NON-PETROLEUM-BASED BINDERS FOR PAVING APPLICATIONS: RHEOLOGICAL AND CHEMICAL INVESTIGATION ON AGEING EFFECTS

NON-PETROLEUM-BASED BINDERS FOR PAVING APPLICATIONS: RHEOLOGICAL AND CHEMICAL INVESTIGATION ON AGEING EFFECTS

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Abstract The massive exploitation of non-renewable natural resources which has taken place in the last decade has led to significant global environmental concerns. In such a context, the use of non-petroleum-based binders for the construction of bound layers of flexible pavements can represent an effective solution to limit crude oil depletion. The research work presented in this paper focused on the effects of ageing on the rheological and chemical characteristics of a non-bituminous binder, indicated in the study as a "biobinder", and a traditional neat bitumen selected as a reference material. Binders were analyzed in four ageing conditions obtained by making use of the Rolling Thin Film Oven and of the Pressure Ageing Vessel. Rheological behaviour of binders was investigated by means of oscillatory tests carried out in a wide range of temperatures and frequencies with a dynamic shear rheometer. Chemical structure was explored via Thin Layer Chromatographic analyses and Fourier Transform Infrared Spectroscopy. The experimental work demonstrated that mechanisms of ageing which are involved in biobinders completely differ from those experienced by petroleum-based binders. Concerns were expressed with respect to the applicability to non-conventional binders of currently available ageing techniques and of chemical characterization methods.

Keywords: biobinders; ageing; rheology; chemical characterization

1. Introduction

For more than a century the use of bitumen as the binding agent of mixtures employed for the construction of flexible pavements has been considered as the only available option. However, in the last two decades several researchers have worked on the formulation of non-petroleum-based binders, also known as biobinders, conceived as potential alternatives to bitumen (Su et al., 2018). These efforts have been spurred by the sustainability-driven need of reducing the exploitation of non-renewable natural resources and by the desire of identifying possible reaction strategies to the increase of crude oil and bitumen costs.

Although the most attractive application of biobinders is full replacement of bitumen, several studies have addressed alternative strategies of use. In particular, they have focused on the development of products which depending upon the case can be employed as bitumen modifiers (to improve low-temperature performance and workability), extenders (to reduce the demand of bitumen) and rejuvenators (in combination with reclaimed asphalt) (Raouf et al., 2010 ; Fini et al., 2016 ; Dashmana et al, 2015; Barco Carrión et al., 2017).

As highlighted by Chailleux et al. (2015), most of the biobinders developed in the course of time for full bitumen replacement are constituted by a combination of a high molecular weight component (usually derived from wood) and a viscous oil. Synthetic polymers and other function-specific materials (such as waxes and fibres) may also be added to the blend. Fabrication conditions and methods vary significantly among the range of products. However, after blending the components at temperatures above their melting point, polymerization reactions usually take place when maintaining the products at high temperatures. In most cases these binders are transparent and can be consequently used in applications in which the natural colour of aggregates is maintained or a specific colour is obtained by means of appropriate pigments.

Despite the remarkable efforts placed in the laboratory characterization of these innovative binders, field experiences have been rather limited, with the placement of few trial sections (Chailleux et al., 2015; Gosselink, 2015). Furthermore, the outcomes of these full-scale trials have been partially disappointing due to the occurrence of failures in a very short time span. It has been reported that mixtures prepared with biobinders tend to excessively stiffen in time, leading to a brittle response under loading. In such a context, it has been postulated that the ageing behaviour of these binders may be quite different from that of bitumen.

As a result of the abovementioned uncertainties, the experimental work described in this paper focused on the assessment of the ageing behaviour of a commercial biobinder which was subjected to several ageing treatments and subsequently characterized from a rheological and chemical point of view. For comparative purposes, a reference standard bitumen was subjected to the same ageing procedures and tests.

2. Materials and methods

Materials considered in the investigation included a biobinder and a traditional neat bitumen, selected as a reference material. As indicated by its manufacturer, the biobinder is made of pitch (obtained as a by-product of the papermaking industry), rosin and SBS. The employed reference bitumen was a conventional 50/70 penetration grade binder. The two binders were analyzed and compared in four ageing conditions: original state, short-term ageing obtained by means of the Rolling Thin Film Oven (RTFO) test (as per AASHTO T 240), long-term ageing obtained by subjecting the RTFO residue to a Pressure Ageing Vessel (PAV) treatment (at 100 °C for 20 h with an imposed pressure of 2.1 MPa, as per AASHTO R 28), and an extra-long term ageing which involved two PAV cycles after RTFO ageing. As a function of their ageing state, samples of both binders were associated to codes U (unaged), R (RTFO-aged), P (PAV-aged) and PP (aged with double PAV treatment).
Rheological properties of the binders were analyzed by means of a dynamic shear rheometer operated by making use of two different parallel plates measuring systems (8 mm parallel plates with 2 mm gap at test temperatures lower than 34 °C; 25 mm parallel plates with 1 mm gap at test temperatures greater than or equal to 40 °C). Linear viscoelastic properties were investigated by means of strain-controlled frequency sweep tests carried out by using angular frequencies ranging from 1 to 100 rad/s and temperatures comprised between 4 °C and 76 °C with 6 °C increments. In order to evaluate the rheological behaviour within the linear visco-elastic domain, shear strains applied to test specimens were varied depending upon temperature and frequency according to preliminary amplitude sweep tests.
Chemical characterization of the binders was performed by making use of techniques which are typical for standard bitumen. These included Thin Layer Chromatography (TLC) and Fourier Transform Infrared Spectroscopy (FTIR).
TLC tests consist in the separation of binder fractions in specific solvents of increasing polarity. This is done by injecting a binder-dichloromethane solution on silica rods which are then oven-dried and subjected to successive elutions in n-hexane, toluene and a solution of dichloromethane and methanol in a volume ratio of 95:5 (Santagata et al., 2009; Holleran and Holleran, 2010). When performed on bitumen, such a test leads to the estimate of the percentages of saturates, aromatics, resins and asphaltenes (of increasing molecular mass, aromatic content and polarity). Since the composition of biobinders is definitely different from that of standard bitumen, in this study the four fractions identified for the considered biobinder were indicated as “p-saturates”, “p-aromatics”, “p-resins” and “p-asphaltenes” (where “p” stands for “pseudo”).
FTIR tests allow the identification of different groups of molecular bonds which are associated to well-defined wavelengths within recorded absorbance spectra. Binder samples are directly spread on the surface of a diamond crystal with high refraction index and FTIR spectra are consequently recorded by using the attenuated total reflectance technology. For both considered binders the FTIR peaks were identified and associated to corresponding bonds by referring to the work performed on bitumen by Petersen (1986) and by Masson et al. (2001).

3. Results and discussion

3.1. Rheological tests

As displayed in Fig. 1, values of the norm of the complex modulus ($|G^*|$) and of the phase angle (δ) retrieved from oscillatory tests were plotted, for both binders and for all ageing states, in the so-called Black space. Such a representation allows a global assessment of the rheological response of a given binder and is also functional for the verification of the applicability of the time-temperature superposition principle.

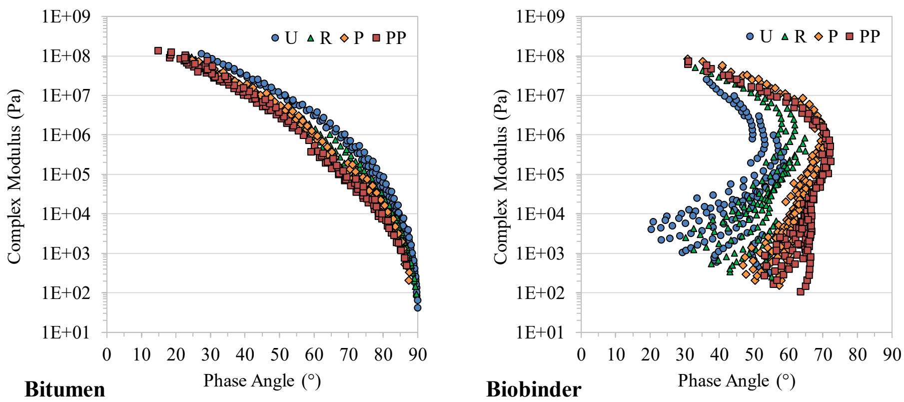


Fig. 1 Black curves of reference bitumen and biobinder

When focusing on the results obtained from tests carried out on materials in their original (unaged) state, a different response was observed for the two binders. The standard bitumen exhibited a single, smooth curve characterized by a gradual transition from the glassy to the viscous state, thus indicating that its behaviour can be modelled according to the time-temperature superposition principle. On the contrary, the biobinder did not show the same type of rheological simplicity, with the presence of several independent curves that did not follow a common trend. In this case it was thus found that the time-temperature superposition principle cannot be applied. Such an outcome can be explained by referring to the composition of the innovative binder, in which the various components may exhibit structural changes due to their different melting points and to the possible formation (and subsequent dismantlement) of semicrystalline domains. These phenomena can significantly affect the relaxation function of the composite material, thus leading to a different sensitivity to temperature and frequency changes.

When considering the effect of ageing, in the case of the reference bitumen it was found that the Black curves were gradually shifted to higher $|G^*|$ and lower δ values. Moreover, it was observed that for the same domain of frequencies and temperatures, the total length of the curves was almost constant, thus indicating that temperature sensitivity was not significantly affected by ageing.

In the case of the biobinder, the effects of ageing on its rheology were totally opposite than those recorded for the reference bitumen. In particular, ageing caused a progressive shift of the Black curves to lower $|G^*|$ and higher δ values. Furthermore, the curves became more consistent and uniform with ageing. These outcomes suggest that the RTFO and PAV treatments caused a progressive loss of internal structure which tended towards a long-term condition closer to rheological simplicity.
For both materials and in all ageing conditions, it can be noticed that at low temperatures the Black curves tend to a zero value of δ and to a constant value of $|G^*|$, of the order of 1 GPa, typical of amorphous materials in their glassy state (Lesueur, 2009). When focusing on the high temperature response, due to the fact that the analysis of Black curves does not easily allow straight comparisons, it was considered beneficial to evaluate the norm of the complex viscosity. In particular, such a parameter was assessed at 76 °C in the investigated range of angular frequency. Corresponding results are displayed in Fig. 2.

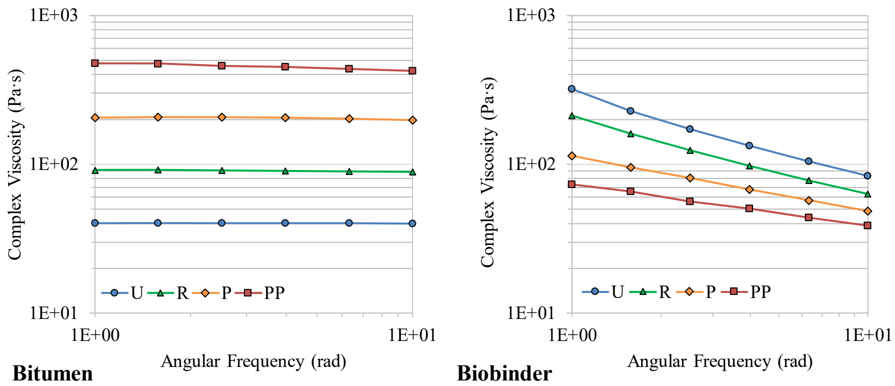


Fig. 2 Complex viscosity at 76 °C of reference bitumen and biobinder

From the plot shown in Fig. 2 it can be observed that the reference bitumen displayed, as expected, an increase of its complex viscosity as a function of progressive ageing. Experimental data highlighted a slight shear-thinning behavior, more evident in long-term aged conditions. When considering the results obtained at low frequency it can be noticed that the complex viscosity tends towards a constant value which can be considered as the zero-shear viscosity.
Due to its unconventional nature, the biobinder exhibited a completely different response. In fact, its viscosity progressively decreased with ageing and in all ageing states the material showed a strong shear-thinning character. Thus, it was clearly observed that the biobinder in the considered conditions behaves like a viscoelastic material and not as a viscous fluid.
In order to quantitatively evaluate ageing effects, the following two indices were calculated after each stage of ageing at several temperatures:

$$AI_{|G^*|} = \frac{|G^*|_i}{|G^*|_O} \qquad AI_{\delta} = \frac{\delta_i}{\delta_O}$$

where $|G^*|_O$ and δ_O are the complex modulus and the phase angle at 10 rad/s in the unaged condition, while $|G^*|_i$ and δ_i are the complex modulus and the phase angle at 10 rad/s measured in different ageing states. Obtained results are listed in Table 1.
From the analysis of the data provided in Table 1 it can be observed that the trends displayed by the values of the ageing indices of the reference bitumen are in line with what has been widely reported in literature. When considering progressively more severe ageing conditions, $AI_{|G^*|}$ increases and AI_δ decreases. The first parameter displays greater ageing-related variations at higher temperatures, where the response is more distant from the glassy state, whereas the second one shows the greatest changes at lower temperatures, which are distant from the viscous asymptote. The trends observed for the ageing indices of the biobinder are totally different. $AI_{|G^*|}$ decreases with increasing temperatures (with the exception of one data point) and displays a dependency upon ageing which is different at low and high temperatures. At low temperatures (4 °C and 28 °C) $AI_{|G^*|}$ is always greater than 1 and increases with ageing; at high temperatures (52 °C and 76 °C) $AI_{|G^*|}$ is smaller than 1 and decreases with ageing (with the exception of one data point). AI_δ is always greater than 1 and does not show a clear trend as a function of ageing and temperature. However, in general terms it seems that AI_δ increases with temperature and ageing (with some exceptions). These outcomes are consistent with the inherent structural complexity of the binder, in which the various components may be affected in different ways by temperature variations and ageing phenomena.

Table 1 Ageing indices of reference bitumen and biobinder

T (°C)	Reference bitumen						Biobinder					
	$AI_{\|G^*\|}$			AI_δ			$AI_{\|G^*\|}$			AI_δ		
	R	P	PP	R	P	PP	R	P	PP	R	P	PP
4	1.1	1.5	1.7	0.82	0.71	0.60	2.0	3.3	3.3	1.07	1.13	0.99
28	2.4	4.7	7.6	0.81	0.76	0.66	1.0	1.3	1.3	1.08	1.22	1.30
52	2.5	6.0	14.3	0.94	0.86	0.80	0.9	0.4	0.5	1.28	1.57	1.69
76	2.2	4.9	10.6	0.98	0.96	0.92	0.8	0.6	0.5	1.08	1.20	1.33

3.2. Chemical analyses

Results obtained from TLC tests carried out on the two binders are listed in Table 2, where they are expressed in terms of the percentages of the classical bitumen fractions (saturates, aromatics, resins and asphaltenes) and of the corresponding "pseudo-fractions" obtained in the case of the biobinder.
It can be noticed that the standard reference bitumen displayed an evolution of its composition which was in line with data published in literature (Wang et al. 2019; Siddiqui and Ali, 1999). While the percentage of saturates did not change significantly, with the progress of ageing both the asphaltenes and resins showed a remarkable increase. It was also noticed that no relevant additional ageing effects were caused by subjecting the binder to a supplementary PAV treatment.

Table 2 Percentages of fractions and pseudo-fractions of reference bitumen and biobinder

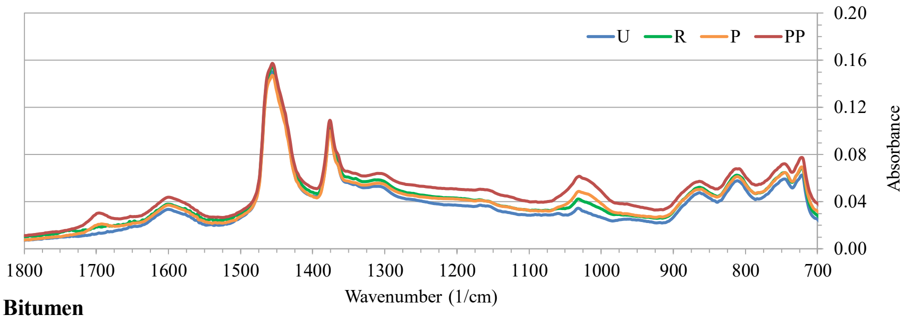
Ageing state	Reference bitumen				Biobinder			
	S (%)	Ar (%)	R (%)	As (%)	p-S (%)	p-Ar (%)	p-R (%)	p-As (%)
U	5.3	42.9	25.2	26.6	0.0	9.7	79.0	11.3
R	5.0	36.9	24.8	33.3	0.0	8.1	68.9	22.9
P	5.6	25.0	35.4	34.0	0.0	7.7	86.4	5.9
PP	5.8	25.8	38.1	30.4	0.0	10.6	82.6	6.8

S: saturates; Ar: aromatics; R: resins; As: asphaltenes
p-S: pseudo-saturates; p-Ar: pseudo-aromatics; p-R: pseudo-resins; p-As: pseudo-asphaltenes

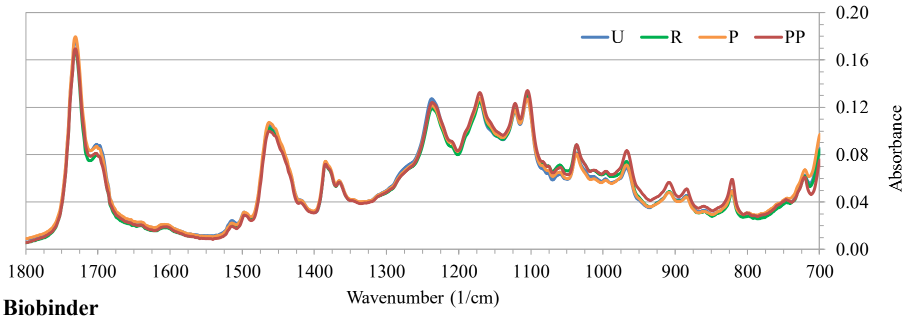
As expected, results obtained for the biobinder were completely different. In particular, it was observed that in all ageing states there was no detectable elution with the first solvent (n-hexane), thus indicating the absence of low polarity molecules in the binder. In practical terms this led to a zero value of the percentage of the pseudo-saturates. It should also be underlined that in all ageing states most of the molecules composing the biobinder were found to belong to the fraction of pseudo-resins. The main chemical changes induced by ageing were found after PAV ageing (either single or double, with no significant differences), which led to an increase of the percentage of the intermediate polarity group (i.e. of the pseudo-resins) that reached 82.6-86.4%. This seems to suggest that the prolonged exposure to high temperatures in the presence of pressure caused a reduction of the degree of internal diversity of the material. Such an outcome is consistent with the rheological results presented in section 3.2 in the form of Black curves, which were found to be progressively more uniform. Finally, it can be noticed that TLC tests carried out on the biobinder after RTFO yielded results which were not consistent with all the others. This may be due to the specific ageing protocol or may have originated by the limitations of the employed characterization technique.

Results obtained from FTIR tests are displayed in the form of absorbance spectra in Fig. 3. From a qualitative point of view, it can be easily recognized that the spectra recorded for the two binders were significantly different and were also sensitive to ageing.

In order to analyze the spectra in quantitative terms, reference was made to previous work performed on bitumen, in which it was shown that the oxidation of hydrocarbons is associated, notably, with the increase of carbonyl groups C=O (corresponding to absorbance signals with wavelengths in the vicinity of 1700 cm^{-1}) and of sulphoxides S=O (corresponding to wavelengths around 1030 cm^{-1}) (Mouillet et al., 2008; Siddiqui and Ali, 1999). More specifically, it was found that changes of the sulphoxides are typical of short-term ageing occurring during plant manufacturing of mixtures, whereas changes in carbonyl groups are relevant for long-term ageing which takes place during the service life of a pavement.



Bitumen



Biobinder

Fig. 3 Absorbance spectra of reference bitumen and biobinder

Processing of the spectra required the calculation of the sulphoxide index (I_S) and of the carbonyl index (I_C), which were obtained by normalizing the areas underlying the spectra in the relevant wavelength bands to the sum of the areas associated to all peaks. Values of I_S and I_C calculated for the two binders in all ageing states are listed in Table 3. As expected, both indices were found to increase with ageing in the case of the reference bitumen. However, tests carried out on the biobinder led to completely different results. It was observed that in comparison to the reference bitumen the biobinder is characterized by a greater percentage of sulphoxides and carbonyl groups: however, the indices do not change significantly with ageing, showing only a slight decrease. This outcome confirms the conclusion, already drawn from TLC tests, that the mechanisms of ageing which are involved in biobinders may significantly differ from those of standard bitumen.

Table 3 Indices derived from FTIR spectra for reference bitumen and biobinder

Ageing state	Reference bitumen		Biobinder	
	I_S (%)	I_C (%)	I_S (%)	I_C (%)
U	2.28	1.39	4.49	13.72
R	2.25	1.85	4.47	12.61
P	2.60	1.76	4.27	13.66
PP	3.31	2.55	3.83	12.84

4. Conclusions

The experimental investigation described in this paper focused on the comparative evaluation of the ageing effects induced in a commercial biobinder and in a reference standard bitumen. It was found that in comparison to the reference bitumen, which exhibited ageing effects in line with data available in literature, the biobinder showed a counterintuitive behavior. From a rheological viewpoint, as a function of progressive ageing, the biobinder displayed a reduction of stiffness and degree of elasticity. Due to the non-conventional nature of the biobinder, changes in its chemical composition caused by ageing, which were assessed by means of Thin Layer Chromatography (TLC) and Fourier Transform Infrared Spectroscopy (FTIR), were quite difficult to identify. However, in general terms it was found that ageing led to a reduction of the degree of diversity of the binder molecules and that there were no significant variations of sulphoxides and carbonyl groups.

It should be mentioned that the investigation described in this paper focused on a single commercial biobinder and that in literature results reported by other Authors on other products are in some cases completely different from those found in this study. Thus, obtained results cannot be considered of general value.

The Authors believe that the performed investigation highlighted two fundamental issues which should be the subject of further research. First of all, there are serious doubts whether the currently available ageing techniques, originally developed for bituminous binders, can be employed for non-petroleum-based products. In such a context, field validation activities are absolutely necessary. Secondly, there are also concerns with respect to the chemical characterization methods to be employed for the monitoring of ageing effects. In particular, it is questionable whether TLC and FTIR, which are extremely valuable for the analysis of standard bituminous binders, can yield relevant results in the case of non-conventional biobinders.

One of the missions of modern research in the area of pavement engineering is to devise new construction strategies in the context of sustainability. Thus, the Authors believe that investigations in the area of biobinders need to be intensified with the final goal of identifying a true alternative to bitumen. The results obtained in the investigation described in this paper are promising, but they need to be supported and expanded by means of further research.

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