Materiales de Construcción
Vol. 67, Issue 327, July–September 2017, e130
ISSN-L: 0465-2746
http://dx.doi.org/10.3989/mc.2017.04516

Evaluation of bio-materials' rejuvenating effect on binders for high-reclaimed asphalt content mixtures

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Received 15 April 2016
Accepted 23 November 2016
Available on line 10 July 2017

ABSTRACT: The interest in using bio-materials in pavement engineering has grown significantly over the last decades due to environmental concerns about the use of non-recoverable natural resources. In this paper, bio-materials are used together with Reclaimed Asphalt (RA) to restore some of the properties of the aged bitumen present in mixtures with high RA content. For this purpose, two bio-materials are studied and compared to conventional and polymer modified bitumens. Blends of these materials with RA bitumen were produced and studied to simulate a 50% RA mixture. The rejuvenating effect of the two bio-materials on RA has been assessed and compared with the effect of the conventional binders. Apparent Molecular Weight Distribution of the samples (obtained by the δ-method) and different rheological parameters were used for this purpose. Results revealed the power of bio-materials to rejuvenate RA bitumen, showing their capability to be used as fresh binders in high-RA content mixtures.

KEYWORDS: Bio-material; Reclaimed asphalt; High content; Rejuvenation; Rheology

Citation/Citar como: Jiménez del Barco-Carrión, A.; Pérez-Martínez, M.; Themeli, A.; Lo Presti, D.; Marsac, P.; Pouget, S.; Hammoum, F.; Chailleux, E.; Airey, G.D. (2017) Evaluation of bio-materials' rejuvenating effect on binders for high-reclaimed asphalt content mixtures. *Mater. Construcc*. 67 [327], e130. http://dx.doi.org/10.3989/mc.2017.04516

RESUMEN: *Evaluación del efecto rejuvenecedor de bio-materiales sobre ligantes para mezclas con alto contenido de asfalto recuperado***.** El interés en la utilización de bio-materiales en ingeniería de pavimentos ha crecido significantemente en las últimas décadas debido a la conciencia ambiental sobre el uso de recursos naturales no renovables. En este artículo, se utilizan bio-materiales para recuperar las propiedades iniciales del betún envejecido presente en mezclas con alto contenido de asfalto reciclado (RA). Para ello, se ha estudiado y comparado el comportamiento de dos bio-materiales con betunes convencionales y betunes modificados con polímeros. Con este objetivo, se fabricaron mezclas de bio-materiales y betún reciclado simulando mezclas asfálticas con 50% de contenido de reciclado. El efecto rejuvenecedor de los bio-materiales se ha evaluado y comparado con el efecto rejuvenecedor de ligantes convencionales mediante el cálculo de las distribuciones de peso molecular aparente y diferentes parámetro reológicos. Los resultados muestran el poder rejuvenecedor de los bio-materiales, poniendo de manifiesto su potencial para usarse como ligantes vírgenes en mezclas asfálticas con alto contenido de reciclado.

PALABRAS CLAVE: Bio-material; Betún; Envejecimiento; Reciclado; Reología

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1. INTRODUCTION

Bio-materials that are used as binders in asphalt mixtures are termed “biobinders” and were defined by Peralta et al. (1) as “asphalt binder alternatives made from any non-petroleum-based renewable resources, which should not rival any food material, and have environmental and economic benefits”. The interest on using biobinders in pavement engineering has significantly grown over the last decades due to the increasing scarcity of raw materials and environmental concerns about the use of non-recoverable natural resources.

According to the literature, biobinders can be used in three different ways to decrease the demand for fossil fuel based bituminous binders: (1) as a bitumen modifier (< 10% bitumen replacement), (2) as a bitumen extender (25% to 75% bitumen replacement), and (3) as a direct alternative binder (100% replacement) (1–3). In this regard, there exist several studies using biobinders as bitumen modifiers (4–8) but less research can be found using them as total replacement of bituminous binders (9–12).

An alternative way to use biobinders in asphalt mixtures is combining them with the aged binder present in Reclaimed Asphalt (RA). Binders in RA are known to be brittle and stiff due to their exposure to climate changes and traffic loading during their service life. This fact could promote the prompt appearance of non-desired distresses in the pavement (such as fatigue and thermal cracking) and prevent authorities and constructors from using RA in high contents (13; 14). In this sense, when RA content in recycled mixtures is aimed to be high (> 30%), soft binders (high penetration grade) are usually added in order to try to restore some of the properties of the aged binder. In this regard, the rejuvenating effect is understood as the decrease in stiffness and increase in fluidity (decreased viscosity) of RA binders. However, soft conventional bitumens are becoming a limited resource and research is needed to try to replace them with other materials.

The aim of this paper is to study the potential of biobinders to totally replace conventional bitumen for the manufacture of asphalt mixtures with high RA content. For this purpose, recycled, bio and conventional binders have been rheologically tested and compared. Then, bio and conventional binders were blended with a reclaimed asphalt binder. The rejuvenating effect of the different materials over the recycled one was assessed using different techniques. Among others, the innovative δ-method developed in IFSTTAR (15) was applied to obtain the Apparent Molecular Weight Distributions (AMWD) of the materials and increase the understanding of the interaction between binders.

2. MATERIALS AND METHODS

2.1. Materials

A Reclaimed Asphalt (RA) source in France was selected for the study. RA binder was recovered following the EN 12697-4:2005 Fractionating Column by distillation (16) procedure. Two different bio-materials were selected to be studied as replacement for conventional virgin binders in high-RA content mixtures. The first bio-material is a binder produced from 100% renewable resources. Specifically, this bio-material is a blend of pine resin (80%) and linseed oil (20%). These types of blends exhibit visco-elastic and thermo-rheologically simple behaviour. The second bio-material is a vegetal binder containing polymers which was selected due to different advantages that polymers provide to binders for asphalt mixtures (17). This material is already patented by EIFFAGE company and known as Biophalt® (18).

In order to compare the behaviour of these two bio-materials with standard ones, a 70/100 penetration grade bitumen and SBS-polymer modified binder were selected as reference binders since they are soft materials usually used as binders in RA mixtures. Finally, a 50/70 penetration grade bitumen was included in the study in order to have a control binder which is often used in standard asphalt mixtures. Conventional properties of the six binders are shown in Table 1. It is worth noting that RA is a highly aged binder with penetration of 8.7 dmm. This penetration value reveals the need for rejuvenation in order for this binder to be further used in high-RA content mixtures.

Table 1. Binders’ characterisation

BINDER	ROLE in the study	NAME	PENETRATION @ 25° (dmm) (22)	SOFTENING POINT (°C) (23)
Reclaimed asphalt binder	Recycled binder	RA	8.7	75.8
80% pine resin + 20% linseed oil	Bio-material	BB	235	40
Biophalt®	Bio-material	BP	147	73.5
70/100 penetration grade bitumen	Reference for BB	70/100	86	46
SBS-polymer modified bitumen	Reference for BP	PMB	85	67
50/70 penetration grade bitumen	Control	50/70	68	47.6

The bio-materials, considered as a total virgin bitumen replacement, and reference binders were blended with RA binder in order to study their rejuvenating effect. The percentage of blend between RA and the different binders was calculated according to the Replaced Virgin Binder (RVB) concept (19–21) for Reclaimed Asphalt mixtures assuming full blending, 50% RA in the mixture and total binder content of 5%. The RVB calculation is shown in Eq. [1].

$$RVB\,(\%) = 100 \cdot \frac{RA\ \text{in the mixture} \cdot DOB \cdot RAb\ \text{content}}{\text{binder content in the mixture}} = 100 \cdot \frac{0.5 \cdot 1 \cdot 0.036}{0.05} = 36\% \qquad [1]$$

Where, *RA in the mixture* is the total RA percentage to be added in the mixture by weight, *DOB* is the assumed degree of blending between RA and virgin binders (100%), *RAb content* is the binder content in the RA and *binder content in the mixture* is the designed final binder content in the mixture, with all the parameters expressed in decimals. Thus, four blends of RA with the different binders were manufactured having 36% of RA and 64% of the other binder in mass. Taking into account binders and blends, a total of 10 different materials were tested.

2.2. Methods

2.2.1. Blends manufacture

For the production of the four blends of RA and bio or reference materials, RA was heated to 160°C (due to its hardness) and the other binders were heated to 140°C. Once the proportions of each material were weighted and put together in a tin, they were introduced into an oven at 150°C for one hour. After that, binders were blended using a vertical propeller coupled to a motor able to control the revolutions per minute (fixed at 200 rpm) in a temperature-controlled environment for 15 minutes.

2.2.2. Rheology testing

Binders and blends were tested in the Dynamic Shear Rheometer (DSR). DSR used was a Kinexus Pro+. Frequency and temperature sweeps were carried out from 1 Hz to 25 Hz and from -10°C to 60°C. For this purpose, two parallel-plate geometries were used: 8 mm diameter parallel-plates from -10°C to 30°C, and 25 mm diameter parallel-plates from 20°C to 60°C with 1 mm gap. Tests were carried in strain-controlled mode at 0.06% strain in order to stay within the linear viscoelastic region of the binders' behaviour. For each binder, correct geometries were selected for 20°C and 30°C depending on results in order to achieve a smooth Black diagram (24).

Using these data, master curves of the norm of the complex modulus and phase angle of the different binders were produced at 15°C for comparison following the procedure developed by Chailleux at al. (25). This procedure minimises errors in the calculation of shift factors for master curves. Then, cross-over frequencies (ω_0) at 15°C and rheological indexes (R) of RA and its blends were determined in order to assess the rejuvenating effect of the different materials. Binder's crossover frequency is that frequency at which the binder's phase angle is equal to 45° at a certain temperature (i.e. frequency at which loss and storage moduli are equal). On the other hand, R-value of a binder is the distance between the norm of the complex modulus at the crossover frequency and the glassy modulus (usually taken as 1 GPa in shear loading). Crossover frequencies of binders decrease with ageing while R-values increase. Therefore, according to several authors (26), crossover frequency versus R-value space can be used to visually evaluate binders' ageing and rejuvenation.

2.2.3. δ-method application

A relationship between rheological properties of bitumen and its molecular weight distribution (MWD) is generally assumed in the literature (27–31). The basic assumption of the δ-method is that for a given frequency, the phase angle of the complex modulus is proportional to the fraction of relaxed molecules at this frequency. Therefore, a relationship can be established between the oscillation frequency and the molecular weight. Moreover, phase angle's master curve can be associated to the cumulative molecular weight distribution of the binder. Consequently, from the differentiation of the phase angle master curve, an apparent molecular weight distribution (AMWD) can be obtained. This differentiation requires a continuous curve, so the data has to be fitted with a continuous model. The Huet-Such model (32–34) has been chosen for this purpose as it is well suited for bitumens.

The Huet-Such model is a combination of one spring (G∞), two parabolic creep elements (0<h<k<1) with one coefficient (δ) that regulates the balance between them and a dashpot (β) placed in series with the other elements. This model and its respective equation are represented in Figure 1. Model parameters were adjusted to the rheological test data obtained on the DSR device after master curves construction at $T_{ref} = 0°C$.

A detailed description of the δ-method can be found in Themeli et al. (2015). The molecular

$$G^* = \frac{G_\infty}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}}$$

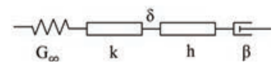

FIGURE 1. Huet-Such model and equation.

weight distribution obtained by δ-method is termed “apparent” because the proportionality condition to the phase angle, proved for polymers, is assumed for bitumen in this study. Therefore, δ-method provides the Apparent Molecular Weight Distribution (AMWD).

3. RESULTS AND DISCUSSION

3.1. Individual materials characterisation

Figure 2 shows the rheological results of the binders in the Black space. This space allows the different nature of the materials under study to be viewed and provides a fingerprint of their behaviour. In this space, all frequencies and temperatures tested are displayed, corresponding higher temperatures to lower values of the norms of the complex modulus. The first remark to be made is that all the tested materials, including biobinders, exhibit thermo-rheologically simple behaviour due to the smooth overlap of the curves in the Black space over the range of tested temperatures (-10°C to 60°C). The 50/70 and 70/100 pen bitumens show similar Black diagrams due to their conventional nature (no modification, ageing or bio-materials presence). RA reveals high elastic response due to the ageing process to which it has been subjected to during its service life. On the other hand, BB is a non-elastic material which reaches phase angles closed to 90° for a wide range of the complex modulus (|G*|). In this regard, BB and 70/100 pen bitumen have a different rheological nature. In terms of RA rejuvenation, increased fluidity (increased viscous response) is one the desired properties for fresh binders to be used in high-RA content mixtures to increase RA fluidity and reduce fatigue and thermal cracking potential. Conversely, BP is a highly modified binder able to show elastic behaviour (low phase angles) at high temperatures. In comparison to the PMB, BP exhibits greater polymer modification features exhibited by bell-shaped black curves and drastically reduced phase angle values (improved elastic behavior) for |G*| values below 1 MPa (higher service temperatures).

3.2. Rejuvenating effect analysis through rheology results

Once the rheology of the individual materials is known, the blends’ rheology is shown in Figure 3 in the Black Diagram. Figure 3 reveals that the blends of RA and the different materials present thermo-rheologically simple behaviour (as it happened for the original binders). This fact allows applying the Time-Temperature-Superposition-Principle (TTSP) for the construction of their master curves and further analysis. Storage (G’) and loss (G’’) moduli master curves and shift factors temperature dependency of RA, 50/70 pen bitumen and blends are shown in Figures 4-6.

In order to further evaluate the effect of the different binders over the RA, cross-over frequencies vs. rheological indexes (R-values) space (26) has been used as displayed in Figure 7. On one hand, cross-over frequencies are related to the elastic/viscous nature of binders, meaning that the higher the cross frequency the more viscous the material (due to the fact that the binder reaches 45° of phase angle at a higher frequency). Therefore, the more elastic materials can be found at the bottom-middle part of these graphs. On the other hand, R-values are the logarithmic difference between the norm of

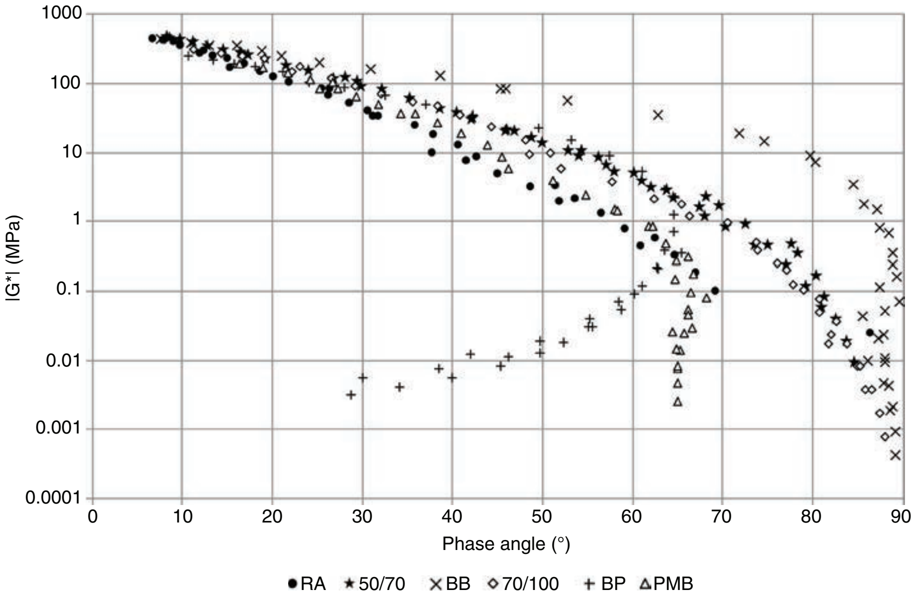

Figure 2. Black diagram of original binders.

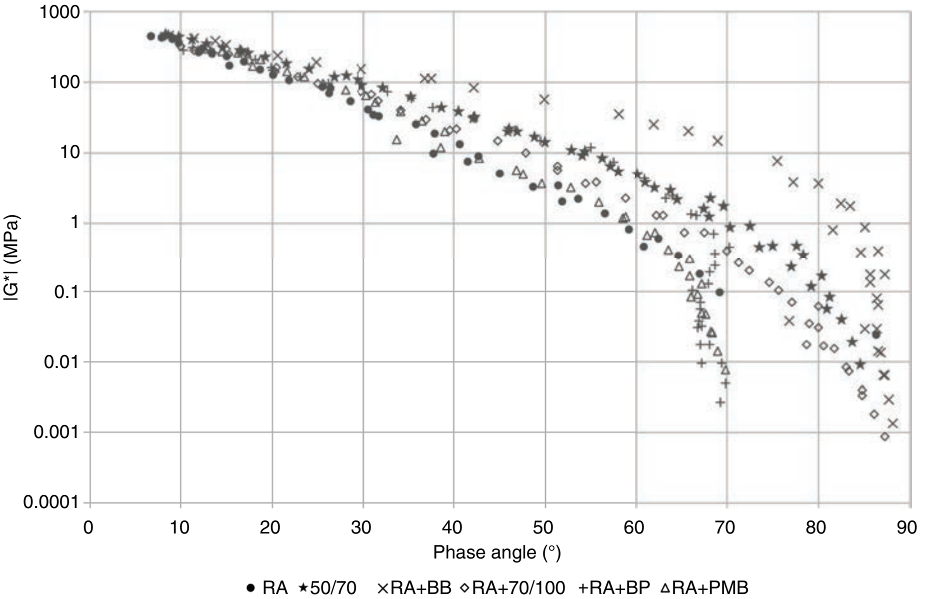

FIGURE 3. Black diagram of blends.

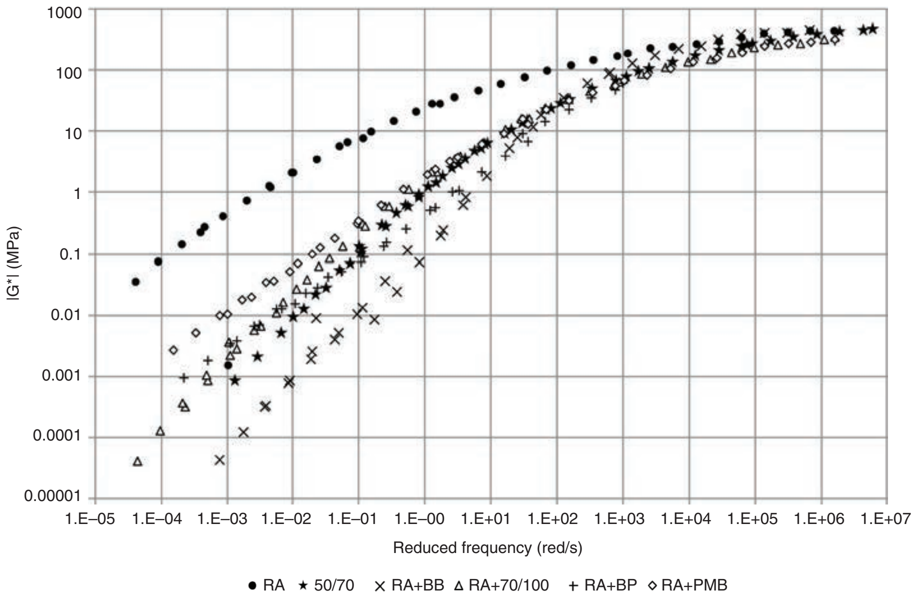

FIGURE 4. Storage modulus (G') master curves at 15°C.

the complex modulus at the cross frequency of the specific binder and the norm of the glassy modulus. This means that R-values provide a measure of the binders' stiffness in an equi-elastic state and at a given temperature. In this sense, at the same elasticity level, the greater the R-value the stiffer the binder. In this regard, Figure 7 shows that RA point is located at the bottom-right part of the plot, having high R-value and low cross-over frequency. Subsequently to the rejuvenating effect, the blend of RA with the different materials produces a shift of this point up and to the left in Figure 4. In this sense, it can be said that bio-materials produced less elastic and softer (at the same level of elasticity) rejuvenated RA in comparison to the reference binders.

Fatigue (G*sinδ) and rutting (G*/sinδ) parameters have been used to evaluate the rejuvenating effect of biobinders and reference binders on fatigue and rutting resistance on RA. For this purpose, G*sinδ = 5000 kPa and G*/sinδ = 1 kPa at 1 Hz were taken as thresholds for obtaining critical temperatures of the different materials for comparison purposes. Figure 8 shows these results. It can be seen that rutting critical temperatures of blends of the different

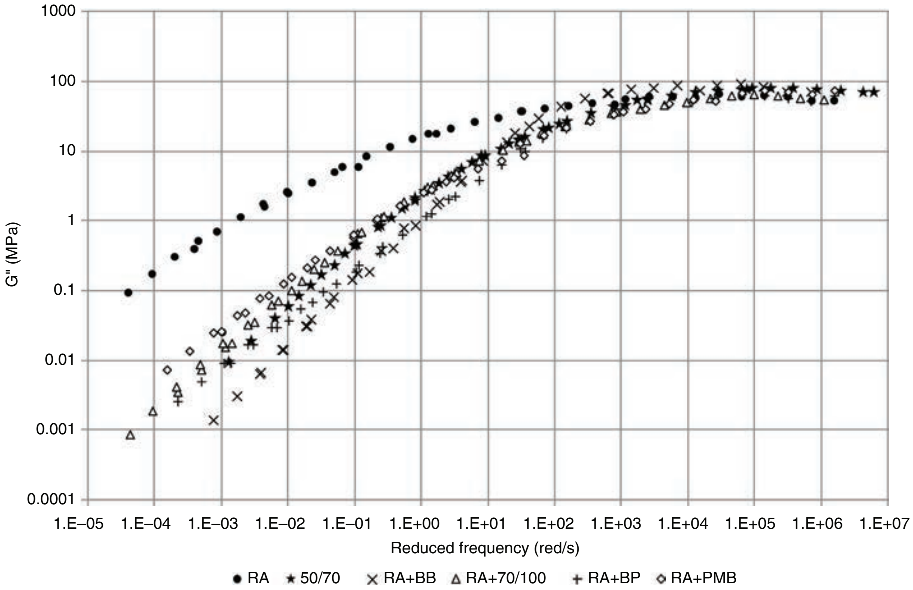

FIGURE 5. Loss modulus (G'') master curves at 15°C.

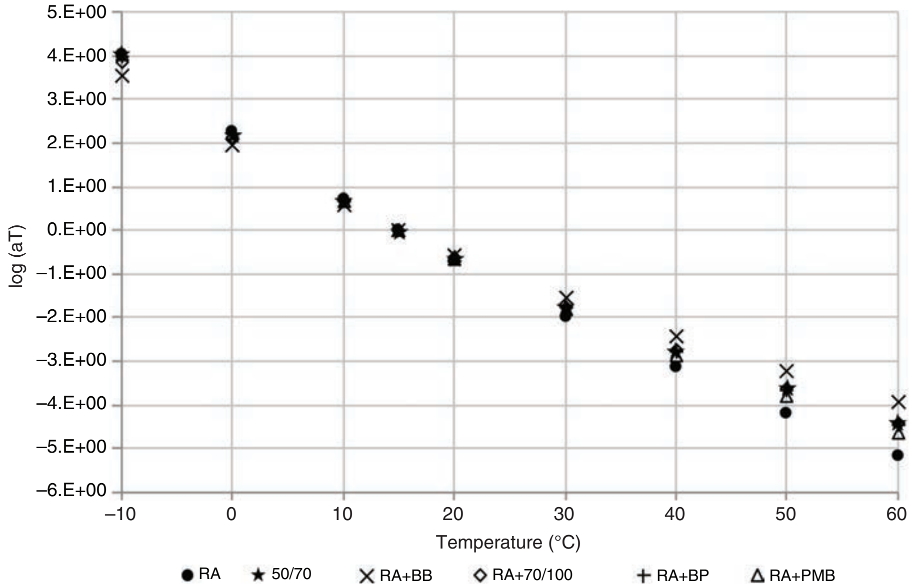

FIGURE 6. Temperature dependency of shift factors.

binders (conventional and bio-materials) are equal or higher than that of the 50/70 pen bitumen. This means that their rutting behaviour is expected to be equivalent to that of the 50/70 pen bitumen. Only the RA+BB blend presents a slightly lower temperature. Regarding fatigue, all RA blends have comparable or lower critical temperature than that of the 50/70 pen bitumen; thus equal or better fatigue resistance can be expected for these binders. In conclusion, blends of RA and biobinders are likely to have a positive rejuvenating effect on RA performance for high-RA content mixtures. This result is in accordance with other investigations about rejuvenating agents (14). However, it is important to note that in this investigation the rejuvenating agents would act as a total virgin bitumen replacement in the mixtures and not simply as an additive.

3.3. Rejuvenating effect analysis through AMWD results

In this section, the Apparent Molecular Weight Distribution (AMWD) for all blends is plotted and compared to that of the RA binder. δ-method

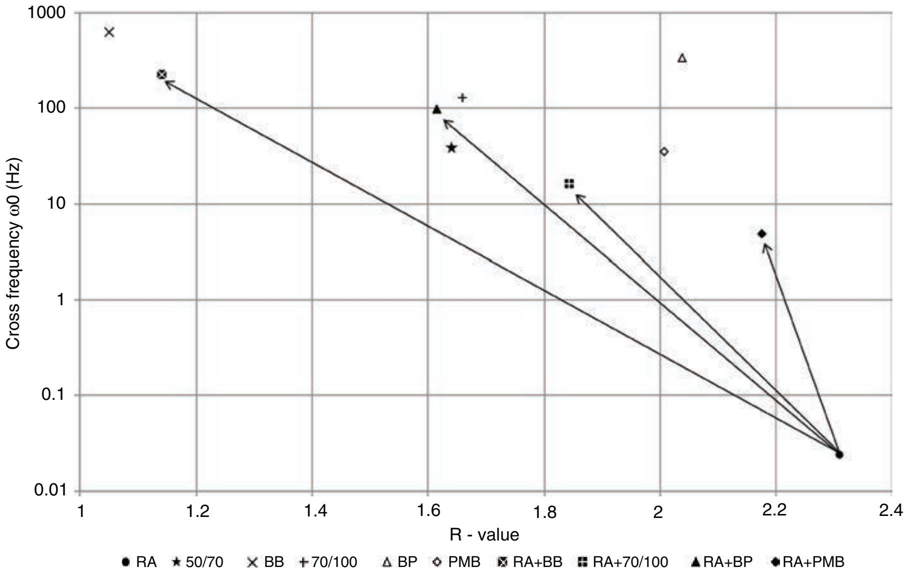

FIGURE 7. Crossover frequencies vs. R-values.

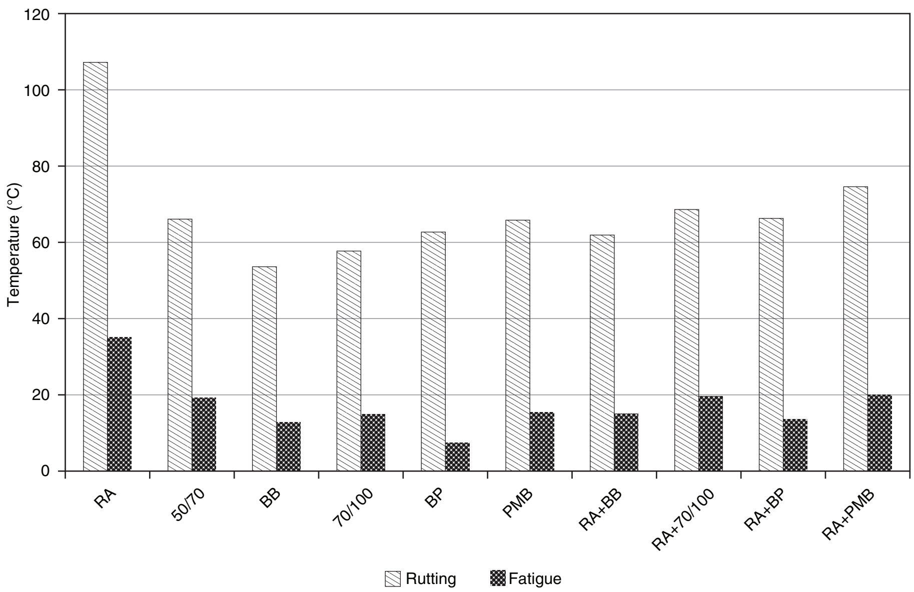

FIGURE 8. Rutting and fatigue performance temperatures.

application is restricted to materials that exhibit a continuous monotonic curve on the Black diagram; therefore, its application was only possible for RA, 50/70 bitumen and blends, and not for the original materials such as BP and PMB (see Figures 2 and 3). For this purpose, Huet-Such model parameters were determined in order to obtain the required continuous master curves of binders for the δ-method and are displayed in Table 2. Master curves at 0°C of the norm of the complex modulus and phase angle of RA binder and its blends are shown in Figures 9 and 10 respectively. The glassy modulus G_∞ represents the value of $|G^*|$ at infinite frequency, remaining almost constant (600 MPa) for all the binders. This value seems consistent with usual values for binders, even if Yusoff et al. (36) and Yusoff (35) suggested values around 1 GPa.

In the case of the RA+BP blend, the modelling is on the limit of δ-method application for this case. The β value seems inconsistent, the increasing accumulative curve for the phase angle achieves a plateau at 70° instead of continue growing towards 90° as the other blends. This may be due to the high content of polymers, limiting at the same time the calculus of parameters and the application of the δ-method, so for the RA+BP AMWD curve the values are indicative. On the other hand, this constraint does not exclude the use of this tool to compare and

TABLE 2. Huet-Such rheological model parameters and WLF coefficients for RA binder and blends at T = 0°C

Bitumen / Parameter	G_∞ (MPa)	δ	k	h	β	τ (s)	C1	C2
RA	627.68	5.15	0.24	0.62	348.22	4.25E+00	25.87	154.27
RA+BB	551.71	2.44	0.30	0.85	3.64	1.12E−01	18.22	126.82
RA+BP	581.51	3.50	0.25	0.73	1.53E15	3.526E−02	20.71	126.93
RA+PMB	579.14	6.14	0.30	0.71	422.04	1.51E−01	22.23	136.56
RA+70/100	623.42	5.17	0.26	0.65	53.32	8.93E−02	19.22	113.74
50/70	661.22	6.96	0.32	0.76	6.50	7.61E−02	27.28	195.75

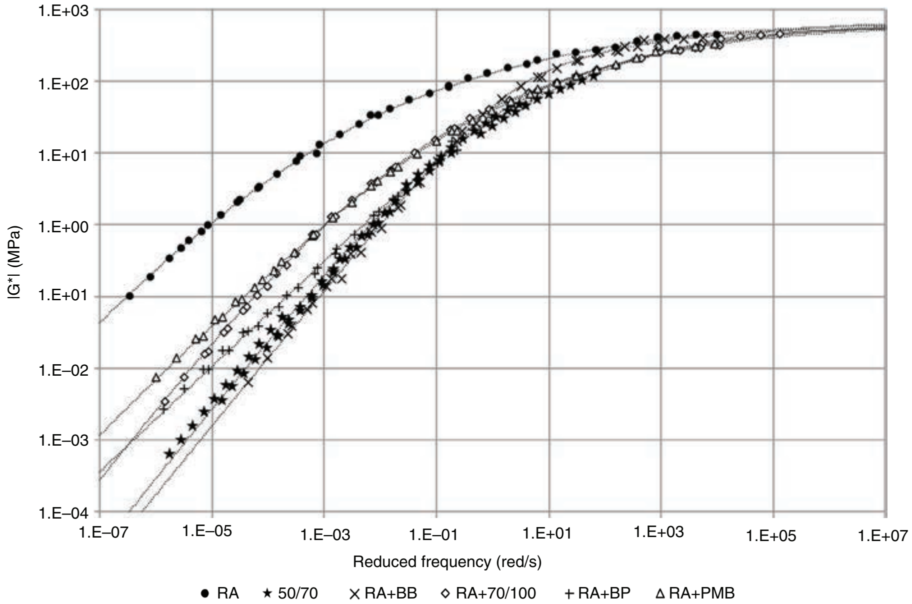

FIGURE 9. Norm of the complex modulus (|G*|) master curves at 0°C and Huet-Such model fitting.

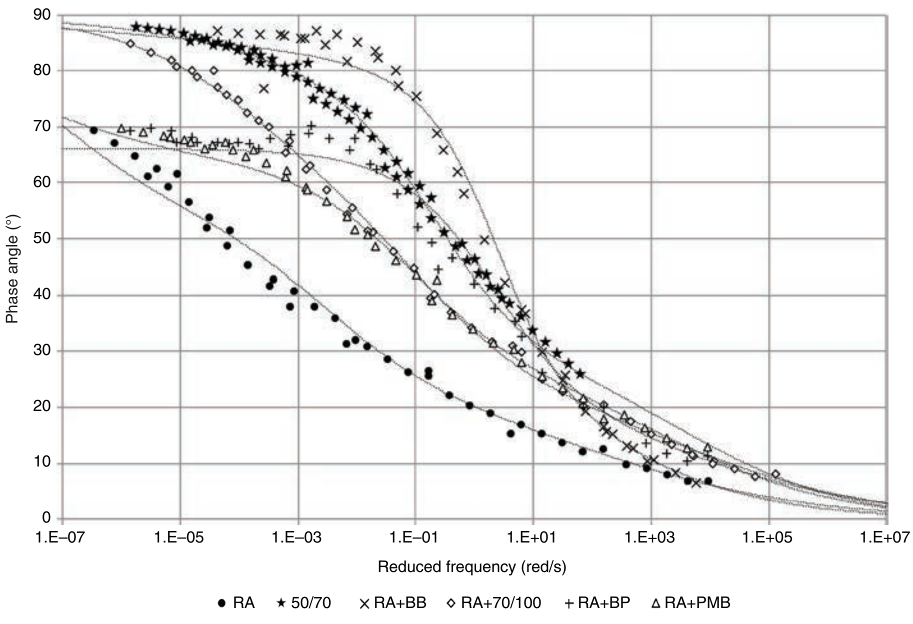

FIGURE 10. Phase angle (°) master curves at 0°C and Huet-Such model fitting.

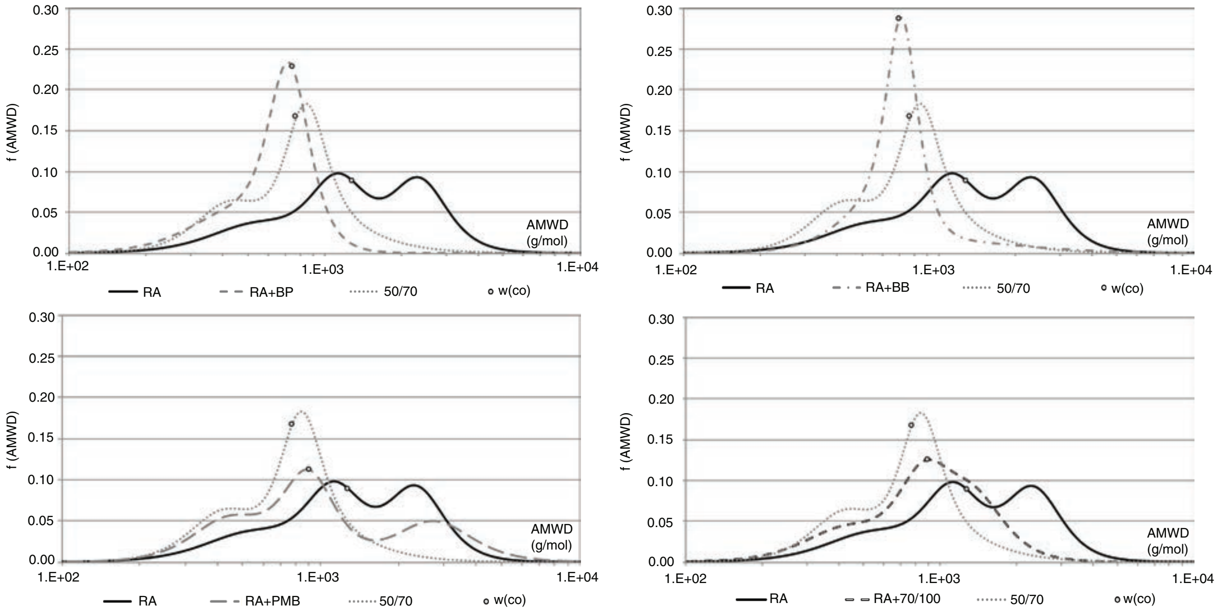

FIGURE 11. AMWD of RA and its blends.

verify the rejuvenating effect induced by the blending between RA and BP.

The AMWDs are plotted with the apparent molecular weight (AMW) in g/mol on the abscise axis and the corresponding probability density f(AMW) on the ordinate in Figure 11. The trend between curves is used as a first approach to quantify the rejuvenating effect of the blending through the apparent molecular weight distributions. In addition, cross-over points (w(co)), points at which phase angle is equal to 45° (i.e. loss and storage moduli are equal), of the different binders have been displayed.

Firstly, Figure 11 reveals the difference between RA, which presents a bi-modal AMWD with one peak around 1000 g/mol and the other at heavier molecular weight (as expected for an aged binder) and 50/70 pen bitumen, which possesses a monomodal AMWD with a peak around 750 g/mol. According to Mullins (2011), asphaltenes are presented between 500-1000 g/mol molecular weights. Therefore, the fact that RA exhibits heavier molecules than 1000 g/mol could mean that molecular clustering may be taking place, showing high molecular weight molecules up to 2500 g/mol. In this regard, the δ-method shows a great potential to provide new information about bitumen ageing.

Regarding the blends of RA with the different binders, the main effect that can be observed in Figure 11 is the shift of RA's AMWD to the left (i.e. to lighter weights) after blending. In terms of biobinders blends, RA+BB and RA+BP exhibit light AMWD (lighter than 50/70 pen bitumen), both with a unimodal distribution below 1000 g/mol. On the other hand, the RA+PMB show their molecular weight peak at nearly the same point as the 50/70 pen bitumen with the PMB being and a second peak at higher AMW induced by the polymers presented on the blend. Lastly, blend RA+70/100 shows a unimodal distribution with a wider base than the other blends.

Nevertheless, rejuvenating effect is clear in all cases, proving the strength of this tool to enhance the identification of the rejuvenating effects of the different bitumen blends. In addition, the movement to the left of the cross-over points from the RA to those of the blends can be seen as a rejuvenation indicator.

4. CONCLUSIONS

The investigation presented in this paper shows that biobinders have the potential to replace conventional and modified binders in the production of high-RA content mixtures (50%) at the binder level of study. For this purpose, two biobinders and two more traditional petroleum-based binders (conventional and modified) have been analysed and blended with RA to study the rejuvenating effect that they produce over RA. This effect has been assessed by means of rheology and the application of the δ-method to obtain their molecular weight distribution.

Rheological characterisation of the biobinders revealed that they are thermo-rheologically simple materials with desired properties, such as high viscous response (BB) or capability to have low phase angles at high temperatures (BP), to produce rejuvenation in high-RA content mixtures. All the biobinders and conventional binders that were studied produced a rejuvenating effect over RA that can be easily appreciated in the cross-over frequencies versus rheological indexes space. In this regard, the blend of biobinders with RA generates less elastic and softer binders, having a comparable effect to traditional petroleum-based binders.

In terms of performance prediction, blends of RA and biobinders show equivalent rutting critical temperatures compared to 50/70 pen bitumen and RA blends with traditionally used binders, which would lead to similar rutting resistance in the asphalt mixture. Blends of RA and biobinders showed improved fatigue resistance in comparison to the rest of blends. The fact that RA fatigue performance can be enhanced with biobinders without compromising rutting behaviour is a desirable rejuvenating effect.

A more fundamental evaluation was undertaken to assess low-temperature properties of the blends. To this end, the materials response was fitted at 0°C with Huet-Such model. Parameters obtained for biobinders seem reasonable in comparison with those of conventional binders (but for the RA+BP blend which is at the limit of its application). From these parameters, δ-method was applied to determine the apparent molecular weight distribution of RA, 50/70 binders and RA blends. This AMWD allowed visualising the rejuvenating effect of binders over RA through the shift of the RA distribution to lighter molecular weights. In this regard, it can be highlighted that RA+BB and RA+BP blends show similar AMWD to the 50/70 pen bitumen, which is not the case of the RA+PMB and RA+70/100 blends having a rejuvenation effect less pronounced. The δ–method seems to be a powerful tool for the quantification of structural evolutions of bitumen blends, giving a clear visualization of the structural modifications induced. These results tend to confirm that a structural interpretation of recycling and the rejuvenating effect through these types of blends is possible with the δ-method.

In summary, biobinders have comparable characteristics and produce comparable or greater rejuvenating effect on RA than traditionally used binders. Therefore, they show great potential to be used in high-RA content mixtures as fresh (virgin) binders. However, these materials are relatively new and need further development in order to fully understand their performance and how they would affect asphalt mixtures in the field. In this regard, future research is now being focused on the study of mechanical performance and ageing of high-RA content mixtures manufactured with biobinders as the virgin binder.

ACKNOWLEDGEMENTS

The research presented in this paper is carried out as part of the Marie Curie Initial Training Network (ITN) action, FP7-PEOPLE-2013-ITN (http://www.superitn.eu). The funding for the research was provided by the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement number 607524.

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