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Short Communication

Molecular Weight Distribution: Bitumen Binders *vs.* Polymers and δ-Method *vs.* Gel Permeation Chromatography (GPC)

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ABOUT THE STUDY

Polymers consist of macromolecules formed by chemical bonding of a variable number of repeating units. Since the repeating units are equal one to each other, the length of the chains is the main parameter determining the cohesive energy and thus the physical properties of the polymer. For this reason, the Molecular Weight Distribution (MWD) dramatically affects thermal, mechanical, rheological, and technological properties of these materials [1-9]. Moreover, the variation of MWD during the processing and the in-service life is also useful in evaluating ageing effects and degradation processes [10]. The most common method to obtain MWD is Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography (SEC)[11]. This technique involves the dissolution of the polymer in a suitable solvent and the elution of the solution through a packed column, consisting of particles of a cross-linked polymer having a defined porosity distribution. The different free paths of the macromolecules throughout the bed determine their separation along the column. The separation mechanism is due to the hydrodynamic size of the macromolecules rather than any chemical interaction between the macromolecules and the stationary phase or between the macromolecules themselves. An alternative to GPC is the "inverse mechanical" approach that derives the MWD from master curves of linear viscoelastic functions [12,13]. This method is an indirect procedure from bulk measurements and the MWD is usually defined "apparent" because in bulk the interactions between the molecules are unperturbed and may result in agglomerates that would not survive in solution.

Both GPC and rheological approach have been also used to determine the MWD of bituminous binders [14,15]. However, it is important to underline the differences between these two materials, especially for the case of chromatography. If in polymers the molecules differ only in molecular weight, in bituminous binders they also have different chemical composition and functional groups so that the whole composition is commonly divided into four categories of compounds having increasing polarity: Saturates, Aromatics, Resins and Asphaltenes (SARA fractions) [16]. Since in a diluted state, molecules with different polarity have different degree of interaction with the stationary phase, the GPC method for bitumen is both size and polarity exclusion. Furthermore, depending on their aromatic or paraffinic nature, molecules in bitumen may have a different correlation between molecular weight and hydrodynamic volume and may have a different visibility for the detector [17]. Nevertheless, GPC remains a very useful tool. As an example, the UV signal, measured as a function of the retention time, is characterized by two main peaks that can be related to light and heavy fractions in the bituminous binder (Figure 1) [18].

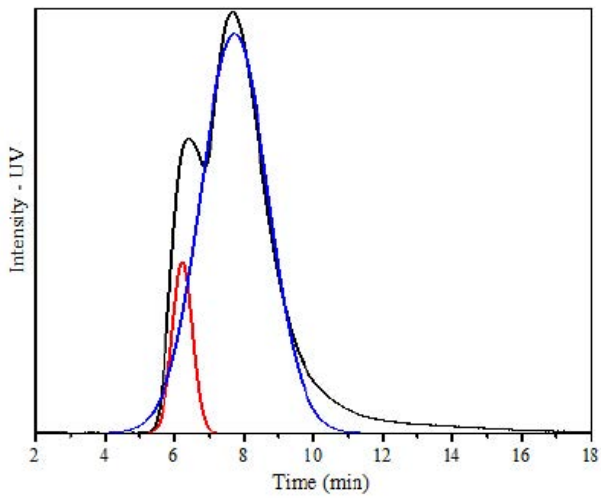

Figure 1: UV Intensity *vs.* retention time of a bituminous binder: Example of deconvolution of the whole curve in two curves related to light and heavy fractions respectively.

Note: — Whole curve; — Light fractions; — Heavy fractions.

During ageing, oxidative phenomena determine a gradual increase of the asphaltenes to maltenes ratio. The corresponding decrease in the light fraction and increase in the heavy fraction can be seen in Figure 2 in case of a bituminous binder artificially aged using a Pressure Ageing Vessel (PAV) system for 25,40,65 and 90 hours [19].

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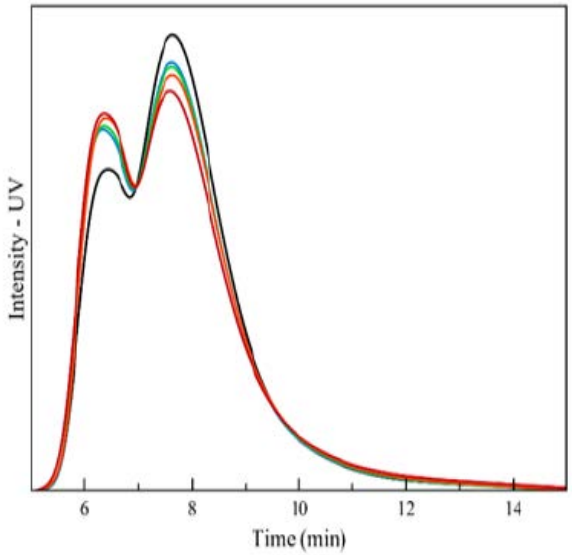

Figure 2: UV Intensity *vs.* retention time of a bituminous binder unaged and artificially aged by PAV for 25, 40, 65 and 90 hours respectively.

Note: —B_U; —B_25; —B_40; — B_65; — B_90.

In addition to the above-mentioned problems, it should be also considered that for bitumen the use of a dilute state is sometime not really useful. In the bulk state, a bituminous binder has a sol-gel colloidal structure, characterized by asphaltenes micelles, of high molecular weight, dispersed in an oily medium, of lower molecular weight, consisting of the maltenic molecules (saturates, aromatics, and resins components), with resins acting as surfactants [20]. This complex structure determines the mechanical properties and performances of the material and may be strongly affected even by small variation in the bitumen composition. However, since the structure is not preserved in the dilute state, GPC may be scarcely sensitive to such effect.

For this reason, the bitumen MWD measured by GPC is not easily correlated to its operating properties and from this point of view the inverse approach may be preferable. In particular, a recently developed procedure is the so-called -method that calculates the MWD from the master curve of the phase angle [21-23]. The procedure is graphically explained in Figure 3 and its basic idea is a direct correlation between molecular weight and relaxation time of a molecule. Being a mechanical solicitation above or below its peculiar relaxation time, determines if the molecule behaves as a liquid or not. The liquid character of the whole material is assumed to be proportional to the fraction of "liquid" molecules in it and the phase angle master curve can be converted into a Cumulative Molecular Weight Distribution (CMWD).

The δ-method is undoubtedly a more useful technique to evaluate variations in the colloidal structure of bituminous materials. The Apparent Molecular Weight Distributions (AMWD) for the same samples of Figure 2 is reported in Figure 3. It is evident that ageing has a stronger influence in the shape of AMWDs than it has on the shape of MWD by GPC. Therefore, AMWD can be used to relate ageing to variations in the colloidal bitumen microstructure [23].

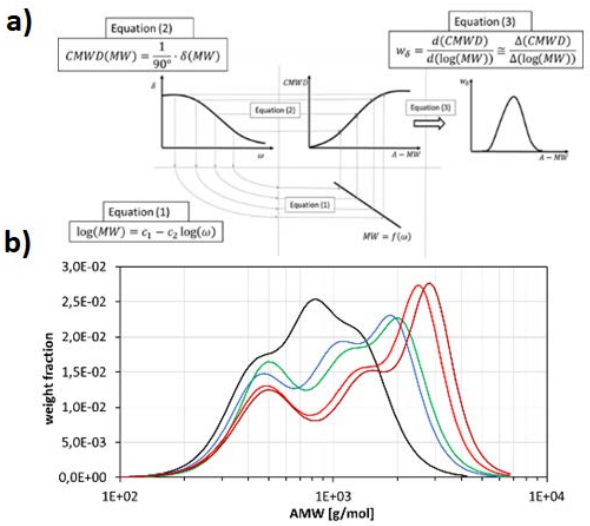

Figure 3: a) Schematic representation of the δ-method approach; b) AMWD of a bituminous binder unaged and artificially aged by PAV for 25, 40, 65 and 90 hours.

Note: — B_U; — B_25; —B_40; —B_65; — B_90.

As a further example, the addition of waste vegetable oils to oxidized bitumen has a rejuvenating effect, aimed at restoring the colloidal structure of the virgin bitumen [24]. Of course, the GPC of rejuvenated bitumen obtained shows the presence of the rejuvenating agent as a small shoulder, but cannot detect modifications of the bitumen structure (Figure 4). On the contrary, δ-method cannot detect the presence of the rejuvenator, but demonstrates how the addition of the waste oil allows restoring the AMWD of the virgin bitumen (Figure 4) [25].

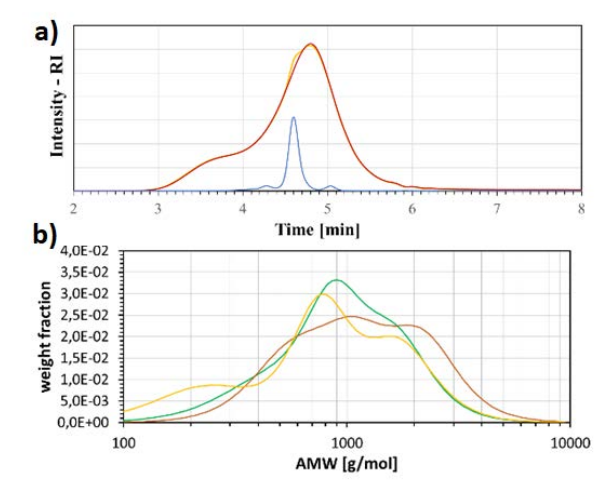

Figure 4: a) RI Intensity *vs.* retention time of an artificially aged (25 h PAV) bituminous binder (B-PAV) and the rejuvenated sample after the addition of 4 wt% of waste vegetable oil (B-4VO-U) compared with the trace of waste Vegetable Oil (VO); b) AMWD of a bituminous binder unaged (B-U), artificially aged by 25 h of PAV (B-PAV) and subsequently rejuvenated adding 4 wt% of waste vegetable oil (B-4VO-U).

Note: a) — B-4VO-U; — B-PAV; — VO; b) — B-U; — B-PAV; — B-4VO-U.

CONCLUSION

In summary, both polymers and bituminous binders are viscoelastic materials whose MWD can be useful to understand or predict their bulk properties. The distributions can be derived from GPC or from rheological measurements being the information from these two techniques somehow complementary. With respect to polymers, the different chemistry of the bitumen molecules implicates an additional cause of uncertainties and artifact in the dilute state. Nevertheless, GPC remains a very useful technique, but should be limited to compare materials deriving from the same base bitumen. This aspect is peculiar of bitumen and is a direct consequence of the variability in bitumen composition depending from the oil source. A similar suggestion, for example, was done by Marsac et al. for oxidative parameters derived from infra-red analysis [25]. At the same time, with respect to polymers, the complex colloidal equilibrium makes the bulk methods very sensitive to any change in the internal structure of bitumen binders. In conclusion, the GPC should be preferred to detect changes in composition due to ageing and or addition of modifiers, while the bulk approach is more useful for changes in the colloidal structure.

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