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NEW EXPERIMENTAL APPROACHES TO ANALYSE THE SUPRAMOLECULAR STRUCTURE OF REJUVENATED AGED BITUMENS

Abstract. Bitumen aging occurs through volatilization, oxidation and supramolecular assembly variations involving drastic changes in the structure of the material. Due to the ageing process of bitumen and its corresponding increase in viscosity, the stiffness of asphalt pavement is increased during its lifetime. Chemically, the relative content between asphaltenes and maltenes in the bitumen shifts towards a lower maltene fraction. Therefore, addition of high amounts of Reclaimed Asphalt Pavement (RAP) in asphalt mixtures may negatively affect the quality and performance of the final mix design. Rejuvenating agents can assist in this process by decreasing the aged bitumen's viscosity and restoring its original properties. An efficient rejuvenating agent favors there organization of the colloidal structure of the oxidized bitumen, thus recreating a supramolecular structure similar to fresh bitumen. Then, novel experimental approaches are needed to evaluate the efficiency of rejuvenators as well as the effect such additives have on aged bitumen properties. To achieve the aforementioned purpose, two advanced experimental approaches able to provide detailed information on bitumen microstructure are examined here. The essential concepts underlying the scattering and NMR techniques will be reviewed and the results of some recent applications of these methods in the evaluation of the effectiveness of the RAP rejuvenation will be synthetically illustrated.

Key words: rejuvenators, bitumen, aging, scattering, PXRD, NMR, relaxometry.

Introduction. Many important physical, mechanical, rheological and other characteristics of asphalt concretes depend considerably on bitumen properties [1-6]. But bituminous materials are easily subject to oxidative aging during pavement service life, especially in conditions of thermal and / or ultraviolet radiation [7, 8]. It is well assessed that oxidized bitumen is characterized by reprocessing temperatures higher than fresh one, because most of the condensed aromatic components and resins, which are responsible for a certain grade of mobility, are converted into highly oxygenated polar and more saturated compounds (asphaltenes and saturates), [9]. Indeed, the depletion of polycyclic aromatic compounds with amphiphilic activity and acting as supramolecular cage surrounding the polar asphaltenes, may lead to an increase of average colloidal sizes dispersed in the continuous a polar maltene phase. This phenomenon in turn gives rise to loss of elasticity and predisposition to material failure. Thus, once removed and processed, the bituminous layers can be recycled as reclaimed asphalt pavements (RAPs), even though their reuse is still limited (less than 20% in the mix design) due to their poor bulk mechanical properties (complex modulus and viscosity), which can cause premature cracking failures. The RAP performances as asphalt binders may be partially restored towards their original state upon addition of several classes of compounds called rejuvenators [10-12]. In particular, at least two classes of rejuvenators can be distinguished on the basis of the mechanism by which they exert their respective regenerating action, namely, softening agents (usually called flux oils, lube stock, slurry oils etc.) able to decrease the viscosity of the aged binder, and real rejuvenators capable to restore the physicochemical properties of bitumen whose virgin microstructure has been altered by volatilization and oxidative processes [13]. To the former type belong the rheological rejuvenators (commonly taken from vegetable oil wastes), which should replenish the volatiles and light chemical fractions that have been lost during aging of asphalts, and rebalance the asphaltene/maltene ratio typical of fresh bitumen. The latter category comprises novel rejuvenators related to the general class of surfactants. Indeed, thanks to its capability to lower the inter-facial energy between two immiscible phases, an amphiphilic molecule can bind on a side the polar phase and on the other side the a polar one, due to the simultaneous presence within its molecular architecture of both polar and non-polar moieties. The overall result of these simultaneous interactions proved to be effective in the stabilization of clusters of polar molecules dispersed in polar solvents [14, 15].

Therefore, amphiphilic molecules are expected to work similarly well in improving the dispersion of asphaltene clusters in the maltene phase, and consequently counteracting the aging process and reverting to rejuvenation eventually [16, 17].

The efficient and targeted use of additives with documented rejuvenating action on RAPs employed in the road paving industry must be based primarily on a rigorous experimental investigation of their effect exerted on the colloidal microstructure of bitumen. However, although these additives play an important role in bitumen recycling methods, their impact on the bitumen supramolecular structure arrangement has not yet been fully investigated in depth. The purpose of the present contribution is to emphasize the potentialities of advanced experimental methods such as scattering techniques and nuclear magnetic relaxometry, which can be considered promising techniques in the elucidation of the dynamics of the complex microstructure in bitumen. In fact, unlike the results acquired through the analysis of the mechanical bulk properties, scattering (in particular X-ray scattering) and NMR experiments can probe from nano- to mesoscale level the effectiveness of a rejuvenator in restoring the microstructure of bitumen subjected to the drastic action of aging processes [18, 19]. This work underlines that the detailed analysis of the microstructural dynamics of bitumen, extending the information taken from commonly used empirical and rapid methods, allows us to better understand the phenomena that occur in such complex materials, providing new tools for the piloted design of ever-performing rejuvenations.

Experimental methods. Information on how rejuvenators can affect the supramolecular structure and distribution of aggregates within the bituminous colloidal network and how this may affect the overall material properties can be achieved from careful analyses of Powder X-Ray Diffraction (PXRD) data and NMR measurements performed at low magnetic fields (^{1}H-NMR Relaxometry), making these techniques very powerful methods to carry out structural investigation in such complex systems [18, 20].

Application of X-ray scattering techniques for the analysis of bitumen. X-ray scattering techniques represent non-destructive analytical methods able to reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy [21]. The PXRD spectrum provides the nano-structural information as well as the crystallite parameter of the molecules that are associated with the asphaltene aggregates [22-24]. For structure investigations on length scales longer than a few nm, Small-Angle X-ray Scattering (SAXS) is best suitable, whereas in the wide angle range (WAXS) the spectrum furnishes precious indications about characteristic distances belonging to various atomic and molecular organizations of different levels of complexity.

Application of Nuclear Magnetic Resonance techniques for the analysis of bitumen. Nuclear Magnetic Resonance (NMR) spectroscopy has been recently found to be an efficient and powerful technique for the characterization of complex materials such as bitumen [25]. One of the advantages of this technique is the ability to simultaneously identify several components of the mixture with the acquisition of a single high resolution^{1}H-NMR spectrum and, consequently, to evaluate the relative amount of the aliphatic and aromatic hydrogens portion in the complex system. In particular, dynamics information can be obtained from ^{1}H spin−spin relaxation time (T_2) measurements according to the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (NMR Relaxometry) [26, 27]. Usually the T_2 varies all over the sample because of the sample heterogeneity or surface relaxation differences; then a multi-exponential attenuation of the NMR spin echo envelope should be observed. The relaxation time probability distribution function can be obtained by applying an inverse Laplace transform (ILT) to the experimental data [28]. The T_2 relaxation time distribution can be considered a structural fingerprint of the bitumen in which the changes in relaxation times reflect the changes that occur in the structure of the colloidal binder. In general, by ILT NMR relaxometry one can monitor the structural evolution of bitumen when additives (polymers, surfactants and so on) are added, since the relaxation distribution is strongly affected by the supramolecular organisation present in the colloids. In particular, the powerful ILT method applied to the experimental NMR echo decay can be exploited to test the effectiveness of the real rejuvenator. Indeed, direct correlation can be made between T_2 and the rigidity of structures in these materials as well as the molecular constrain causing dynamic hindrance [29].

Results and discussion. The bulk mechanical properties of bituminous materials such as, e.g., ductility and rigidity, are empirically determined by the amplitude oscillatory rheometry through the measurement of the complex modulus G^*consisting in its real (elastic modulus G') and imaginary (viscous modulus G'') components [30-33]. However, more sophisticated experimental investigations such as NMR relaxometry and X-ray scattering are being proposed as emerging methods for the comprehension of the microscopic/molecular processes underneath the observed behaviour of a bituminous material subjected to both physical and chemical treatments. Indeed, the application of low-field NMR spectroscopy has been used for the determination of physical properties of petroleum fractions [25, 29] and the Inverse Laplace Transform analysis of the NMR echo signal decay gives the transverse (or spin-spin) relaxation time T_2 that can be connected to different domains characterized by different rigidities [20]. The chemical reasoning for this lies on the molecular constrain causing dynamic hindrance and lowering T_2, an effect that can be considered quite general and already found also in different systems [34-36]. In bitumen, the T_2 relaxation time distribution profile is usually characterized by two distinct peaks.

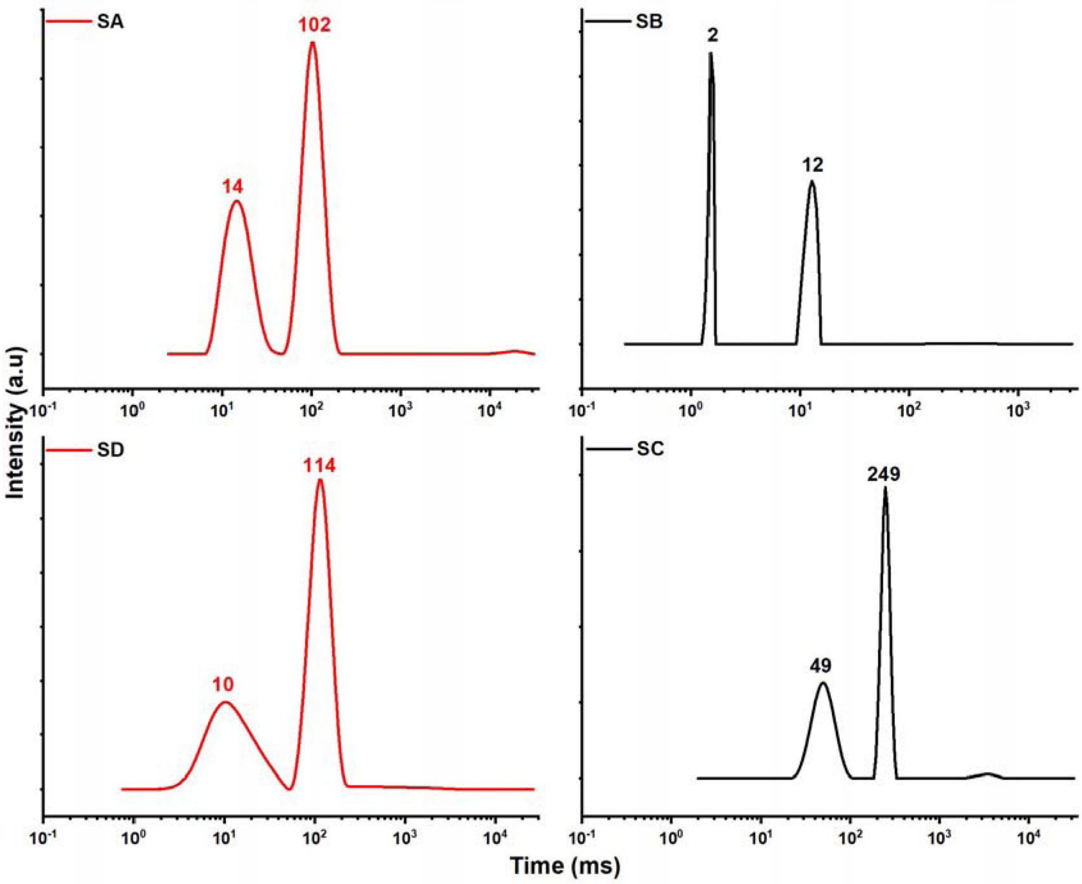

Figure 1 - T_2 relaxation time distribution functions obtained for pristine bitumen (SA) at 50°C, PAV bitumen (SB) at 70°C, PAV bitumen + 2 wt% vegetable flux oil (SC)at 60°C and PAV bitumen + 2 wt% green rejuvenator (SD) at 60 °C

The short T_2 times (around 10 ms) arise from slow tumbling of more rigid supra-molecular aggregates; hence they can be reasonably attributed to the dynamics of asphaltenes. Conversely, long T_2 times (around 100 ms) connected to low intra-molecular interactions can be referred to the maltene fraction of the sample under examination. The T_2 profiles illustrated in figure 1 provide an example of the application of the ILT method in the choice of the right rejuvenator through a quick comparison of the T_2 distributions for different treatments subjected to the same bituminous matrix. Indeed, one can easily verify that the addition of a green rejuvenator to the oxidized bitumen (PAV bitumen), has the effect of restoring the original probability density function compatible with fresh pristine bitumen (compare SA with SD). On the other hands, the pattern is only partially recovered when a flux oil (a softening agent) is used (compare SA with SC).

Structural features of the asphaltene clusters self-aggregated in the maltene phase can be also investigated by the X-ray scattering technique in order to gain new results on the role played by some additives in the rejuvenation action of bitumen whose colloidal structure has been seriously compromised by the aging processes. Indeed, the eventual presence of an additive triggers the formation of further intermolecular interaction in competition with those responsible for this self-assembly, causing a change of the size and shape of these aggregates. A representative X-Ray scattering spectrum of bitumen together with the Lorentzian deconvolution reported in figure 2 as a function of scattering vector $q = 4\pi \sin \theta / \lambda$, illustrates several important features.

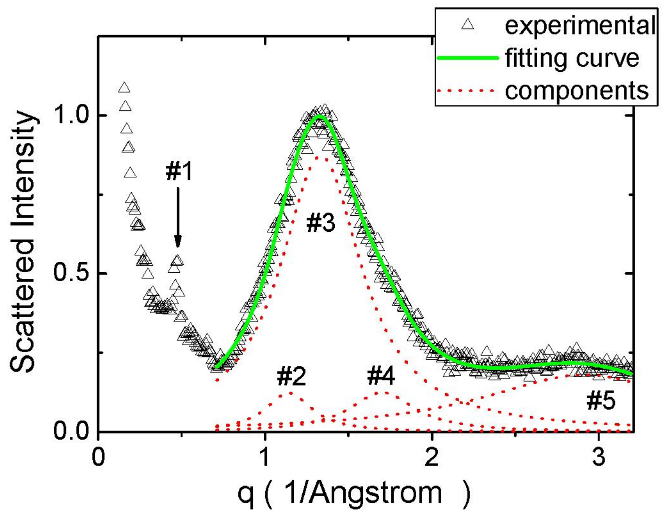

Figure 2 – Typical Wide AngleX-Ray diffraction pattern of asphalt binder with peak profile analysis

The most prominent band centred at around 1.3 $Å^{-1}$gives a characteristic of 4.4-4.7 Å, which can be attributed to the typical intermolecular lateral distance commonly present in disordered fluids. This length parameter results to be slightly higher than that identified from the band of graphene (lateral distance of about 3.6 Å) and coming from the stacks in the aromatic compounds. However, owing to the coexistence of aliphatic components in the bitumen it is reasonable to treat this band as an unresolved superposition of these two contributions. Therefore, deconvolution procedures in terms of bell-shaped curves are necessary to discriminate all the signals. Besides, an eventual low-intensity reflection in the range 0.3-0.8 $Å^{-1}$ can be attributed to the occurrence of a supra-molecular aggregation and would be therefore associated to a repetition distance between one asphaltene local aggregate and its neighbouring one, in accordance with a model of a complex system with different levels of complexity. Finally, for $q<0.3$ $Å^{-1}$ the fractal aggregation generated by an ensemble of asphaltene clusters can be examined. In principle, the formation of self-similar, fractal structures in bituminous materials cannot be excluded. In such case, the interfacial boundary is not sharp and a scaling law between the mass M (or particle number N) and the enclosed volume is established, which can provide an indication of how efficiently the particles are packed. The presence of additives may modify not only the fractal structure but also the intermolecular assembly as probed by the band centred at 1.3 $Å^{-1}$ and the peak around 0.5 $Å^{-1}$.

Conclusion. The restoring of the aged bitumen structure to the original conditions is a challenging task due to its complex organization at the supra-molecular scale. It has been emphasized that scattering techniques and nuclear magnetic relaxometry represent promising methods of investigation that deserve attention for a deeper analysis of bituminous materials. In fact, they can probe the effectiveness of a rejuvenator in restoring the bitumen microstructure after the aging process, while the mechanical properties alone do not allow reaching this degree of microstructural knowledge. In conclusion, we want to bring to the attention the fact that the detailed analysis of the physics of molecular bitumens allows us to better understand the phenomena that occur in bitumen, providing new tools for the piloted design of new rejuvenators with ad-hoc performances.

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ЖАСАРТЫЛҒАН ЕСКІРГЕН БИТУМДАРДЫҢ МОЛЕКУЛАЛЫҚ ҚҰРЫЛЫМЫН ТАЛДАУҒА АРНАЛҒАН ЖАҢА ТӘЖІРИБЕЛІК ТӘСІЛДЕР

Аннотация. Битумның ескіруі материал құрылымындағы өзгерістермен байланысты болатын булану, тотығу және молекулалық қосылыстардағы өзгерістердің нәтижесінде орын алады. Битумның ескіру үдерісіне және оның тұтқырлығының артуына байланысты асфальтбетон жамылғысының қаттылығы пайдалану кезінде арта түседі. Химиялық тұрғыдан түсіндіргенде, битумдағы асфальтендер пен мальтендердің салыстырмалы үлесі мальтендердің төмен құрамына қарай жылжиды. Сондықтан, қайта қалпына келтірілген асфальт жамылғысын (ҚАЖ) асфальт қоспаларына көп мөлшерде қосу асфальтбетон жамылғысының сипаттамасына теріс әсер етуі мүмкін. Жасартқыш реагенттер ескірген битумның тұтқырлығын азайту және оның бастапқы қасиеттерін қалпына келтурі арқылы осы үдерісті жақсартуы мүмкін. Тиімді жасартқыш реагент тотыққан битумның коллоидті құрылымының ұйымдасуына қолайлы жағдай туғызып, жаңадан дайындалған битумның молекулалы құрылымын қалпына келтіреді. Одан басқа, жаңа тәжірибелік тәсілдер жасартқыш реагенттердің тиімділігі мен мұндай қоспалардың ескірген битумның қасиеттеріне ықпалын бағалау үшін қажет. Жоғарыда аталған мақсаттарға қол жеткізу үшін, осы мақалада битумның микроқұрылымы туралы толық ақпарат беретін неғұрлым перспективалық тәсілдер қарастырылады. Сейілу және ЯМР әдістерінің негізі болған басты тұжырымдамалар қарастырылады, сондай-ақ ҚАЖ жасартудың тиімділігін бағалауда осы әдістерді синтетикалық пайдалану нәтижелері көрсетілді.

Түйін сөздер: жасартқыш реагенттер, битум, ескіру, сейілу, рентген дифракциясы (ҰРД), ядролық-магниттік резонанс (ЯМР), релаксометрия.

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НОВЫЕ ЭКСПЕРИМЕНТАЛЬНЫЕ ПОДХОДЫ К АНАЛИЗУ НАДМОЛЕКУЛЯРНОЙ СТРУКТУРЫ ОМОЛОЖЕННЫХ СОСТАРЕННЫХ БИТУМОВ

Аннотация. Старение битума происходит из-за выпаривания, окисления и изменений в надмолекулярных соединениях, связанных со значительными изменениями в структуре материала. В связи с процессом старения битума и соответствующего увеличения его вязкости, жесткость асфальтобетонного покрытия увеличивается во время эксплуатации. В химическом смысле относительное содержание между асфальтенами и мальтенами в битуме сдвигается в сторону более низкого содержания мальтенов. Поэтому добавление большого количества регенерированного асфальтового покрытия (РАП) в асфальтовые смеси может отрицательно повлиять на качество и характеристики окончательного состава смеси. Омолаживающие реагенты могут поспособствовать улучшению данного процесса путем уменьшения вязкости состаренного битума и восстановления его первоначальных свойств. Эффективный омолаживающий реагент благоприятствует организации коллоидной структуры окисленного битума, тем самым восстанавливая надмолекулярную структуру свежеприготовленного битума. Затем, новые экспериментальные подходы необходимы для оценки эффективности омолаживающих реагентов, а также какое влияние оказывают такие добавки на свойства состаренного битума. Чтобы достичь вышеуказанной цели, в данной статье рассматриваются два наиболее перспективных подхода, способные предоставить подробную информацию о микроструктуре битума. Будут рассмотрены основополагающие концепции, лежащие в основе методик рассеивания и ЯМР, а также будут проиллюстрированы результаты некоторых недавних синтетических применений этих методов в оценке эффективности омолаживания РАП.

Ключевые слова: омолаживающие реагенты, битум, старение, рассеивание, рентгеновская дифракция (ПРД), ядерно-магнитный резонанс (ЯМР), релаксометрия.

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