morphology or the aggregation behavior of asphalt supramolecular structure.

4.2. *Simulation method*

The microscopic phase structures and intermolecular interactions of asphalt aggregates could be investigated by molecular dynamics (MD) simulation and then to further predict the macroscopic properties of asphalt (Cai et al., 2019; da Costa et al., 2012). The dissipative particle dynamics (DPD) method simplifies the interactions between particles and could be used in the characterization of the colloid aggregation structure of asphalt. The evaluation on intermolecular interactions at the electronic level could be carried out by quantum chemical methods such as the density functional theory (DFT), including the calculation of interaction energy and the determination of stable molecular configurations. Above simulation methods have been applied widely in the investigation of asphalt supramolecular system, giving rise to many literatures shown in Table 2.

5. Effects of supramolecules on the properties of asphalt

The macro properties of asphalt binder are driven by the polar association and intermolecular interactions in the micro structure of asphalt (Holleran et al., 2020). Factors such as the hydrogen boning interaction, noncovalent π-π stacking and heteroatoms have impacts on the mechanical properties and phase behaviors of asphalt (Kabir et al., 2022; Samieadel et al., 2017). It was reported that the viscosity of asphalt was related to the size and composition of aggregation structure (Lemarchand et al., 2015), and was more sensitive to the intermolecular interactions concerning the active hydrogen (Liu and Long, 2018). Moreover, intermolecular interactions played a vital role in the binding of asphalt binder, aggregate and water (Du et al., 2021; Guan et al., 2020; Liu et al., 2020).

The supramolecular structure could be used to explain for the chemical aging of asphalt and the restorative effect of the modifier on the aged asphalt. Intermolecular interactions increased with the aging of asphalt, which may lead to low dispersibility and increased association behaviors between asphalt molecules (Pahlavan et al., 2018b; Sreeram et al., 2019). The increment of intermolecular interactions induced a higher glass transition temperature of asphalt (Luo et al., 2021). Hu et al. (2022) suggested that the asphalt components presented higher agglomeration and lower compatibility with the increment of the molecular polarity and the intermolecular binding energy of asphaltene after aging, resulting in the poor cracking resistance of asphalt. In the regeneration of the asphalt, it has been proved that the incorporation of the rejuvenator promoted the segregation of asphalt molecule agglomeration, contributing to the regeneration of aged asphalt (Ding et al., 2021; Pahlavan et al., 2018a). Fini et al. (2020) indicated the deagglomeration of oxidized asphaltene was presented as the increase of both crossover modulus and crossover frequency, and the two indicators were recommended to evaluate the rejuvenation of asphalt. Pahlavan et al. (2018b) suggested the bio-rejuvenator alleviated the impact of polar substitution in aging process of asphalt, so that intermolecular interactions decreased, giving the aged asphalt molecules more mobility to regenerate into a more stable and ordered structure. Hu et al. (2021) insisted the electrostatic interaction between asphalt molecules enhanced with the generation of polar groups in the aging, while the hydrogen bonds between molecules were destroyed after the incorporation of rejuvenator, leading to the decrease in the electrostatic interaction and the deagglomeration between asphalt molecules.

The compatibility between the modifier and asphalt is also proved to be linked with hydrogen bonding, π-π stacking, van der Waals, acid-base interaction and other noncovalent interactions (Induchoodan et al., 2021; Wang et al., 2018; Yang et al., 2021). Zhang et al. (2021a) demonstrated the high temperature properties of asphalt increased by the modifier with high energy of hydrogen bonding between molecules and the low temperature properties improved by the modifier with more amount of hydrogen bonding. Shu et al. (2017) found that the multiple-walled carbon nanotubes improved the properties of SBS modified asphalt by the strong adsorption between them created by the π-π interaction. Mousavi et al. (2016b) proved that the uniformity of the π-electron density in the aromatic region was disturbed by the interaction between the bio-modifier and the asphaltene, resulting in the variations on the binding distance and energy of the π-π interaction so that the aggregation extent was changed, having an impact on the morphological and rheology properties of asphalt including the resistance to fatigue and cracking. Bao et al. (2020) indicated that the bio-asphalt could be utilized as a lubricant to limit the intermolecular interactions so that the modified asphalt presented better anti-rutting properties.

Except that supramolecular network could be formed by molecular self-assembly in the asphalt, the polymers with supramolecular structure also could be applied in asphalt, particularly in the modification, to improve asphalt performance. Wang et al. (2012) suggested that the UV aging resistance and rheology properties of asphalt increased after modification with the layered double hydroxides (LDHs), a nano-material with the host-guest supramolecular structures. Zhao et al. (2016) recommended that the interlayer of LDHs was more beneficial to the compatibility of LDHs with asphalt.

6. Discussions

The aggregation of asphaltene molecules has been the attention of petrochemical researchers. However, the asphaltene molecule in the pavement asphalt usually disperses well, and only exhibits aggregation in the aging status. The aggregation of asphaltene and resin molecules affect the mechanical properties of pavement asphalt significantly since the asphaltene molecule is dispersed by resin. Therefore, the supramolecular structure composed of asphaltene and resin molecules should be the primary subject on the research of the chemical structure of asphalt.

The supramolecular structure of asphalt is formed by the synergistic effect of various intermolecular forces. Experimental methods only detect a certain type of functional group or chemical structures. Describing the synergy of various intermolecular forces is the advantage of the simulation method. Moreover, it is necessary to calculate intermolecular forces and their synergies in the asphalt molecular model to evaluate the effect of supramolecular structures on the mechanical properties of asphalt.

Force fields and computational methods significantly affect the accuracy and efficiency of simulation method. The current force fields for the simulation of asphalt are developed based on single-molecule evaluation, which could not be applied on the description of the synergy of various intermolecular forces. In addition, the understanding of the synergistic effect of intermolecular forces requires larger-scale molecular models. The current simulation methods based on molecular dynamics approaches could not deal with the large-scale molecular model of asphalt. Therefore, the advanced force fields and high-throughput calculation methods suitable for asphalt are the priority for the research of the supramolecular structure of asphalt.

7. Conclusions

(1) Supramolecular theory focuses on the supramolecular system constructed through the intermolecular noncovalent interactions. Asphalt as a colloidal material has a wide range of aromatic ring structures and heteroatoms, allowing for the asphaltene molecules to form supramolecular systems through intermolecular interactions. There are various interactions between asphalt molecules such as π-π stacking, hydrogen bonding, acid-base interaction and metal coordination, which are prerequisites for the formation of supramolecular structures in asphalt. In addition, intermolecular interactions are related to the mechanical properties of asphalt. Consequently, the introduction of supramolecular theory provides a new view for investigating the relationship between the micro structure and the macroscopic properties of asphalt from the perspective of weak noncovalent forces of asphalt.

(2) Existing supramolecular structures in asphalt system include the colloidal structure, the asphaltene aggregation models and so on. Studies have concentrated on the commonalities of asphalt molecular structures due to their complexity, and there is no unified conclusion on the main driving force of asphalt molecular association. The natures of intermolecular interactions, the major driving force and behaviors of supramolecular aggregation need to be further investigated.

(3) Research on supramolecular system of asphalt can be conducted in experimental and simulation analysis. Experimental methods consist of FTIR, NMR, scattering method and other microscopic tests. Simulation methods include MD, DPD, DFT and other methods. A single method cannot completely characterize the asphalt supramolecular structure. It is recommended that MD is used as the basis, combined with quantum chemical methods, mesoscopic dynamics methods such as DPD, and fine-scale technologies such as finite element and discrete element, to extend the research scale of asphalt supramolecular systems and to achieve an effective link between microstructure variations and macroscopic properties of asphalt.

(4) More studies focus on the asphaltene aggregation especially in the petrochemical field at present. In the road engineering, some literatures showed the physical, chemical and mechanical properties of asphalt are related to the supramolecular structures. Analysis of supramolecules could also be introduced in the studies on the aging, modification and regeneration of asphalt. It is recommended to further investigate the essence of the supramolecular systems in asphalt and the mechanism of supramolecules to macroscopic properties of asphalt.

Conflict of interest

The authors do not have any conflict of interest with other entities or researchers.

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