Understanding the Microstructure of Bitumen: A CLSM and Fluorescence Approach to model Bitumen Ageing Behavior

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ABSTRACT

Confocal Laser Scanning Microscopy (CLSM) allows the detailed study of the microstructure of bitumen and is capable of the visualization of fluorescent centers in bitumen. The origin of this fluorescence has been the subject of ongoing debate in the community. However, by the use of chromatographic separation and fluorescence spectroscopy, we were able to obtain new evidence regarding the composition and ageing behavior of asphaltene micelles. In fact, the aromatic mantle, serving as a stabilizing agent around the micelle, is responsible for high intensity fluorescent emissions in the visible range, and not the asphaltenes themselves. These facts serve as the basis for an updated micelle model, capable of describing both the visualized microstructure and the ageing behavior of asphalt concrete in respect to thermal healing of asphalt.

Moreover, based on this micelle structure model a new mechanical model for bitumen ageing was derived, in the framework of continuum micromechanics. Thereby, the bitumen is considered as a viscoelastic four-phase composite, consisting of an asphaltene phase embedded in a maltene phase. A third phase, built up by resins and highly polar aromatic structures, triggers the interaction between asphaltenes, and mechanically describes the age-dependent microstructure of bitumen. This model could be validated by means of shear rheometer tests on differently aged bitumen.

Keywords: fluorescence spectroscopy, bitumen micro-structure, bitumen ageing, bitumen modeling, confocal laser scanning microscopy

1. INTRODUCTION

Asphalt concrete is one of the most prominent materials in road engineering. Due to rising crude oil prices and increased manufacturer liability the economic situation for producers, engineering companies, and customer become less and less favorable. Additionally, mineral concrete as a competitive material has become ever more popular over the last decade. This leads to the exploration of new technical processes, like warm mix asphalts and advanced recycling strategies that enable the production recycling asphalt mixes of equal quality levels compared to the original product. However, all these strategies depend on the understanding of bitumen microstructure, which is the defining factor for ageing properties of asphalt.

Bitumen is broadly defined as a *virtually not volatile, adhesive and waterproofing material derived from crude petroleum, or present in natural asphalt, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperatures* [1]. This definition is as exact as possible, given the diversity of bitumina.

Since materials researchers started investigating bitumen several models for the bitumen microstructure and asphalt concrete were developed. This study is based on the micelle theory [2], [3] and the extended 5+1 scales of asphalt observation model [4], which points out the importance of the molecular and bitumen scale analysis for the material properties (**FIGURE 1**). Basically, this model assumes bitumen to be a colloidal system of asphaltenes micelles dispersed in a maltene matrix.

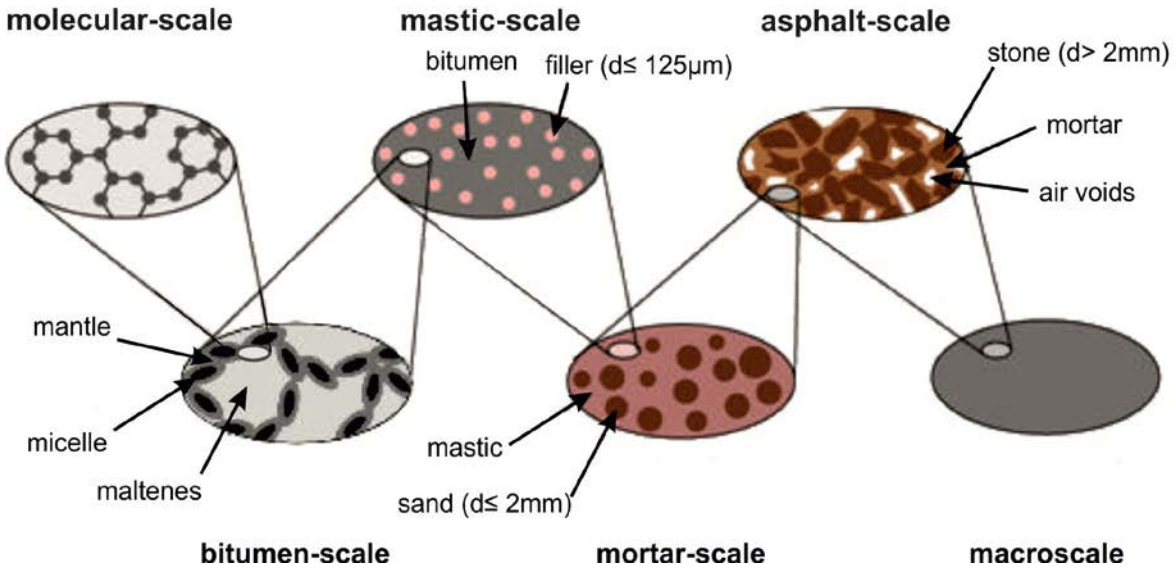

FIGURE 1: The 5+1 scales of asphalt observation, explaining the relations of material properties to the different scales of study [4]

CLSM is an imaging technique capable of analyzing highly localized fluorescence emission and was used to visualize the bitumen microstructure. Additionally, fluorescence spectroscopy was employed to obtain integrated spectra of bitumen and bitumen fractions. By combining the information, we were able to develop a new model hypothesis for bitumen ageing.

Previous studies employing CLSM on bitumen have mainly been focused on SBS-modified bitumina [3], [5], [6], [7], [8]. The analysis of pure bitumen with this intriguing method was seldom conducted [9], [10], [8]. The discussion of the nature of the fluorescent centers that can be visualized by CLSM is an ongoing debate in bitumen research [11]. Contradictory identifications range from asphaltenes [10], [9] to waxes [12]. Some of these hypotheses can be discarded easily, since certain constituents are not capable of fluorescent emission in the visible range due to their very physical and chemical nature. This study has identified the origin of these fluorescent centers and found conclusive evidence that the aromatics fraction is the source of the strong fluorescent signals in bitumen that can be visualized by CLSM.

2. MATERIALS AND METHODS

BITUMEN AND BITUMINOUS SPECIMEN

The materials used in this study were carefully chosen for their material properties and their respective position in the production cycle of bitumen (**TABLE 1**). The precursors were studied to examine, if they exhibit a similar structural composition to their respective end products. Bitumen B50/70 was chosen as a typical material used in road construction, while B70/100 bitumina are often used for the production of SBS-modified bitumina.

TABLE 1: Samples and Description

Sample	Description
Precursor 1	Vacuum flashed, cracked residuum
Precursor 2	Residuum of vacuum distillation
B50/70	Bitumen for asphalt concrete production
B70/100 1	Bitumen for asphalt concrete production or for production of SBS-modified Bitumina
B70/100 2	Bitumen for asphalt concrete production or for production of SBS-modified Bitumina

ANALYTICAL EQUIPMENT

We employed an ECLIPSE TE2000 (Nikon Corporation, Tokyo, Japan) as a confocal laser scanning microscope. The microscope hosts both a transmission and a CLSM (Confocal Laser Scanning Microscope) array. The light source for the transmission array is a T-DH 100W Illumination Pillar (Koehler Type). An Argon-ion laser is used as source of excitation radiation. Typical for CLSM, laser optics is configured to allow a scanning of the surface and the image is created point by point and line by line. The advantages mentioned above in combination with the highly sensitive detector are key features for the successful application. However, the capability to scan volumes below the surface, a key advantage of the CLSM technique, cannot be applied here, because of the high absorption cross section in the visible range of all bitumina. For sample preparation, the bitumen was heated to about 150-200°C as necessary for melting the sample. Then a small quantity of bitumen was applied to a glass slide with a piece of wire and a second glass slide was placed onto the sample. After a short period of cooling, the sample was measured. Early experiments showed that this procedure had to be modified. The first step towards a significant improvement in picture quality is the replacement of the standard object carriers by extremely thin glass slides (<0,5mm). Second, an additional heating period was implemented, allowing the bitumen film to spread and become thinner. These very thin films could then be examined by CLSM.

For fluorescence spectroscopy, an Edinburgh Instruments FSP920 photoluminescence spectroscopy setup was at our disposal. As an illumination source, a XE900 Xenon Arc Lamp is used, which provides high intensity radiation on a broad spectrum. The setup employs double Czerny-Turner monochromators (type TMS300) at both excitation and emission arms, guaranteeing a very narrow spectral bandwidth. The detector is a S900 single-photon photomultiplier (type R928). The spectrometer was used to conduct both excitation and emission measurements. For sample preparation, the bitumina were heated to 150°C and a drop of

bitumen was applied to a standard microscopic slide. This slide was stored at the same temperature for 5 minutes to allow the drop to spread and increase its surface. Afterwards the samples were cooled to room temperature and subjected to fluorescence spectroscopy. For bitumen fractions, this treatment was not necessary, because the maltene phase and its components are viscous liquids at room temperature and can be applied directly to the glass slide. The asphaltenes were taken up with toluene and then dripped slowly on the warm glass surface (80°C) to allow the formation of a thin film.

Chromatographic separation was conducted according to ASTM Standard 4124 [13], which is the most prominent and widely used method [11] and based on the Corbett procedure [14]. However, the nomenclature was changed to fit the SARA (Saturates Aromatics Resins Asphaltenes) scheme, deviating from the standards nomenclature (aromatics – naphthene aromatics; resins – polar aromatics). First bitumen was separated into maltene and asphaltene phase by extraction with n-heptane. However, the n-heptane extraction was conducted in a Soxhlet-extractor. The further separation is conducted in a 1000mm chromatographic column with alumina as the stationary phase with three different solvents/solvent combinations. The eluate was collected in 50ml beakers, which were sealed, cooled, and then stored at -15°C to slow oxidative degradation. Then each fraction was warmed to room temperature and subjected to distillative separation under vacuum. The sample was then cooled to room temperature before breaking the vacuum. Afterwards, the fraction was weighed. The sample was then again subjected to escalating distillation (max 185°C, 10mbar, 10min) and weighing until constant weight was reached to assure gravimetric exact measurements. Then the sample specimens were prepared for fluorescence spectroscopy.

3. RESULTS

3.1 Microstructure of Bitumen, Bitumen Precursors

It was possible to obtain new and enhanced pictures of the bitumen microstructure by application of CLSM to pure bitumina. These images proof the existence of a microstructure, which implicates agglomeration processes and phase separation processes in bitumen, as implicated in the micelle model. The fluorescent centers detected are of roughly ellipsoid shape, vary in size and amount, and their spatial distribution seems to be statistical and unordered. Exemplary, two images are shown in FIGURE 2. Their exact size distribution and population density varies for each sample and is characteristic for specific bitumina. The micelle model describes bitumen as a colloidal system of dispersed asphaltenes in a continuous maltene phase, which makes the spatial distribution of the fluorescent centers an important issue [3], [11]. Thus, a strong connection to the mechanical and rheological properties can be assumed. Preliminary experiments with picture analysis software have been conducted to assess the particle size distribution for the tested bitumina and whether significant differences between the samples can be found. Although the necessary picture processing is a rather complicated task due to high background fluorescence in bitumen, first results are promising and future experiments and process automation could provide a powerful tool for bitumen analysis.

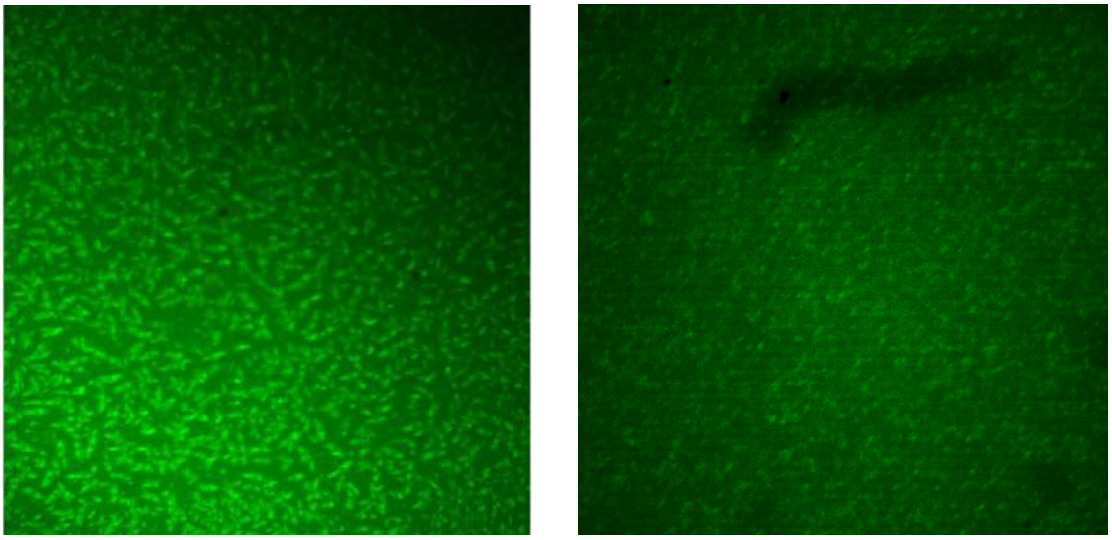

FIGURE 2: CLSM images of bitumen precursor PE1005 (left) and bitumen B70/100 (right), fluorescent centers characteristic for the respective sample

3.2 Fluorescence Analysis and Chromatographic Separation

Initially, fluorescence experiments have been conducted to support the use of CLSM as an imaging technique on bitumen. However, this study found that besides the distribution of fluorescent centers, the fluorescent behavior of bitumen and bitumen fractions can provide additional evidence regarding the actual microstructure of bitumen. Fluorescence spectroscopy yields an integrated spectrum that is not capable of visualizing spatial distributions. Information about the fluorescent centers and their composition in bitumen must be obtained indirectly through inference. A closer look on the basic physicochemical properties of bitumen reveals that bitumen contains only three fractions that could theoretically be the origin of the fluorescent signal. The asphaltenes, the resins, and the aromatics are, based on their general description, capable of fluorescence. Saturates can easily be dismissed as a source of fluorescent emission, due to the well defined chemical nature of fraction. There are two kinds of spectra presented here, excitation scans (variable excitation, fixed detection wavelength) and emission scans (fixed excitation, variable detection wavelength). For the excitation scans, the same detection wavelength as used at the microscope was chosen, 515nm, and a spectral range of 200-500nm was observed. For the emission spectra, two wavelengths have been studied carefully. First the excitation wavelength of 488nm was selected, because this is one of the excitation wavelengths available in the CLSM setup. To check for high energy fluorescence transitions, we employed a wavelength of 280nm. (**FIGURE 3**).

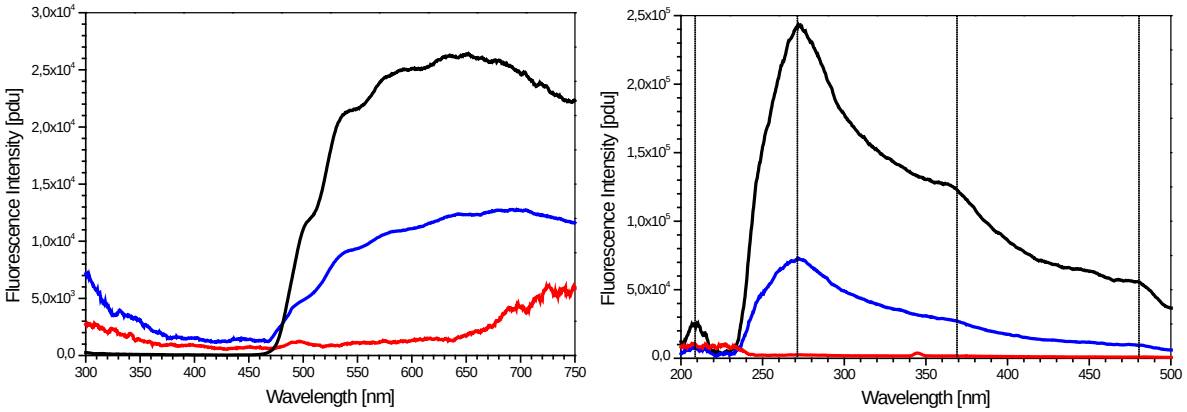

FIGURE 3: Emission fluorescence spectra of bitumen B50/70 (blue), asphaltenes (red) and maltenes (black) at 280nm excitation wavelength (left) and excitation spectrum of bitumen B50/70 at 515nm detection wavelengths;

The excitation fluorescence spectrum of pure bitumen allows the identification of four wavelength of particular interest (**FIGURE 3**, right): 210nm, 270nm, 370nm, 480nm (dotted lines) for CLSM at a detection wavelength of 515nm. These are a local and the absolute maximum, as well as the two shoulders visible in the excitation scan of the pure bitumen. The distribution of the fluorescent centers excited at these wavelengths would be of particular interest. Since fluorescence transitions can also be triggered by wavelengths lower than the necessary minimum, it is impossible to visualize the higher energetic transitions exclusively. For the CLSM studies, an excitation wavelength of 488nm was chosen, because it is very close to the shoulder at 480-490nm. Also it is one of the spectral lines providing the highest intensity available at the Argon-ion laser and is frequently used for CLSM. The technique was capable of revealing the origin of the fluorescence signals of the different species spatially distributed.

After the completion of the CLSM imaging, soon investigating the source of the fluorescence became a primary goal of further experiments. Usually a detailed interpretation of the fluorescence spectra could be attempted, but for bitumen, this is a rather difficult task. The dependency of fluorescence phenomena on the chemical vicinity of the molecules is very well documented and the effects of the surroundings are hardly assessable for bitumen [15]. Hence, a more empirical approach was chosen. The fractionation by chromatography is a well-known and reliable standard method in bitumen analysis [14], [13], [11]. It is often employed for characterization of bitumina by their relative contents of fractions. The fractions themselves again are complex mixtures of molecules, but exhibit similar chemical/physical behavior. In previous publications, the origin of fluorescence emission was suspected to be the asphaltenes fraction. This theory was explored to full extent. In general asphaltenes are defined as insoluble in n-heptane. While the basic extraction protocol for standardized testing is based on a simple extraction with n-heptane [13], for these experiments, a Soxhlet-extractor was used for the removal of asphaltenes, which guarantees as pure asphaltenes as reasonably possible. The fluorescence spectra of these fractions were surprising. Our experiments strongly indicated that the origin of the fluorescent centers can be found in the maltene phase and not in the asphaltenes phase, as proposed by other researchers [10]. The spectra of the asphaltenes show almost no fluorescent capabilities at either the detection wavelength or the excitation wavelength used by the CLSM (**FIGURE 3**). The maltene phase exhibits strong fluorescence in these areas. The

absolute intensity ratings, although being only general tendencies, suggest that the residuum somehow dampens the fluorescence of the pure bitumen 50/70 as it dilutes the extract. Obviously, the fluorescence of the asphaltenes is shifted to wavelengths higher than 750nm, into the near infrared region, which is not accessible to the fluorescence spectroscope used in this study.

Further fractioning of the maltene phase into saturates, aromatics, and resins, was conducted to obtain their respective spectra. Although the spectra differ within reasonable bounds, all bitumina show the same behavior: Only the aromatics fraction shows significant fluorescence in the relevant areas. Taking into account the micelle model and that the fluorescent centers are spatially distributed and the fluorescent species seem to agglomerate, they can be interpreted as a stabilizing mantle, composed mainly of aromatics, surrounding the asphaltenes micelles. FIGURE 4 shows the normalized spectra of the bitumen fractions and show that the aromatics exhibit very strong fluorescence at 480nm excitation. However, it has to be added that normalization removes the information of fluorescent emission intensity, which is by several orders of magnitude higher for the aromatics than for both resins and saturates.

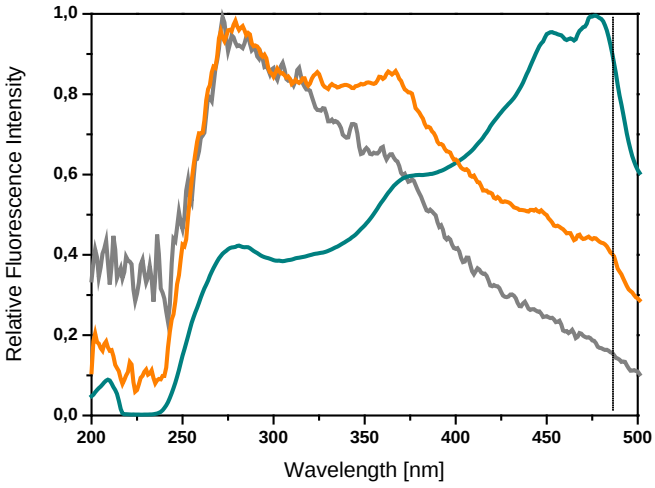

FIGURE 4: Fluorescence spectra of bitumen fractions: saturates (grey), aromatics (green), resins (yellow), detection wavelength of CLSM: 488nm

3.3 The Micelle Model and Ageing

Considering this new information about the chemical structure of the micelle we formulated a new thesis regarding bitumen ageing. This model is a refinement of the micelle model and takes the research conducted upon the oxidative properties of bitumen and bitumen fractions [16], [11] into special consideration. The saturated fraction is considered the least reactive, almost inert by comparison, of all fractions. The asphaltenes seem to have a very strong capability for oxidation in liquid state (i.e. melted or in solution), but show low reactivity at ambient conditions due to their highly associated and solid state. Both aromatics and resins show significant susceptibility for oxygen uptake [16]. Due to this research, for mixing and construction, i.e. the first short term ageing step, oxidation can take place across all phases, with the exception of saturates, but for long term ageing, the oxidation of the asphaltenes fraction has to be considered insignificant. Based on the micelle structure model and its structural and

chemical constraints, a pathway for oxidative species diffusing through the material can be plotted (**FIGURE 5**, left).

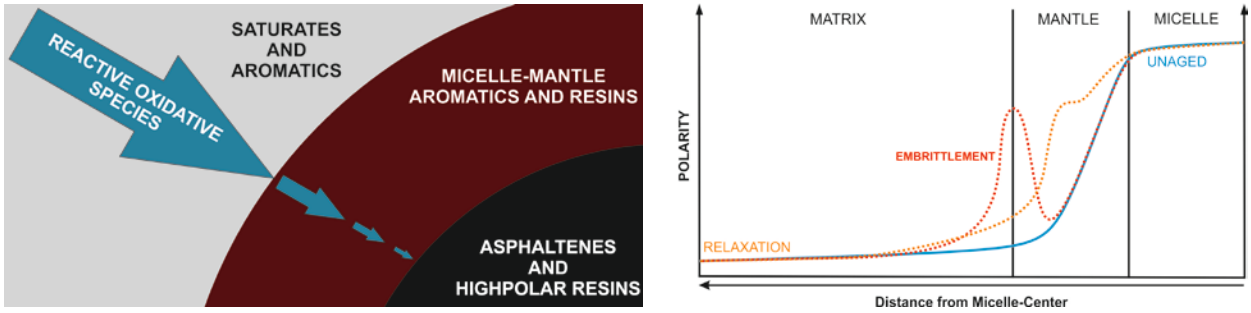

FIGURE 5: Reactive oxidative species (ROS) pathway in bitumen (left). Polarity of bitumen in the micelle structure in fresh (blue), long term aged (red), and relaxed (orange) state (right)

The continuous phase is largely inert, so the first contact between oxidative species and reactive material happens at the surface of the micelle mantle, which is composed of aromatics and resins. There oxidation can occur and the ammount of reactive oxidative species reaching the asphaltenes has to considered reduced strongly by the oxidation happening in the mantle. This is also conclusive with studies on asphalt oxidation which generally show a declining amount of nonpolar aromatics and a buildup of resins and asphaltenes as a result of ageing. This oxidation process has to be considered very slow in nature, due to the low temperature and the stability of most carbohydrates to oxidation at ambient conditions. However, experience in road engineering show that road damages due to asphalt ageing can occur few months after the construction. Furthermore, experiments regarding asphalt healing in lying asphalt concrete roads show that heating the asphalt can significantly increase road lifetime by enabling self healing [17]. Based on this research we developed a new model hypothesis for asphalt ageing. If the low mobility of molecules at ambient conditions is taken into account, it can be understood that oxidation leads to the formation of a high polar layer on the outside of the micelle mantle. If the polarity reaches a certain limit, then phase separation at this new boundary occurs and the whole, larger micelle plus mantle particle basically forms another immobile center. This reduces transduction of elastic properties and leads to a hardening of the material. If the asphalt is heated, then the diffusion rate significantly increases and the now highly polar resins/aromatics migrate into the center of the micelle and the functionality of the mantle is restored. This also explains why the ageing at road construction is not as destructive as it would have to be considered. At the high temperatures, the high polar oxidation products can simply be transported into the inside of the micelle. However, the increase in micell volume means that the mantle becomes thinner and thus the polarity gradient more extreme and micelle mobility in the matrix decreases. This limits the capability of relaxation by inclusion of high polar molecules in the micelles.

4. MICROMECHANICAL MODELING OF BITUMEN MICROSTRUCTURE

Based on the micelle model introduced before, delivering a basic concept of the bitumen microstructure, and the knowledge gain through the proposed results of chemical analysis, a mechanical model which takes the bitumen microstructure into account could be derived.

Therefore, the framework of continuum micromechanis was chosen, allowing for a description of the viscoelastic response of bitumen depending on the volumetric composition and the physical properties of its constituents. Moreover, the interaction between material phases can be taken into account through different so-called homogenization schemes [18], [19], [20], [21], [22], [23]. Thereby, a material is considered as a micro-heterogenous body filling a macro-homogenous representative volume element (RVE). Quasi-homogenous subdomains [20], [21], [22], also known as material phases, with known physical properties describe the microstructure within such an RVE. Correlating the homogeneous deformations acting on the boundary of an RVE with the resulting (average) stress, the mechanical behavior of the overall material can be estimated. Such an approach is refered to as homogenization.

On the basis of the chromatographic separation mentioned before, a reasonable subdivision of bitumen into distinct material phases for the micromechanical modelling were possible (see **FIGURE 6**). Therefore, an RVE of bitumen is built up by a contiguous matrix phase, representing aromatics and resins, in which spherical inclusions are embedded, describing the saturates. While the asphaltenes, acting in the center of micelles, are also modelled by spherical inclusions, the micelle mantles are assumed to form a network-like structure and for this reason are represented by needles with randomly distributed orientations.

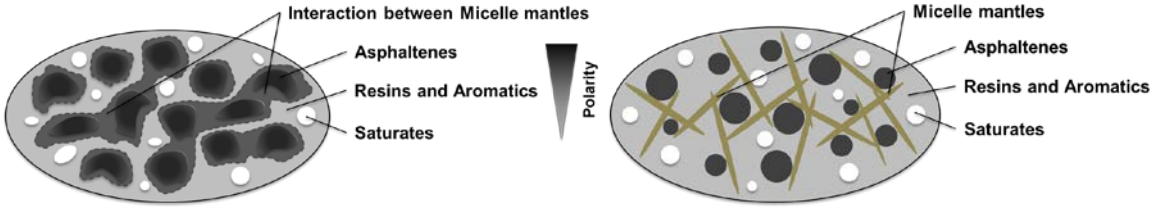

FIGURE 6: Concept of bitumen microstructure based on micelle model and therefrom derived RVE considered in micromechanical model

Identification of the viscoelastic behavior of the maltene phase (matrix phase and the inclusions representing the saturates) was done by static shear creep tests using a dynamic shear rheometer (DSR). As asphaltenes and their mantle material (highly polar resins and aromatics) act together in the micelle structure, the same effective viscoelastic behavior is assigned to both phases. To access this effective behavior, static shear creep tests on bituminous mixtures with different (known) asphaltene contents were carried out and by comparison of experimental and model results on a best-fit basis the material behavior could be obtained. In addition, the increase of needles, representing the interaction between micelles, with increasing asphaltene content could be determined, revealing an exponential relationsship for asphaltene contents between 0 % and 20 %. For a detailed validation of these assumptions and the introduced micromechaincal model we refer to further publications.

The influence of longterm ageing was investigated on B70/100 bitumen samples, aged in laboratory using PAV and RTFOT equipment [24] . From static shear creep tests on these samples it was found, that the mechanical behavior of asphaltenes as well as maltenes due to ageing is negligible. However, a significant increase in asphaltene content, and consequently the micelle mantle content, could be observed (detailed information also presented in further publication). This increase, and thus the effect of ageing, can be described satisfactorily by the derived micromechanical model, as can be seen in **FIGURE 7**.

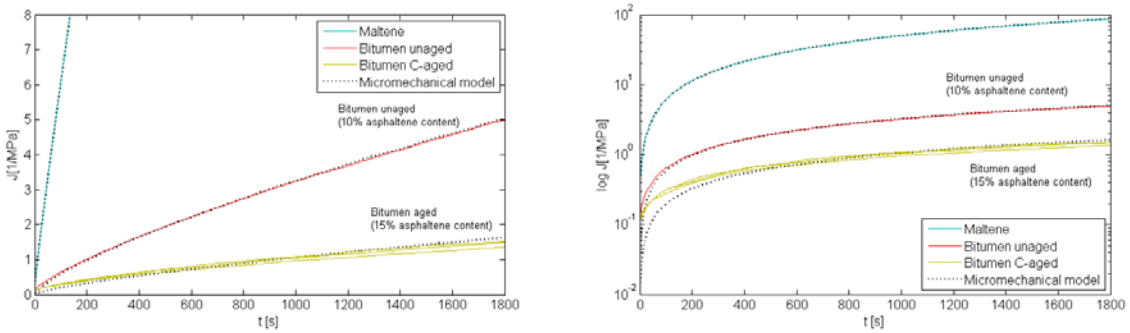

FIGURE 7: Comparison of experimental results on aged and unaged bitumen (B70/100 at +5°C) from static shear creep tests with predictions from micromechanical modeling

5. CONCLUSION

Confocal laser scanning microscopy is an important tool for bitumen analysis, because of its capability to visualize the microstructure of bitumen. It proves the existence of two separate phases in bitumen, as predicted by the micelle theory. Also, it was possible to identify the fluorescent phase in bitumen by chromatography and fluorescence spectroscopy as the aromatics fraction. The aromatic phase contains the molecules that exhibit strong fluorescence capabilities at 488nm excitation and 515nm detection and seem to agglomerate. Although other phases also show activity under these conditions, it is by several orders of magnitude lower in intensity, if compared to the aromatics. Thus, an ongoing debate in the scientific community has found its end.

The realization that the fluorescent phase in bitumen is actually the aromatics phase indicates that this is a critical phase regarding ageing and embrittlement. Basically, we developed an enhanced micelle theory for ageing that is capable of explaining the different effects of short term and long term ageing as well as thermal healing of asphalt concrete. This is an early step on the road to upstream recycling of asphalt concrete and bitumen, because the identification of problematic structural and chemical changes is necessary to overcome their effects.

Based on the introduced micelle model, a mechanical model is derived in the framework of continuum micromechanics considering bitumen as a four-phase composite consisting of asphaltenes, micelle mantles, and saturates embedded in a contiguous matrix of aromatics and resins. The microstructure was implemented in a homogenization scheme to predict the overall viscoelastic response. An increase of asphaltene content, and thus volume content of the micelles, is identified to be responsible for ageing effects, which can be described by the micromechanical model very well.

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