Cold recycling process using renewable resources: contribution of rheological and chromatographic methods for rejuvenating mechanism and duration assessment

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ABSTRACT

Recycling end-of-life road products can be performed in various ways, involving a combination of sustainable techniques. A first level in sustainability is reached by the use of a bitumen emulsion, which enables processing at moderate temperatures. This technique is already commonly used, according to specific guidelines.
Further improvement is achieved if the emulsion contains a rejuvenating agent manufactured from renewable resources. In this context, the key issue in laboratory study is to find a proper way to highlight the rejuvenating effect and to follow its evolution. Suitable test methods, described in this paper, have been identified and used for this purpose.
The general principle is to compare binder characteristics after extraction from RAP, and from mixes obtained after recycling process and in situ-aging ; several aging steps are considered. The rejuvenating effect is supposed to end when the characteristics of binder from mix after recycling are back to those of the RAP binder.
Dynamic Shear Rheometer (DSR) enables to determine the binder stiffness modulus as a function of temperature: thus, thermal sensitivity is monitored, along with binder hardness. In the first weeks after recycling process, the binder tends to soften, due to the progressive rejuvenating effect. Afterwards, the binder hardens slowly throughout months. After 1 year in situ, a rejuvenating effect is still observed.
Chromatographic methods such as gaseous chromatography (simulated distillation) enable to monitor the chemical evolution of the rejuvenating agent itself, within the blend with RAP binder and rejuvenation bitumen. After 1 year aging in situ, the rejuvenating agent is no longer detected, through its effect can still be seen though rheological properties.
Considering results obtained by both kinds of techniques, a hypothesis can be proposed, in order to explain the action mechanism of the rejuvenating agent. This latter is most likely to have delayed binder hardening. Hence, the efficiency of rejuvenating process has been improved by lengthening its effect, in comparison with performances attributed to a pure bitumen emulsion.

Keywords: Chemical properties, Durability, Emulsions, Rejuvenators, Rheology

1 Introduction : Rejuvenation Techniques

A variety of techniques are available for recycling end-of-life road materials. The material can be recycled in situ, using appropriate mobile plant, or crushed and recycled in a coating plant. In all cases, a rejuvenating binder must be incorporated into the material. This is because, after several years of in-situ ageing, the binder in the material has hardened considerably due to its high asphaltene content, and lost some of the viscoelastic properties which give the bituminous material its cohesion. The role of the rejuvenating binder is thus to restore these rheological properties and compensate for the oxidative ageing of the bitumen by adding aromatic and resinous compounds to modify the chemical composition and bring it closer to that of a fresh binder.

This can be carried out after heating, with the added binder in anhydrous form, but the environmental benefits are much greater if recycling is conducted at ambient temperature using an emulsified binder.

These rejuvenation techniques have been widely tested, and are usually applied on the basis of empirical knowledge. Publications are mostly focused on studies carried out on the binder right after rejuvenation, without any data on follow-up throughout time [1] [2]. The studies consist mainly of mechanical characterisation, either on the mix [2] or on the extracted binder itself [3].

On a jobsite-oriented point of view, the various techniques that are available for cold in-situ recycling have been described in several guides [4] [5] [6], each one being related to local specifications.
For example, the French SETRA guide: “Retraitement en place à froid des anciennes chaussées” [4] contains specifications for the material after the recycling process. With regard to the coated material, the specifications relate to its water resistance as evaluated by the Duriez test, and its rigidity modulus. The binder that has been recovered from the coated material has to meet a specification with regard to its ring and ball temperature. This must show a reduction of between 5°C and 15°C compared to the value obtained with the aged binder. This specification only applies to the fresh binder. There is no specification concerning change over time, i.e. the durability of the rejuvenation effect.
In other cases [5] [6], long-term performances are dealt with on an empirical point of view, without any laboratory test to support the evaluation of rejuvenating effect durability.

Therefore, the choice of a rejuvenating technique usually remains empirical. The contradicting requirements for bituminous materials on one hand and binders on the other means a compromise must be made when choosing a rejuvenating binder and its dosage. If the added binder is too soft and/or if an excessive amount is used, the mechanical performance of the mix will be impaired. On the contrary, if the added binder is too hard and/or added in an insufficient amount, the rejuvenating effect will be short-lived.

It therefore seems advisable to use an additive which would extend the rejuvenating effect of the added binder without causing excessive softening in the initial stage, and which implements a mechanism which differs, or compliments, the mechanisms responsible for the changes in pure bitumen. The ageing of pure bitumen is governed by three types of phenomena [7]: the evaporation of light fractions, the transformation of aromatic oils into resins and resins into asphaltenes (chemical change), and the steric rearrangement of compounds in the bitumen (physical hardening). While these changes are of course inevitable, it seems possible to prolong the effectiveness of rejuvenation by adding a compound that delays the occurrence of at least one of these phenomena.

2 Monitoring the Rejuvenating Effect using Rheological and Chromatographic Techniques

Two techniques, whose results complement each other, can be used to characterise binders following the rejuvenation procedure. They are:

- Characterisation using the Dynamic Shear Rheometer (DSR) in order to monitor the rheological characteristics of the binder, in particular its hardening;
- Characterisation of the volatile fractions introduced by the rejuvenating binder using a chromatographic technique, simulated distillation.

2.1 Study of Rheological Properties

Characterisation with the Dynamic Shear Rheometer (DSR) is already used to investigate the mechanical performance of binders. The results obtained for a pure or modified bitumen generally allow us to predict its in-situ performance: suitability for use in a high modulus mix, ability to withstand high temperatures (creep) and/or low temperatures (cracking).

In the context we are concerned with, this technique enables us to monitor the viscoelastic properties and thermal susceptibility of the binder during a temperature sweep which can be repeated at different stages of binder ageing in order to monitor any changes. Every time this test is performed it is necessary to recover some of the binder in the bituminous material, but only a few grams are required for each sample.

2.2.1 Test Principle

A sample of bitumen is placed between two parallel metallic plates with a diameter of 8 mm which are 1 mm apart. This assembly is placed in a temperate regulated cell as shown in Figure 1. One of the two surfaces is subjected to sinusoidal harmonic oscillation at a predefined frequency and rate of strain. The rheometer software computes the complex modulus G*(which is the ratio between the amplitude of the stress and the amplitude of the strain) and the phase angle δ, which expresses the phase difference between the stress and the strain [8]. These measurements are made during a temperature sweep. The determination of the phase angle makes it possible to situate the behaviour of material between two extreme cases, presented in Figure 2, that of purely elastic material, and that of a purely viscous material. It is thereby possible to perceive the contribution of each of these components of the rheological behaviour:

- the elastic portion which represents the ability of the material to store energy,
- and the viscous portion which represents its ability to lose it.

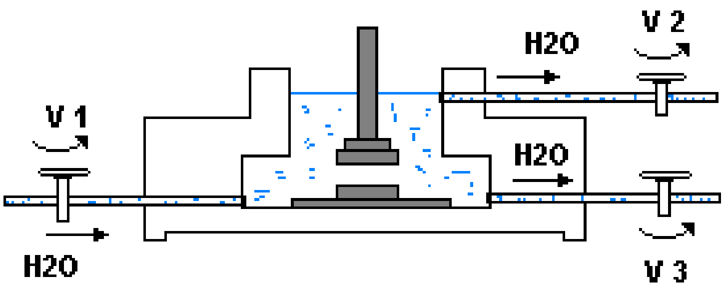

Fig. 1 The cell used in DSR to measure the complex modulus and the phase angle

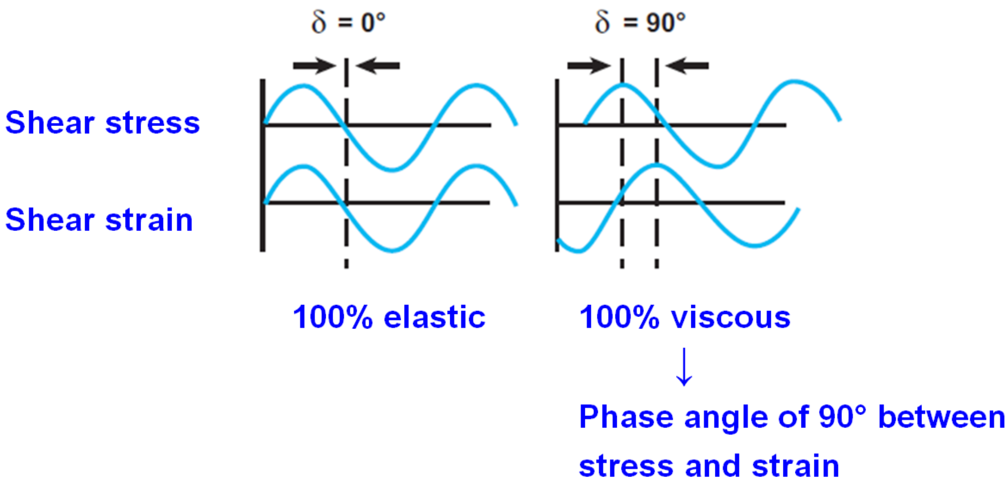

Fig. 2 Phase angle δ between stress and strain during a harmonic sinusoidal movement.

2.2.1 Results Obtained

The complex modulus and the phase angle are plotted against temperature for different types of binder or the same binder at different stages of ageing. Figures 3 and 4 show some examples of plots of this type, for a binder after in-situ ageing and for the same binder that has undergone rejuvenation.

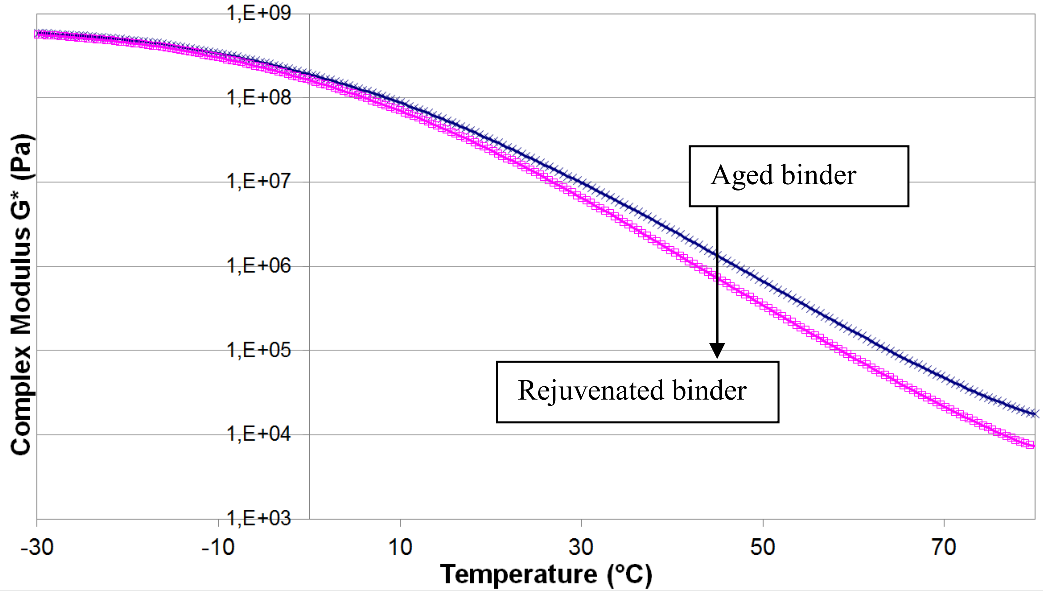

Fig. 3 Plot of complex modulus versus temperature

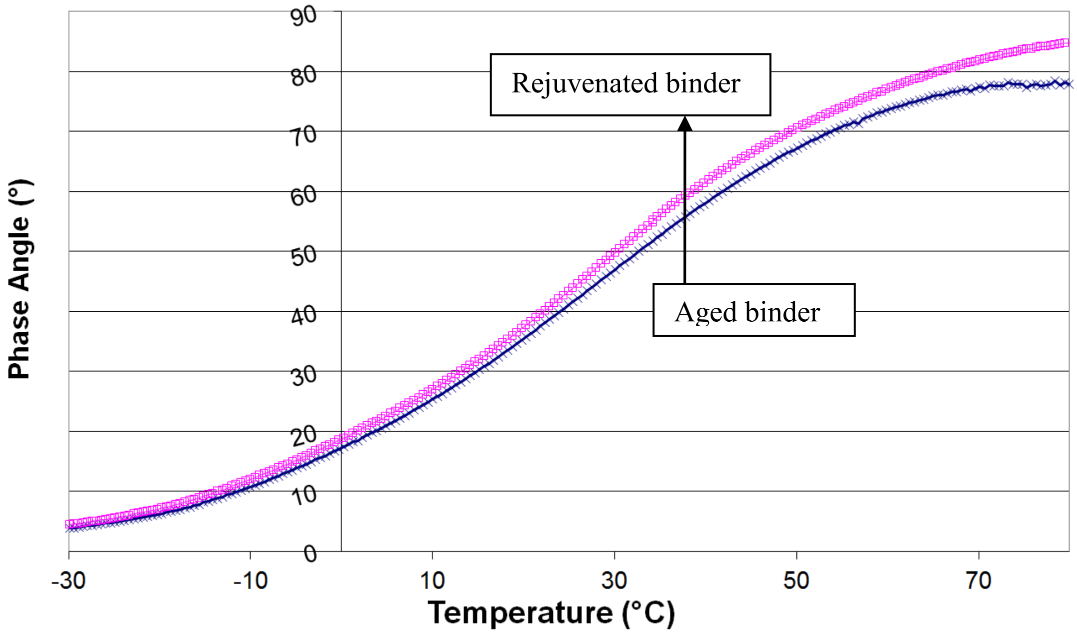

Fig. 4 Plot of phase angle versus temperature

After rejuvenation, the complex modulus at a given temperature is lower, which, as one would expect, is due to the softening of the binder. This is consistent with the only parameter which is generally determined during a study of rejuvenation (reduction of the ring and ball softening point). But the rheological study provides considerably more information than this test. It shows the increase in the thermal susceptibility of the binder, which is apparent from a general increase in the gradient of the curve. Moreover, the increase in the phase angle reveals a modification in the rheological behaviour, in favour of the viscous portion.

2.2 Study of Chemical Composition: Simulated Distillation

Simulated distillation is a type of chromatography that is able to detect and measure the volatile compounds present in bitumen. The amount and nature of these compounds depends on the origin of the crude, the methods employed in the refinery, the addition of additives, etc.

2.2.1 Test Principle

The fundamental principle of simulated distillation by gas chromatography is the elution of the chemical compounds that make up the specimen in order of increasing boiling point. It is possible to establish a correlation between the retention time of compounds in the chromatographic column and a boiling point standard consisting of a mixture of n-paraffins (n-c7 to n-c44). The heavier the compound, the higher its boiling point and the longer its retention time.
Prior to the analysis, a known quantity of nC7, is added to each sample as an internal standard, as the surface area of the peaks is directly proportional to the quantity of product detected.
In the case of bituminous coated materials, the binder is extracted directly by dissolving it in dichloromethane, and is therefore not heated. This means that it is possible to detect the most volatile fractions. Figure 5 shows the migration of the sample through the column.

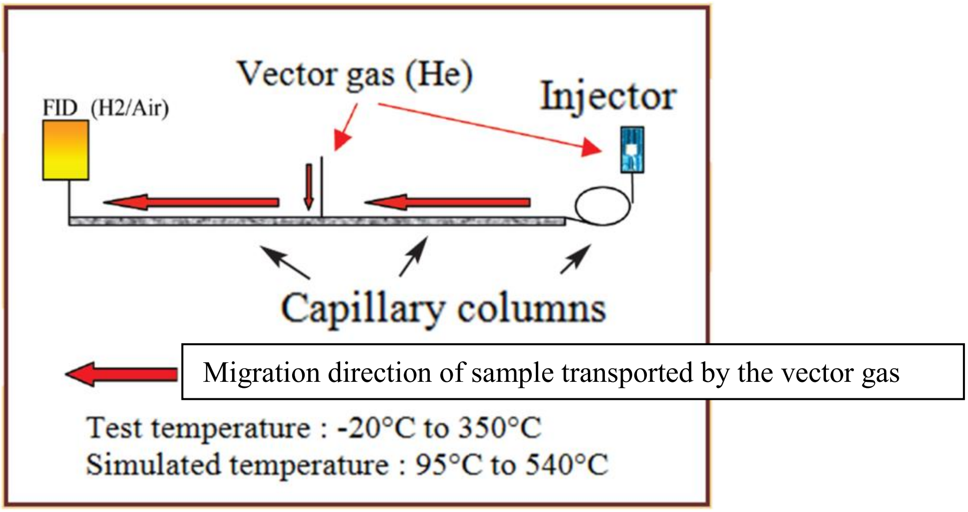

Fig. 5 The simulated distillation apparatus

2.2.2 Results Obtained

The chromatogram is the plot of the response of the Flame Ionisation Detector (FID) against time. The peaks are allocated according to their corresponding boiling points. Figure 6 presents some chromatograms obtained with a bitumen that has aged in situ and the same bitumen that has been recycled with the addition of a rejuvenating agent manufactured from renewable resources.

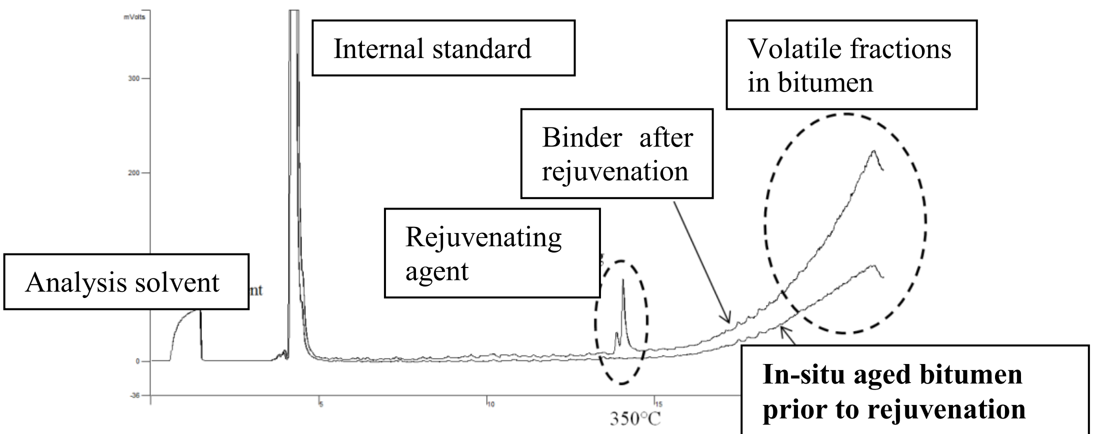

Fig. 6 Simulated distillation chromatograms

3 Study of a Concrete Case

The above techniques have been used to study changes in the binder in the years following its rejuvenation. The case in question was the in-situ recycling of the wearing course of a county road to a depth of 10 cm using a 160/220 pen bitumen emulsion additivated with a rejuvenating agent manufactured from renewable resources. A total surface area of 18,000m² underwent this treatment.

The binder extracted from the RAP was used as a control. In addition, the binder was extracted from the mix immediately after the recycling stage, then after 17 days of in-situ ageing, and last, after one year in situ. The characteristics of the binder were determined at each stage.

3.1 Characterisation using Conventional Tests

The penetration rate and softening point of the binders were characterised as specified in the Setra guide [1]. The results are set out in Table 1.

Table 1 The characteristics of the binders during ageing

	Penetration (1/10mm)	Softening point (°C)
Before rejuvenation (RAP)	11	68.4
Day (t=0)	19	64.6
T = 17 days	20	61.4
T= 1 year	13	64.2

These results confirm that the addition of a rejuvenating emulsion, i.e. soft bitumen (160/220 pen) and a rejuvenation agent, leads to a softening of the binder. Furthermore, they show that after one year in situ, the binder is still softer than it was before recycling. The rejuvenating effect of the emulsion is therefore still apparent. However, these results provide no information about the mechanisms involved in the rejuvenation process and provide little information about the differences between the state of the binder immediately after rejuvenation and its state after one year. More in-depth investigation was therefore performed using simulated distillation in order to monitor changes in the rejuvenating agent in the binder, and by rheology in order to monitor the overall effect of the rejuvenated binder.

3.2 Analysis of Light Fractions: Simulated Distillation

Samples of binders taken at the different stages of ageing were analysed by gas chromatography or, more precisely, simulated distillation. The resulting chromatograms are shown in Figure 7.

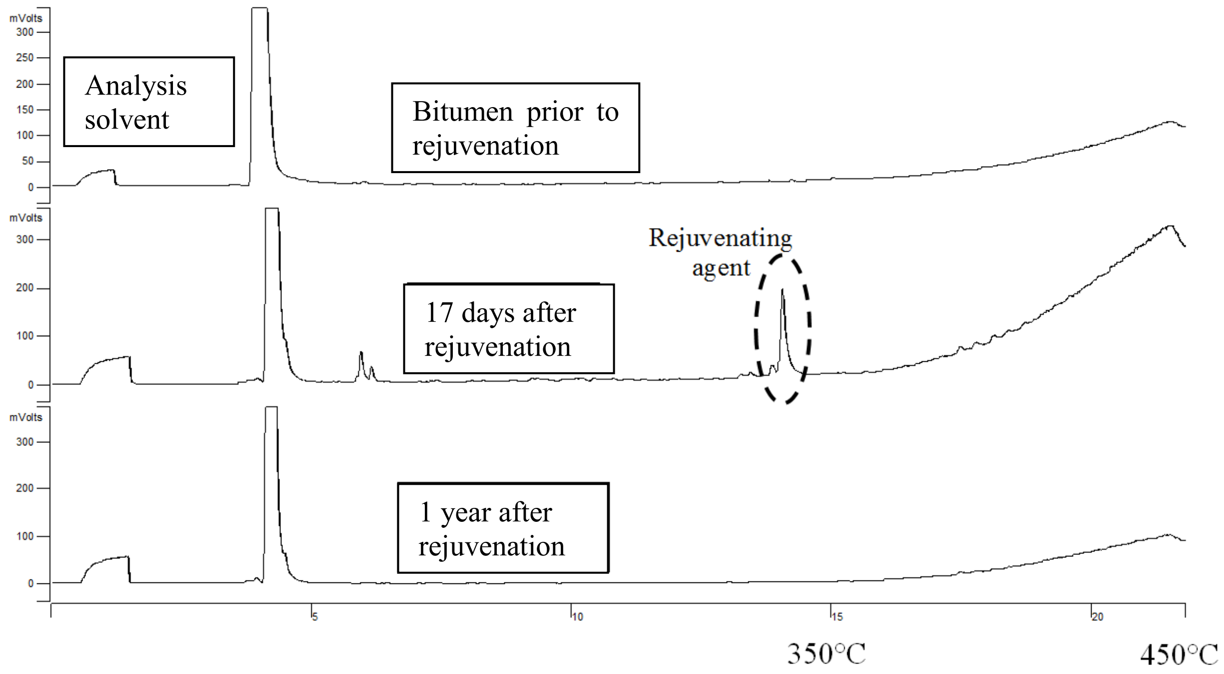

Fig. 7 Monitoring of the rejuvenating agent in bitumen, after recycling

These chromatograms show that the rejuvenating agent, which was clearly visible in the early age binder, is no longer detected after one year in situ because of the changes it has undergone within the binder. This finding is completely consistent with those of a study conducted on a pure rejuvenating agent at different stages of laboratory ageing which showed there to be a marked change in the shape and height of the peaks, as shown in Figure 8.

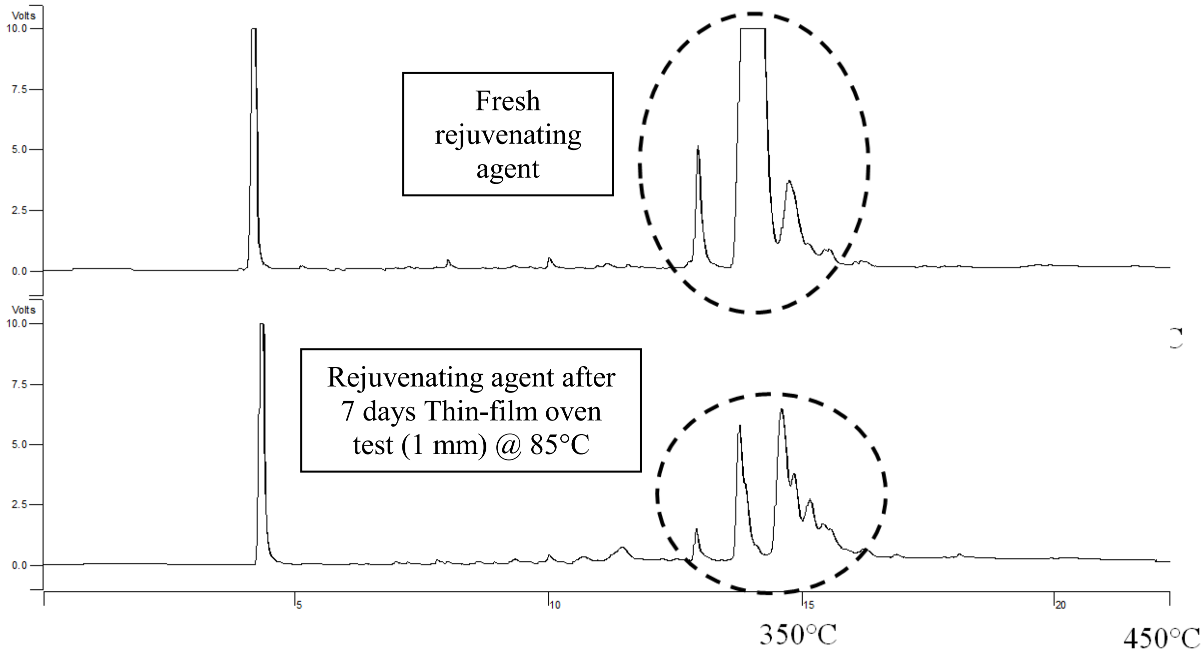

Fig. 8 Monitoring of pure rejuvenating agent, fresh (top) and after aging simulation (bottom)

A comparison between the chromatograms shows that the reduction in the characteristic peaks of the rejuvenation agent is due to intrinsic chemical changes. Analysis of binders recovered from core samples taken at the rejuvenation worksite showed that the rejuvenation agent was clearly detected at early age and changes chemically throughout the first year until it becomes undetectable.

3.3 Rheological Characterisation

In addition to simulated distillation analyses, we also carried out rheological characterisation of the binder recovered from the bituminous material. The differences in the modulus and phase angle at different temperatures and after different durations of ageing are presented in Figures 9 and 10 respectively.

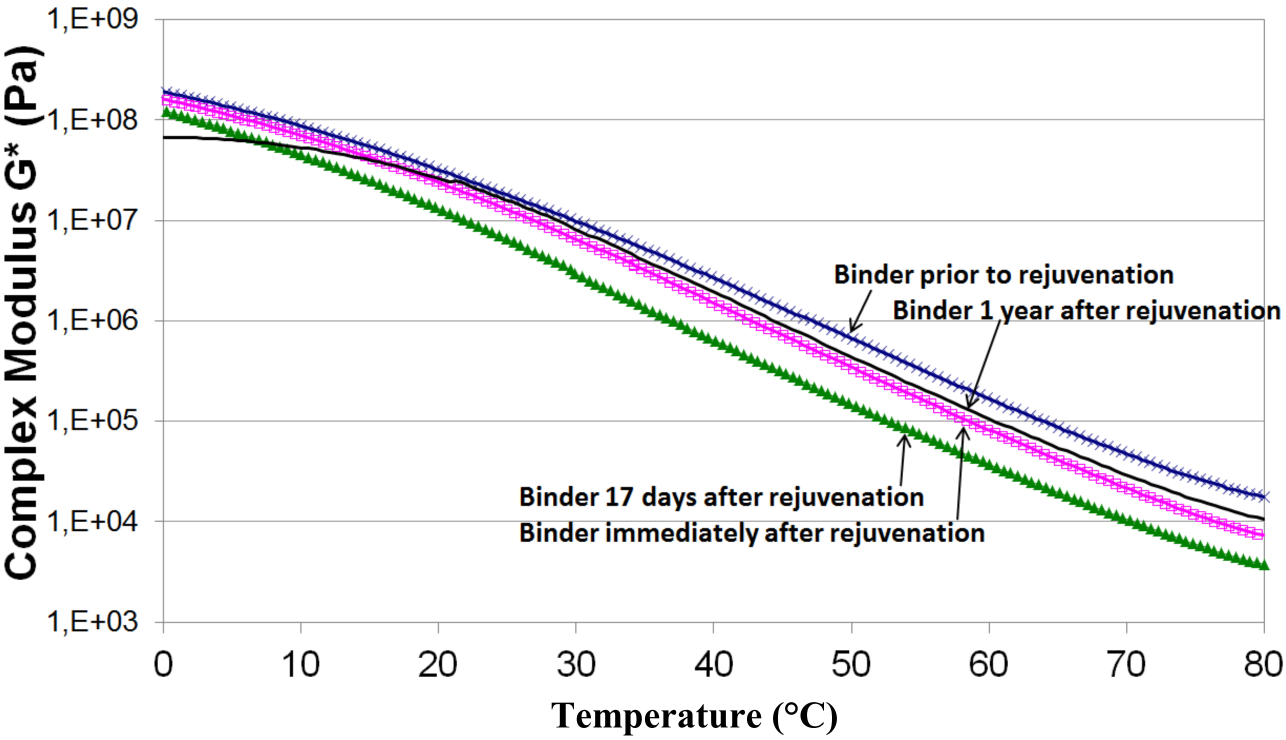

Fig. 9 Complex modulus versus temperature

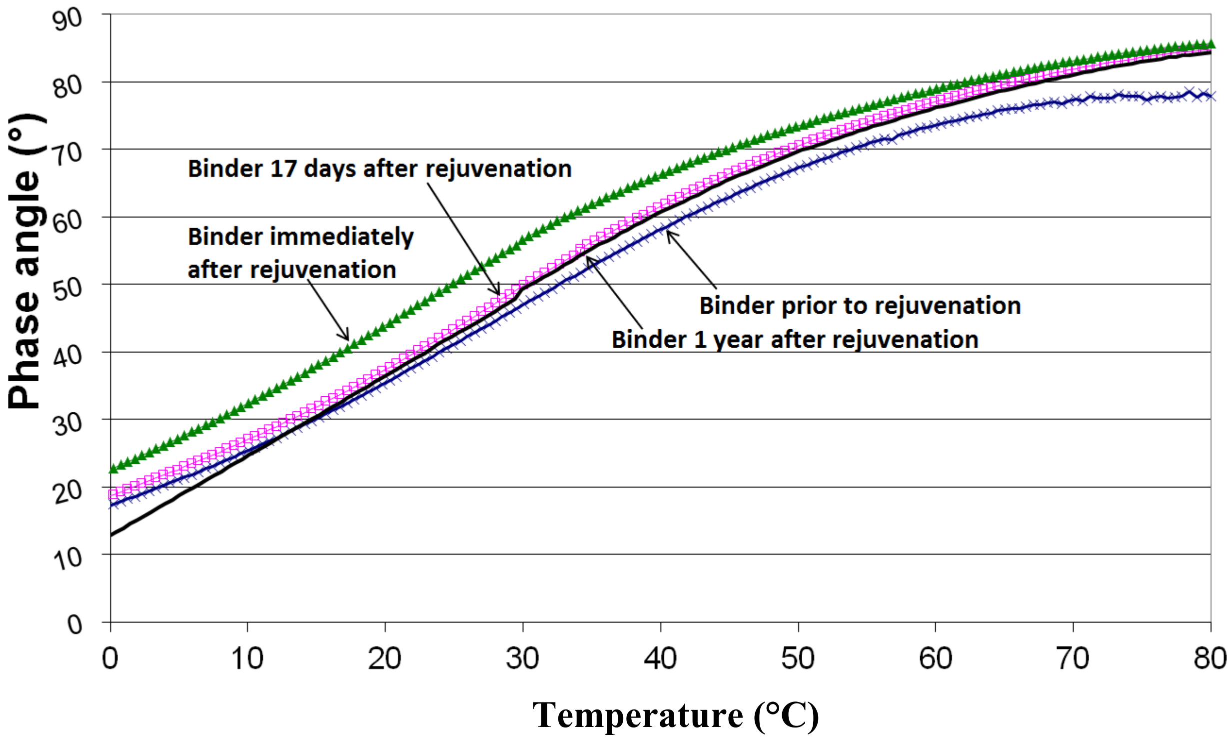

Fig. 10 Phase angle versus temperature

These graphs show the existence of two stages. In the first, between rejuvenation and 17 days, the complex modulus (or rigidity modulus) falls, which is the result of softening of the binder, and the phase angle increases which is the result of an increase in the viscous portion of its rheological behaviour. It is very likely that this softening stage continues during the weeks that follow, and is revealed by the DSR in a much more precise way than by the penetration values or softening point.

In the second stage, the opposite changes take place: the complex modulus increases and the phase angle decreases, which indicates a reduction in the viscous portion of rheological behaviour.

After a year in situ, the penetration of the rejuvenated binder is similar to that of the binder in the RAP, from which one can assume that the rejuvenating effect would be practically undetectable.
DSR characterisation after one year gives plots of the complex modulus and the phase angle against temperature which are between those of the binder in RAP and the binder after rejuvenation.
To summarise, the rejuvenation effect of the additive in early age led to a softening of the binder in the first few weeks. We can assume that the hardening that appeared in the second stage is the result of the gradual attenuation of the rejuvenation effect.
After one year, the rejuvenation effect that is still apparent from the rheological characteristics is probably due to the added binder rather than the rejuvenating agent. However, we can assume that use of the rejuvenating agent has delayed the hardening of the binder, and therefore extended the duration of the effectiveness of the rejuvenation procedure compared to the use of pure bitumen.

4 Conclusion

Chromatography and rheological techniques are of great value for understanding the changes that occur in a binder during recycling. Their benefits have been confirmed with regard to the use of a rejuvenation agent that contains compounds other than bitumen.
The changes that affect a bituminous material that has been rejuvenated using a bitumen emulsion can be evaluated empirically by monitoring the penetration and softening point of the binder recovered at different stages of ageing. What is observed is a gradual hardening of the binder, until it returns to the characteristics of the binder prior to rejuvenation.
When a rejuvenating agent manufactured from renewable resources is added, ageing of the binder is governed by a two-stage mechanism which we have been able to observe by applying chromatography and rheological techniques. The rejuvenating effect, which is still clearly apparent after one year of ageing in situ, seems to last longer than that produced by a pure bitumen emulsion.

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