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Research paper

Effect of thermal maturation on chemical structure and nanomechanical properties of solid bitumen

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A R T I C L E I N F O

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A B S T R A C T

An abundance of organic matter is present as solid bitumen in highly mature shales. Changes in chemical structure of solid bitumen during catagenesis could alter the way its mechanical properties evolve. This study considers a series of solid bitumen samples artificially produced from the pyrolysis at 420–618 °C of soluble organic matter which originated from Maoming shale, to examine alternations in their chemical structure, nanomorphological and mechanical properties during maturation. Solid-state ^{13}C nuclear magnetic resonance spectroscopy and elemental analysis were employed to characterize the structural changes. Young's modulus and microstructures were determined by atomic force microscopy. The results show that both structural (including C/H atomic ratio and carbon aromaticity) and mechanical (Young's modulus) variations in solid bitumen exhibit two staged evolutions (i.e., wet gas stage and dry gas stage) during maturation. In the wet gas stage (EasyRo 1.85%–2.64%), the C/H ratio and carbon aromaticity increase substantially with maturation, and the solid bitumen is relatively compliant with an average Young's modulus varying from 2.7 ± 0.6 to 3.0 ± 0.6 GPa. When maturity reaches to dry gas stage (EasyRo 2.64%–4.59%), structural parameters do not change greatly, whereas solid bitumen becomes much stiffer with modulus rising sharply to 7.2 ± 1.1 GPa at EasyRo 3.49% and further gently to 8.8 ± 1.4 GPa at EasyRo 4.59%. Concomitantly, great variations are observed on surface morphology, and the degree of heterogeneity in solid bitumen is recorded to be increasingly high along thermal simulation. Given the strong correlation between structural parameters and Young's modulus, we suggest that the stiffening of solid bitumen is extensively affected by its structural condensation due to the loss of aliphatic carbons and the increase of aromaticity.

1. Introduction

Shales have intrinsically heterogeneous microtextures and chemical compositions, which include organic matter (OM) and minerals, indicating that the macroscale mechanical performance depends on their microstructural mechanical properties (Emmanuel and Day-Stirrat, 2012; Eliyahu et al., 2015; Bobko and Ulm, 2008). The mechanical properties of minerals commonly present in shales have been well characterized (Deirieh et al., 2012; Zhu et al., 2007; Alstadt et al., 2015; Veytskin et al., 2017; Bennett et al., 2015), whereas little research has been conducted on the properties of OM, especially those of solid bitumen.

Shale gas evaluation and exploration have made great achievement in the lower Paleozoic marine shales of the Upper Yangtze region, South China (Chen et al., 2011; Wei et al., 2012; Tan et al., 2014; Zou et al., 2010). Gas shales in China commonly have high total organic carbon (TOC) contents of 2%–5%, and are characterized by high thermal maturity (vitrinite reflectance, Ro = 2.0%–3.5%) compared with North America shales (Xiao et al., 2015). Because marine shales have typically entered the gas stage, they contain an abundance of OM presented as solid bitumen due to thermal cracking of crude oil (Tian et al., 2015; Tuo et al., 2016; Liao et al., 2015). OM is a major component of the highly mature shales found in South China, and thus its elastic properties, especially those of solid bitumen, would partially affect the geomechanical behavior of gas shales by affecting seismic expression and sonic measurements. Therefore, an accurate understanding of the nanomechanical behavior of solid bitumen in response of maturity is essential for compiling rock models to predict seismic signatures (Avseth and Carcione, 2015; Han et al., 2015), evaluate borehole stability and optimize hydraulic fracturing design of shales in South China (Zargari et al., 2016; Chen et al., 2015; Eliyahu et al., 2015; Shukla et al., 2013).

Investigation into nanomechanical properties of solid bitumen may also be of great relevance to explain its associated stages of nanopore

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development. Due to the secondary cracking of bitumen at high maturity, the presence of solid bitumen could aid nanopore development in organic-rich shales, as porous solid bitumen has been widely observed in shales at the gas generation stage (Curtis et al., 2012a, 2012b; Juliao et al., 2015; Mastalerz et al., 2008; Milliken et al., 2013). However, the contribution of solid bitumen to nanopore generation varies greatly among different gas stages (Duan et al., 2016; Chen and Xiao, 2014; Liu et al., 2017). Previous research indicates that the evolution of micropores and fine mesopores associated with solid bitumen in shales increases rapidly in the wet gas stage, but much slowly in the dry gas stage (Liu et al., 2017). This difference may be attributed to changes of solid bitumen's mechanical properties. Studies about kerogen indicate that cleavage of aliphatic C–H bonds and shrinkage between residual aromatic sheets result in structural condensation and carbonization of OM during maturation (González-Vila et al., 2001; Craddock et al., 2015; Mao et al., 2010; Smernik et al., 2006; Cao et al., 2013; Burdelnaya et al., 2014). Thus, the process can alter the mechanical properties of residual OM, and it solidifies into brittle semi-coke or coke, of which the cracking may lead to destruction, merging, and collapse of OM-hosted nanopores at high maturity (Duan et al., 2016; Liu et al., 2017; Eseme et al., 2007). This mechanism may also hold for solid bitumen, that is, nanopore development in solid bitumen is potentially governed by its mechanical properties.

Solid bitumen comprises complex macromolecular moieties, which can undergo considerable structural changes during maturation. Such structural variation could facilitate the formation of diverse microstructures and alter the mechanical properties of residual OM (Okiongbo et al., 2005; Yu et al., 2015). Therefore, it is important to characterize the structural changes as they occur during maturation to understand the alternations in the morphological and mechanical properties of solid bitumen. Various analytical methods, especially solid-state nuclear magnetic resonance (NMR) spectroscopy, have been employed to elucidate structural changes of kerogen during maturation (González-Vila et al., 2001; Craddock et al., 2015; Mao et al., 2010; Smernik et al., 2006; Cao et al., 2013; Burdelnaya et al., 2014). The most extensively used solid-state NMR technique for kerogen is ^{13}C cross polarization/magic angle spinning (CP/MAS) (Lille et al., 2003; Werner-Zwanziger et al., 2005; Wei et al., 2005). However, few works have examined the structural variations of solid bitumen at high maturity.

Numerous studies have characterized the relationship between the elastic properties of kerogen and maturity by nanoindentation (Zeszotarski et al., 2004; Bobko and Ulm, 2008; Ahmadov et al., 2008; Kumar et al., 2012; Shukla et al., 2013; Zargari et al., 2013; Alstadt et al., 2015) and atomic force microscopy (AFM) (Emmanuel et al., 2016; Eliyahu et al., 2015; Wilkinson et al., 2015), but the elastic properties of solid bitumen at high maturation remain poorly understood. Previous research has generally concentrated on solid bitumen *in situ* at various maturities (Zargari et al. 2013, 2016; Emmanuel et al., 2016), the nanomechanical behavior of which depends on both thermal maturation and the supporting action of the stiff kerogen and mineral matrix (Emmanuel et al., 2016). In contrast, thermal simulation of solid bitumen at different temperatures could eliminate the effect of matrix, while maintaining maturation as the single variable. However, no studies have yet concentrated on the artificially matured solid bitumen and characterized its mechanical behavior in response of maturity.

AFM is a powerful technique in characterizing mechanical properties, such as stiffness, rigidity, resistance to breakage and adhesive properties on the nano-to micro-scale. The PeakForce quantitative nano-mechanical mapping (PF-QNM) mode can provide nanoscale quantitative mapping of mechanical properties at high resolution (Pittenger et al., 2014), which has been widely used to characterize the nanomechanical properties of biological materials (Sweers et al., 2011; Iwamoto et al., 2009; Adamcik et al., 2012), polymers (Schön et al., 2011; Dokukin and Sokolov, 2012), cement minerals (Trtik et al., 2012; Li et al., 2016), and shales (Emmanuel et al., 2016; Eliyahu et al., 2015). This method is based on the acquisition of force curves recorded with the real-time calculation of the elastic modulus at each pixel of the image. In this study, we used PF-QNM to characterize the elastic properties of solid bitumen by acquiring high resolution quantitative modulus maps.

Table 1
Geochemical data of Maoming oil shale.

TOC (wt.%)	T_{max} (°C)	HI (mg/g TOC)	OI (mg/g TOC)	S1 (mg/g TOC)	S2 (mg/g TOC)	S3 (mg/g TOC)
16.83	430	716	15	0.87	104.39	2.19

In this work, we measure the chemical structural changes of a series of artificially prepared solid bitumen by using solid-state ^{13}C NMR spectroscopy and elemental analysis, determine the variations in nanomechanical properties by applying AFM to map the elastic modulus, and establish the relationship between chemical structure and mechanical properties of solid bitumen at high maturity.

2. Experiments

2.1. Samples

2.1.1. Original sample

The oil shale sample, which was collected from the Eocene Youganwo Formation of Maoming in Guangdong Province, Southeastern China, is immature with Ro of 0.5%. Organic geochemical parameters of the oil shale are presented in Table 1. It is organic-rich, with a TOC content of 16.83%. Rock-Eval analysis shows a T_{max} of 430 °C, with a hydrogen index (HI) of 716 mg/g TOC and oxygen index (OI) of 15 mg/g TOC. The kerogen is type I–II. And the minerals in the oil shale are mica (42.6%), quartz (21.2%), kaolinite (20.2%), montmorillonite (7.9%), calcite (2.3%), dolomite (2.8%), and pyrite (3%).

2.1.2. Preparation of soluble organics at the peak oil-generating stage

A semi-open pyrolysis system was used to prepare the samples at the peak of oil generation, which was described in detail by Liu et al. (2017). The crushed oil shale powder was sealed in a stainless steel vessel (5 cm o.d., 3 cm i.d.), and then compacted with a jack under a vertical pressure of 50 MPa. The vessel was heated in an oven at 370 °C for 24 h, equivalent to a Ro of 1.1%. After cooling, both seals were removed to collect the matured sample.

The artificially matured sample was Soxhlet extracted with a dichloromethane–methanol mixture (93:7 v:v) for 72 h to collect the soluble organics, and the TOC content is 84.5%. A quantitative analysis show that the soluble organics consists of 43.6% saturates, 23.0% aromatics, 18.1% resins, and 15.3% asphaltenes.

2.1.3. Preparation of solid bitumen

Pyrolysis of the soluble organics was performed under anhydrous conditions in sealed gold tubes (4.7 mm o.d., 4.2 mm i.d., and 40 mm length). Aliquots of 10–20 mg were placed in gold tubes. Each tube was flooded for 20 min with high-purity argon to expel air, and then sealed and loaded separately into stainless steel vessels.

The pyrolysis was conducted at a constant pressure of 50 MPa with temperature ranging from 420 to 618 °C (10 sampling points) at a heating rate of 2 °C/h. Pressure and temperature deviated from the set values by less than 1 MPa and 1 °C, respectively. Each stainless steel vessel was withdrawn from the oven at its set temperature and rapidly cooled by quenching in water. The solid residue collected after pyrolysis at each temperature was soaked in dichloromethane for 5 h to dissolve its soluble components, and the insoluble residue was considered as solid bitumen. Based on a method suggested by Sweeney and Burnham (1990), the corresponding thermal maturity during the whole