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Rheological and phase behaviour of paraffin wax/bitumen blends with thermal storage characteristics

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ABSTRACT

This paper analyses the thermomechanical properties, heat storage characteristics and compatibility of bitumen blends with a paraffin wax, having a melting point around 60 °C, as phase change material. To that end, temperature sweeps in the linear viscoelastic range, technological properties, Modulated Differential Scanning Calorimetry (MDSC), and cross-polarised optical microscopy observations were carried out on blends and pure compounds. The obtained results reveal a partial compatibility between the compounds and the development of a multiphasic microstructure, where the paraffin-rich or bitumen-rich domains form the continuous phase depending on the concentration, with the phase inversion around 20 wt% wax. Below this threshold concentration, the disperse paraffin-rich phase acts as filler that reinforces the continuous bitumen matrix until it reaches the melting transition. Above the critical concentration for the phase inversion, the continuous paraffin-rich phase controls the rheological response. However, both phases retain their own identity and show their individual transitions and relaxations. Despite the partial compatibility, a high degree of crystallinity is found, especially for high paraffin contents, which would result in a significant capacity to store thermal energy, for applications such as solar thermal collection or thermoregulation materials for buildings, etc.

1. Introduction

Bitumen is a by-product obtained by treating the heaviest fraction during the crude oil distillation process, which presents a very complex chemical composition, mainly constituted of hydrocarbon molecules, together with small amounts of other heteroatoms (sulphur, nitrogen and oxygen) [1–3].

The adhesive, thermorheological and waterproofing properties of bitumen make it a suitable material for civil engineering long-established uses [4,5]. The most extended traditional application of bitumen is as a binder for mineral aggregates in road paving construction, but it also has been extensively used in bitumen-based roofing and waterproofing membranes and, less often, in other related applications (coating for water pipes, bitumen paints, sealing materials, etc.) [1,6].

The forthcoming development of the petrochemical industry depends in part on the commercialization of new products and technologies designed to improve the energy efficiency. In this sense, these trends are pushing towards the transformation of crude refineries into diversified energy parks where renewable energy technologies tend to be integrated. This is all encouraged by the growing prices of energy forcing the industry and public administrations to design strategies oriented to save energy and reduce energy losses. Therefore, there is an economic incentive to develop new energy efficient technologies of thermal energy storage, where new low cost and effective materials are required. In relation to this, recent publications have explored the feasibility of using bituminous products in energy field applications, taking advantage of its black colour that gives rise to a low reflectance and, therefore, to a high solar absorption capacity [7–9]. As a result, on the one hand, emerging technologies such as solar pavements may turn roads into an environment-friendly energy harvesting system and, on the other hand, modified bituminous based membranes can be potentially employed to build novel passive thermal regulation materials for building applications [9]. A common aspect between these two technologies is the use of the solid-to-liquid phase change materials (PCMs), which are able to store/release large amounts of thermal latent energy during the melting/crystallization processes, in a narrow temperature interval. In this sense, the use of phase change materials (PCMs) result very attractive for both solar thermal energy harvesting and thermoregulation proposes [7]. Even though three categories of solid–liquid phase change materials can be found in the market (organic compounds,

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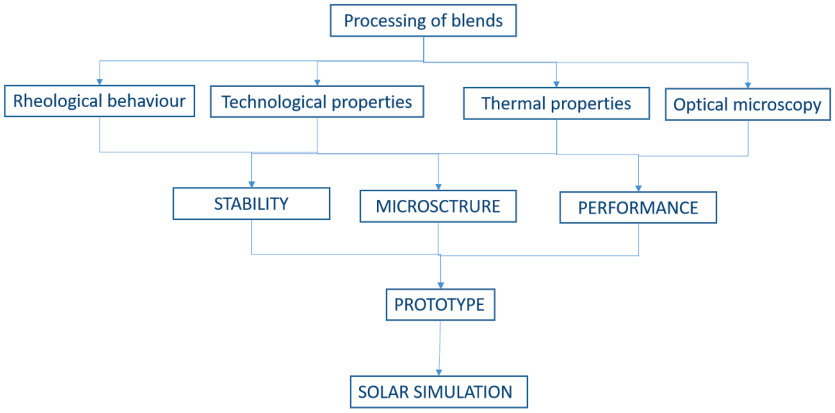

Fig. 1. Experimental design for this study.

inorganic salt hydrates and eutectic compounds), organic PCMs are the most efficient ones and, therefore, preferred for energy applications [10]. More precisely, paraffin waxes have received considerable attention to that end because of some unique features such as large energy storage density, low supercoiling, good chemical and phase change stability, low cost, etc. [11].

In a simplified way, PCMs can be dispersed homogeneously throughout a supporting engineering material, such as bitumen, by two methods: direct incorporation or previous encapsulation of PCM before mixing. In general, the addition encapsulated PCM is considered a more mature technology by means of which bituminous materials have been successfully modified to provide them with new thermal functionalities [11]. Thus, in the case of pavements, microencapsulated PCMs, at selected phase change temperature have proven to be effective to dampen temperature changes in roads and, then, can contribute to minimize the distresses related to extreme performance temperatures, such as rutting and cracking [8]. In addition, they can be also employed to build road pavement solar collectors systems where the harvested solar energy can be further employed in buildings, reducing the energy consumption [9,11]. Regarding building applications, encapsulated PCM in roofing materials may work as de-icing or thermo-regulating agents contributing to thermal comfort and energy savings [8].

However, the technology of PCM encapsulation presents a number of drawbacks that may limit its implementation at an industrial scale [8,10]. Firstly, the complexity of the methods used to obtain the microcapsules represents a significant cost overrun that has an impact on the product's final price. Moreover, the low thermal conductivity of the compounds used in encapsulation significantly decreases the heat transfer rate and, consequently, reduces the efficiency of the heat storage and release processes. Finally, the presence of the protective shell reduces the effective concentration of the PCM in the microencapsulation, often exceeding 20% of the total weight [8].

Therefore, even though the direct addition of PCM to bitumen is a less widely-used technology, it may prove to be a lower cost production method, and would also avoid the thermal resistances of the shell surrounding the PCM core that delay the heat transfer process.

Unfortunately, the lack of knowledge about the miscibility or compatibility between bitumen and the selected PCM limits the development of such products at an industrial scale. On the basis of the extensive experience of polymer bitumen modification in the literature, an intermediate solubility of PCM and bitumen is needed for energy storage applications, i.e. between the two limiting cases of perfect and totally absent solubility [4]. If both components are fully miscible, PCM molecules would be dissolved in the bitumen at molecular scale, limiting their ability to crystallize and, then, losing the latent heat storage capacity. By contrast, in the case of very low solubility, the resulting dispersion would present a very high trend towards phase separation. This would result in lower mixture quality that would lead to poor performance and more vulnerability to leakage of liquid PCM. Therefore, for an adequate implementation, a partial solubility and compatibility between bitumen and PCM molecules is required to achieve a homogenous dispersion at a micro scale. Therefore, PCM morphological structure is preserved and, then, its physical properties and especially crystallinity are retained [4,5,12,13].

Among all theoretically proposed PCMs, paraffin waxes are chosen for a variety of reasons including low cost, negligible supercooling, chemical inertness, high specific phase change enthalpy, small segregation of components, and small changes in structure during transitions, low vapour pressure, etc. The goal of this paper is to assess feasibility of using blends of a model bitumen and a paraffin wax, as PCM for thermal storage applications, in terms of compatibility between both compounds and thermorheological properties. To that end, binary mixtures were prepared over the complete compositional range (0–100 wt%) and analysed by means of rheological measurements, differential scanning calorimetry, technological properties, and cross-polarized optical microscopy to determine the phase morphology. Depending on the concentration range, the results will be of great significance for diverse thermal energy-related applications. Thus, at low PCM content, the obtained outcomes could be potentially applied to thermal solar pavements in order to harvest solar energy or dampen extreme temperature peaks. At high PCM concentration, the results would be of interest for the design of novel bitumen-based membranes for solar capture and energy storage for thermoregulation of buildings.

2. Experimental

A schematic illustration of an experimental design for this study is shown in Fig. 1.

2.1. Materials

As phase change material, a commercial paraffin wax was selected, with melting temperature around 60 °C supplied by Panreac-AppliChem (Spain). In this study, a paving bitumen with penetration grade within the range 100/150 were used as base material for the mixture formulation and was gentility donated by REPSOL S.A. (Spain). This binder has a ring and ball softening point of 41.0 °C, a penetration of 105 dmm, and a SARA composition of 7.4 wt% saturates, 57.6 wt% aromatics, 15.1 wt% resins and 19.9 wt% asphaltenes, and presents.

2.2. Sample preparation

Bitumen/paraffin wax mixtures were prepared by hot blending at 150 °C using a rotor–stator homogenizer (Silverson L5M-A) working at 3500 rpm for 15 min. Both compounds were previously tempered at the processing temperature and, next, approximately 250 g of each

formulation were blended in the high-shear device to achieve sample macroscopic homogeneity. After mixing, the resulting dispersions were separated in small containers and let cool down to ambient temperature. As for the nomenclature, bitumen/paraffin wax mixtures were labelled as BP followed by wax concentration (e.g., BP5 is a mixture containing 5 wt% paraffin wax).

2.3. Tests and measurements

2.3.1. Rheological and technological characterisation

The rheological characterisation of blends and pure components was carried out in the following two different rheometers and suitable geometries, depending on the testing temperature range:

- A controlled-strain ARES-G2 rheometer (TA Instruments, USA) was employed for tests from −80 to 30 °C. In this case, rectangular torsion bars were used, having dimensions of 50.0 ± 0.1 × 12 × 2.65 mm.
- A controlled-stress Physica MCR-301 rheometer (Anton Paar, Austria) was used from 30 °C up to the maximum possible temperature for reliability in the measurements, with a profiled plate-and-plate geometry of 25 mm in diameter, and with 1–2 mm gap.

In both cases, oscillatory-shear temperature sweep tests, were performed at a fixed frequency of 10 rad/s, at a heating rate of 1 °C/min, and by selecting strains so as to ensure a linear viscoelastic response within the whole experimental interval.

For the sake of reproducibility of the rheological tests, samples were submitted to the same preparation protocol. Thus, they were heated to 100 °C in an oven for thermal stabilization, poured into cylindrical or rectangular silicone moulds and, then, let them slowly cool down to room temperature and, finally, stored in a freezer at −20 °C before testing. This protocol allows preserving the micro-structure until tests are subsequently conducted. Finally, samples were equilibrated for at least 30 min at the testing temperature, when placed in the rheometer measuring system.

Finally, two selected technological tests typically used for bitumen characterisation (ring-and-ball softening temperature and penetration) were carried on all samples according to EN 1427:2015 and EN 1426:2015 standards, respectively.

2.3.2. Optical microscopy

Polarised optical microscopy was used to study the morphology and microstructure of the bitumen/paraffin wax blends by means of an Olympus BX51 (Japan) microscope coupled to an LTS-350 Heating-Freezing Stage controlled by a Linkam TP94 (Linkam Scientific Instruments, UK). Small amount of sample was placed on standard microscope slides (76 × 26 mm) and heated up to 100 °C for 5 min on a Heating-Freezing Stage. Then, samples were cooled down at the controlled rate of 1 °C/min for observation at 25 °C under crossed polarisers.

2.3.3. DSC

Modulated Differential Scanning Calorimetry (MDSC) tests were carried out on all samples by means of a Q-250 DSC calorimeter (TA Instruments, USA). Tests were carried out under N_2 atmosphere at a flow rate of 50 ml min^{-1} using 10–20 mg samples sealed in hermetic aluminium pans. Measurement cycles were carried out with a heating and cooling rates of 3 °C per minute, with a superimposed sinusoidal thermal oscillation having an amplitude of ± 0.5 °C and a period of 60 s. In order to ensure the same recent thermal history, samples were heated up to 120 °C for 10 min and, then, subjected to the cooling ramp up to −80 °C, kept at this temperature for 10 min to reach the thermal equilibrium, and, finally, to the heating cycle to 120 °C.

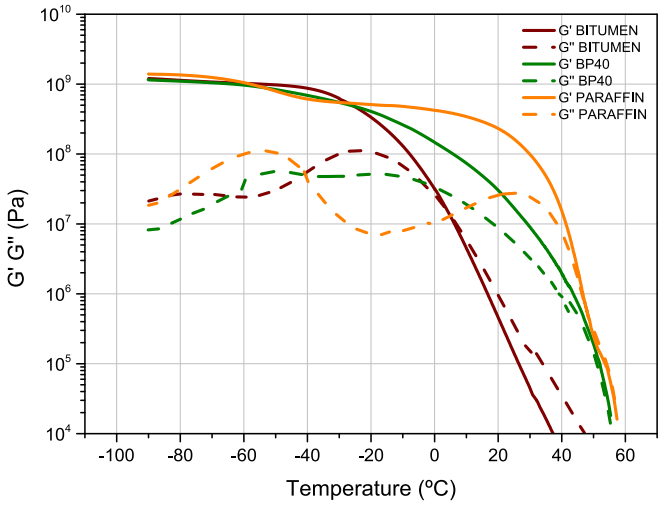

Fig. 2. Evolution of the elastic (G') and viscous (G") moduli, obtained from temperature sweep tests in oscillatory shear, at 10 rad/s, for neat bitumen, paraffin wax and their mixtures, at low temperatures..

3. Results and discussion

Temperature sweep tests in the linear viscoelastic region combined with MDSC measurements are commonly used not only to characterise the viscoelastic and thermal properties of materials as a function of temperature but also to provide reliable information about thermo-rheological and structural transitions [1–2,6].

Fig. 2 reports the evolution of elastic and viscous moduli for neat bitumen, paraffin wax and a selected binary mixture BP40, at the constant frequency of 10 rad/s.

As shown, at low temperatures, the glassy region is mainly observed for all the samples, which is characterised by constant values of G' of roughly 1 GPa, clearly larger that G" [1,14]. As temperature increases, a crossover between the elastic and viscous moduli happens. Then, both moduli undergo a notable decrease of several orders of magnitude, tending to reach the terminal or flow region, at higher temperatures. However, notable differences among samples can be found that deserve to be analysed individually. While neat bitumen displays the well-known direct transition from the glassy to the Newtonian behaviour and the absence of a plateau or rubber-like region [14], paraffin wax and the binary mixture present a more complex evolution, due to the presence of several intermediate stages [15].

3.1. Thermorheological behaviour of paraffin wax: Phase transitions

There are few publications in the way of characterizing the thermorheological behaviour of industrial paraffins and n-alkanes, due to the experimental difficulties associated with the low-temperature fragility, the low molecular weight and the unusual phase behaviour. According to the data presented in the literature [16,17], the evolution of the rheological behaviour with temperature, shown in Figs. 2 and 3, can be regarded as typical and representative of other industrial paraffins and n-alkanes. In general terms, it is characterised by the presence of three distinct regions:

- Firstly, in the low temperature zone (approximately below 30 °C the so-called crystalline region appears, which corresponds to the glassy state of the mechanical spectrum [15].
- Secondly, at intermediate temperatures, both moduli begin to decrease and, next, undergo a flattening in the slope prior to the melting transition. This points out the so-called mesophase region, where paraffins may present several layered plastic crystalline mesophases or solid–solid transitions [15–18].

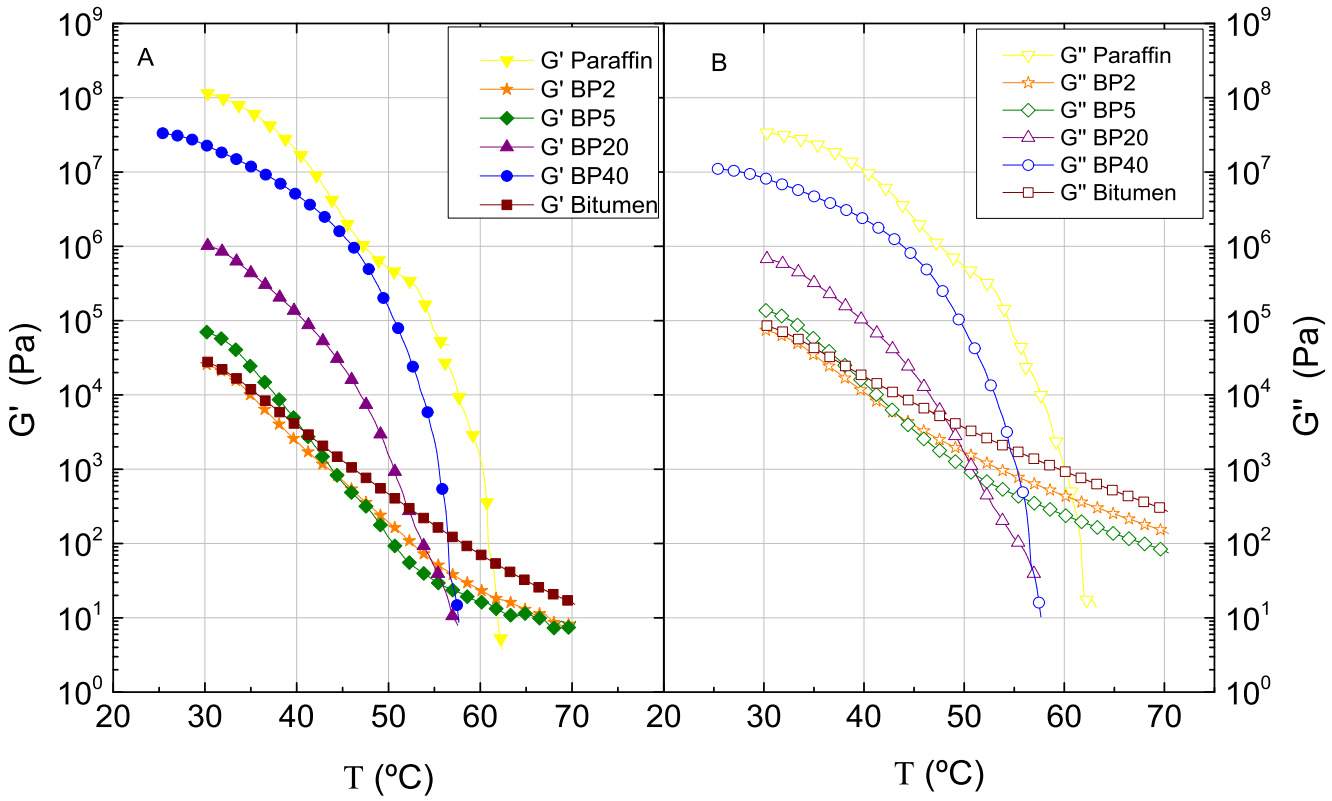

Fig. 3. Evolution of the elastic (G') and viscous (G") moduli, obtained from temperature sweep tests in oscillatory shear, at 10 rad/s, for neat bitumen, paraffin wax and their mixtures, at intermediate and high temperatures.

- Finally, at high temperatures, as a consequence the melting of the ordered structures, both moduli present a sharp drop and reach the terminal region of the mechanical spectrum, referred to as the isotropic liquid or melt region [16,18].

The glassy region of the paraffin wax is extended over a wide low temperature interval, as shown in Fig. 2. In the glassy state, as the convolution of chain backbones are largely immobilised, the viscoelastic properties can only reflect local molecular motions. However, the thermo-dynamic equilibrium is not completely reached. Thus, the material may undergo slow transitions due to side-chain motions along with local short range rotations of the main chain. In general, even for pure paraffins, the number of transitions, their magnitude and temperature of the event depend on many factors such as the crystallinity, molecular weight, polydispersity, impurities, thermal history, etc. [16–18].

The paraffin wax used here displays two well defined relaxations in the crystalline region, characterised by two local maxima of the viscous modulus placed at −54.0 °C (accompanied by a subtle drop in G' curve) and 24.8 °C (Fig. 2). In order to analyse the structural origin of these events, this result may be compared with pioneer publications on n-alkanes in terms of molecular weight [19,20]. As it has been widely reported in the bibliography, paraffin waxes are composed of a mixture of linear n-alkanes with mainly saturated isomers having minimal branching [21]. Even though a precise determination of the molecular weight has not been performed on our sample, a roughly calculation of the molecular composition can be done from the melting peak temperature and, therefore, the paraffin wax may be considered a mixture of alkanes in the range C25-C28 [22]. Thus, according to the data reported for n-alkanes and pure polycrystalline n-paraffins [19,20,23], the observed G" peak, at −54.0 °C, is attributed to the so-called α-relaxation of polyolefins. Thus, considering the estimated molecular composition of the paraffin wax, this peak temperature of viscous modulus approximately matches the correlation reported for pure n-paraffins [19]. In addition, this transition also follows the expected quantitative dependence with the melting point for n-hydrocarbon molecules, since the obtained temperature ratio $T^{max\_G"}/T_m = 0.65$ fits to the range of 0.6–0.65, as it has previously been established [20].

The molecular origin of the α-relaxation is attributed to motions of the interfacial regions, e.g., tie molecules, folds, loops etc. which require chain mobility in the crystal as a precursor [24,25]. This transition is typically observed for polyolefins with a high crystallinity (above of 55 %) and is associated with the crystalline domains with an ordered lamellar structure [24,26]. However, even though paraffins and polyethylenes are constituted of the same chemical repeating unit (–CH_2-) and present a similar molecular arrangement of the crystalline phase, the temperature ranges of the α-relaxation are quite different. Therefore, for n-paraffins this transition appears at about 75 °C below those of polyethylenes due to the huge differences in the molecular weight. Thus, the much larger chain lengths of polyethylenes give rise to chain folding at the crystal surface and shifts the interfacial relaxation to higher temperatures [23,25]. Finally, it is important to note that according to Fig. 4 the α-transition is not detected by DSC, probably due to the small group chain segments involved in this process.

On the other hand, Fig. 2 also points out a second maximum in G" for paraffin, placed at 24.8 °C, accompanied by an abrupt change in the slope of Ġ and followed by the decay process of both viscoelastic functions. This temperature approximately matches the onset of the endothermic DSC peak of the heating scan shown in Fig. 4, and can be considered the transition from the highly ordered crystalline region to the mesophasic phase, prior to the melting [15,27]. Then, from this temperature, a series of weakly structured mesophases are triggered by heat-induced segmental mobility in the crystal lattices, in which the rotational degree of freedom of molecules is increased while retaining their positional order [15,18]. These mesophases are usually referred to as rotator phases, because of the higher degree of orientational disorder

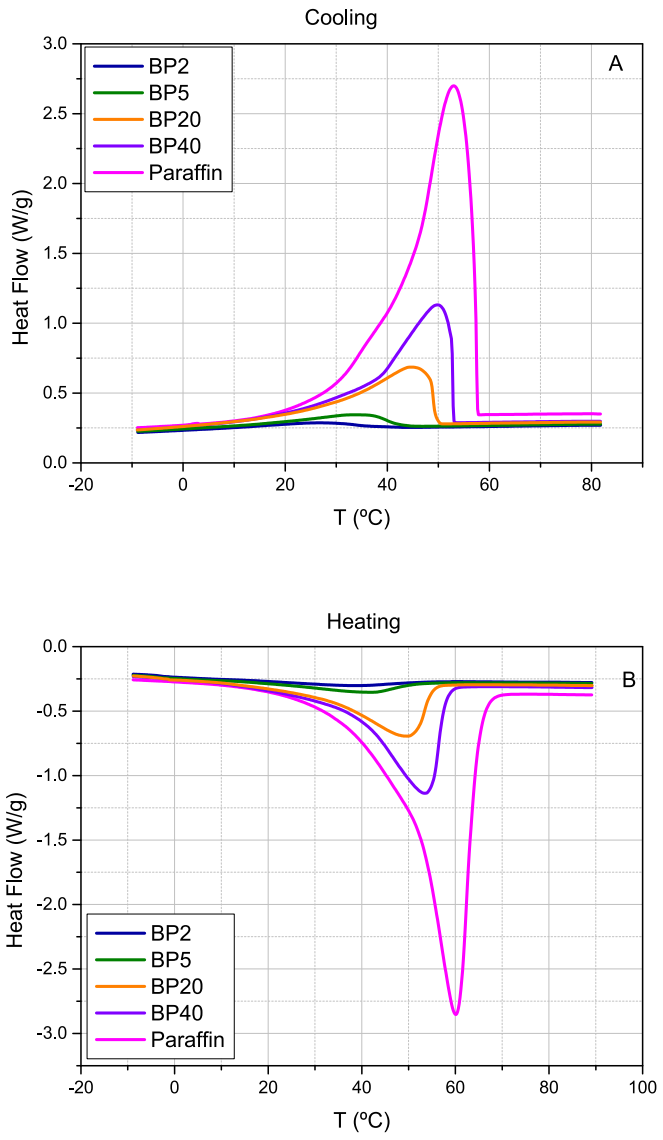

Fig. 4. DSC thermograms for the different systems studied: (a) cooling cycle (b) heating cycle.

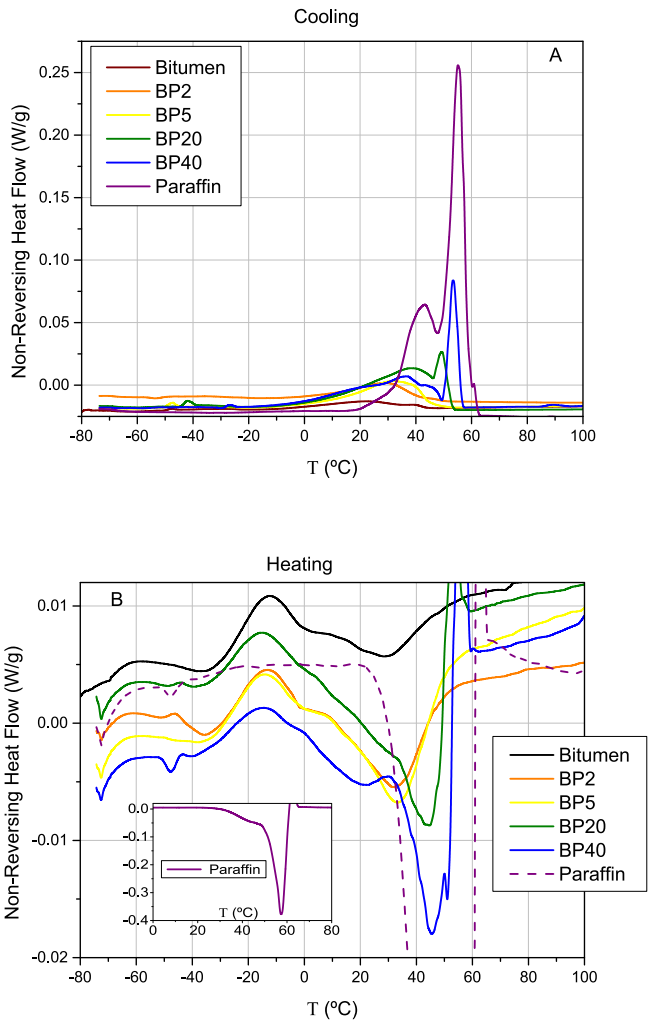

Fig. 5. Non-Reversing Heat Flow curves obtained from MDSC experiments for the different systems studied: (a) cooling cycle (b) heating cycle.

of molecules that favours their rotation along the main chain [18,27]. From a rheological point of view, the appearance of these mesophases give rise to a flattening in the slope of both elastic and viscous moduli prior to the melting transition, as can be seen in Fig. 3. This indicates that the developed mesophasic structures are clearly softer than the fully ordered crystalline phase, before the melting happens. In general, this rheological behaviour is similar to that reported by other authors for pure n-alkanes [15,17,18].

However, the structural evolution of the mesophase is much more complex than a progressive transition to the fluid-like behaviour, since up to five intermediate phases have been identified for n-alkanes in the literature [15,27]. Therefore, several solid–solid or polymorphic phase transitions may happen in the mesophase region depending on the composition, molecular weight, odd or even carbon numbers, etc. [18]. Thus, it has been proven that paraffin waxes will pass through at least one of these phases before the fusion, exerting a significant impact on the thermomechanical properties of the material [15,18,26]. In general, the reported evolution of the viscoelastic functions with temperature is consistent with DSC scans, presented in Fig. 4. As may be observed, DSC curves of the neat paraffin wax exhibit a wide asymmetric endothermic and exothermic peaks mainly associated to the melting of the crystalline structures (during the heating cycle) and further crystallization from the melt (in the cooling scan) [28]. On the one hand, the broad melting and crystallization ranges are indicative of the presence of mixtures of molecules with different lengths and melting points [29]. On the other hand, the signal asymmetry and large difference between the onset and peak temperature of the endothermic event suggests the presence of other overlapped first order transitions [30].

In fact, it has been widely reported that paraffin waxes often present an additional peak in the heating thermogram just below the main melting, attributed to solid–solid or polymorphic phase transitions as a consequence the movement of the material into its initial rotator phase [26,28,29]. The presence of overlapped transitions is confirmed in the non-reversing component of the modulated heat flow, that allows the separation of these events.

Then, Fig. 5 clearly shows that, in the cooling scan, exothermic peak is split into a doublet whereas a shoulder appears in the heating curve, to the solid–solid phase transitions [29,30]. Therefore, the temperature interval from 30 to 55 °C, where the flattening in the slopes of G' and G", happens (Fig. 3), matches with the premelting solid–solid transition range in Fig. 5A, pointing out the development of the intermediate mesophase stage [21]. Finally, at temperatures close to the peak maximum of the DSC melting scan, a sharp drop in both moduli is noticed due to the extensive melting process. As a consequence of the above mentioned results, the exothermic enthalpy for the paraffin wax (209 J/g), which is consistent with the values found in the literature for

Table 1
Glass transition temperature (T_g^{MDSC}) and cold crystallization temperature (T_{cc}^{MDSC}) of blends obtained from MDSC experiments.

	T_g^{MDSC} (°C)	T_{cc}^{MDSC} (°C)
Bitumen	−30.8	−12.2
BP2	−29.5	−13.1
BP5	−31.0	−13.8
BP20	−32.4	−14.8
BP40	−35.5	−14.9

paraffin waxes of similar composition, is the summation of both first order events [15,28].

3.2. Thermorheological behaviour of neat bitumen

As shown in Figs. 2 and 3 neat bitumen displays the expected rheological evolution, characterised by a direct transition from the glassy to the flow region, as temperature increases [14,31]. Then, two distinct temperature regions can be considered and associated with two different rheological relaxation mechanisms, according to the colloidal model of bitumen [1].

At high temperature, a gradual transition from a viscoelastic material to a viscous liquid is noticed, usually termed as bitumen α-relaxation happens (note that this is different to the α-relaxation of the paraffin phase). This bitumen relaxation has been traditionally associated to the Brownian motion of the asphaltenes micelles into a continuous molten maltenic matrix and its temperature point is difficult to evaluate by temperature sweep tests [1,12].

Besides, at low temperatures, a wide glassy region is clearly noticed, showing the presence of a major peak of G" centred at −24.2 °C. Given the complex chemical composition and the developed microstructures in bitumen, it is difficult to correlate this maximum with molecular arrangements. However, from a practical point of view, for bituminous materials, it is widely accepted that this peak corresponds to the "mechanical" glass transition temperature, at the selected frequency, which accounts for the onset of the glassy domain [31]. Then, this process evidences the so-called bitumen β-relaxation mechanism mainly associated to the vitrification of maltene compounds with a minor influence of their coupling with the dispersed asphaltene micelles [1,32]. In addition, the broad shape of this curve is considered a general feature of bitumen because of the heterogeneous freezing of different compounds that leads to the coexistence of liquid and glassy micro-phases [14]. However, from a microstructural point of view, the physical interpretation is not so simple since bitumen develops time-dependant structures not easily detectable with rheological techniques. In this sense, all samples were also subjected to Modulated Differential Scanning Calorimetry (MDSC), a technique that allows the separation of some overlapping thermal events and provides information about minor transitions of bitumen [1–3,31]. Thus, the non-reversing component of the heat flow displays several well define thermal events (Fig. 5) in which bitumen SARA compounds (saturates, aromatics, resins and asphaltenes) are ordered upon cooling from melt. As can be seen in Fig. 5, a broad endothermic background is clearly observed for neat bitumen from − 60 °C to 80 °C, associated to the melting of ordered mesophasic bitumen structures mainly composed of aromatic compounds and, in a minor extent, to crystallized saturates. In addition, several exothermic peaks are superimposed on the broad endothermic background, with a major exotherm centred at − 12 °C, associated to cold crystallization processes of segments of saturated and aromatic compounds, according to their molecular weight [1–3,31]. This is a time dependent phenomenon where small imperfect crystals that developed in the cooling cycle now act as nucleating [33].

In addition, the peaks of the derivative reversing heat capacity allow calculating a well-defined glass transition temperature (Table 1), resulting from the overlapping of glass transition processes corresponding to saturates and aromatics in the maltenic fraction [2,31,34].

Once again rheological transitions correlate with MDSC results. Therefore, above the frozen state, defined by the DSC glass transition, chain mobility of some bitumen compounds is increased allowing the cold crystallization of crystallizable segments ($T_g^{MDSC} < T_{cc}^{MDSC}$), making possible the refereed bitumen β-relaxation.

3.3. Thermorheological behaviour of paraffin wax/bitumen blends

Figs. 2 and 3 point out that binary mixtures present an intermediate rheological behaviour between that of bitumen and paraffin wax, that deserves to be analysed separately in the low and high temperature regions.

3.3.1. Thermorheological behaviour at low temperatures

In the low temperature interval, the binary mixture BP40 also displays a wide glassy region of the mechanical spectrum, with the presence of transitions arising from both components. Therefore, it is expected the development of a multiphasic system in which both phases contribute to different extents to the bulk thermomechanical properties depending on the testing temperature and miscibility [4]. In addition, given its high paraffin wax concentration (40 wt%), which is highly crystalline (see melting peak in Fig. 4), this phase will exert a major influence on the thermomechanical response [1].

Then, Fig. 2 shows the presence of two G" maxima at temperatures close to that of the pure compounds. Thus, the lower temperature peak in BP40, centred at −49.0 °C, matches the subtle drop in G' curve as in the case of the wax paraffin and, therefore, is associated to the α-relaxation of the paraffin phase. The reduced intensity of this relaxation, compared with the pristine paraffin, is obviously due to the lower concentration in the blend. It is noteworthy that the transition temperature of this event is shifted to a higher value, a fact that seems to indicate molecular interactions between some bitumen molecules and the paraffin wax. This is not surprising since saturates compounds of bitumen are chemically similar to paraffin wax and, therefore, thermodynamically compatible. In this sense, it has been widely reported that the temperature of the paraffin α-transition increases as the lamellar thickness does [13], a fact that happens when other molecules diffuses within the crystalline lamella. Even though, only limited experimental evidence of this behaviour can be found in the literature, this effect has been reported for oil/paraffin wax oleogels, where oil molecules are trapped between the crystal lamellae [16].

The glassy modulus, taken as the lower asymptote for the temperature-dependent complex shear modulus, is a dynamical property and valuable parameter to characterise the low temperature rheological behaviour. Then, the glassy modulus of samples results slightly increased with paraffin wax concentration (1.12, 1.20 and 1.40 GPa for bitumen, BP40 and paraffin, respectively) attributed to a larger proportion of crystalline material in the mixture [35]. These values are in line with other reported data for similar asphaltic compounds [1,6,14].

Finally, by comparing BP40 curves with those of neat bitumen, the second peak, centred at −19.2 °C, is attributed to previously mentioned β-relaxation of the bituminous phase, that marks the "mechanical" glass transition of the mixture. Paradoxically, this transition is shifted to a higher temperature value with respect the neat bitumen while the calorimetric glass transition temperature (T_g^{MDSC}) slightly decreases with paraffin content, as can be observed in Table 1. However, both parameters are obtained from different techniques. Thus, the rheological glass transition is a consequence of the mechanical relaxation of the components of the mixture and their contribution to the thermomechanical properties, while calorimetric glass transition is associated to amorphous phases in the blend [3,31]. Then, the evolution of the mechanical T_g reveals a coupling effect of bitumen with the paraffin wax phase, because the paraffin wax phase still remains in the crystalline state in the blend. Thus, the paraffin transition from the crystalline to the

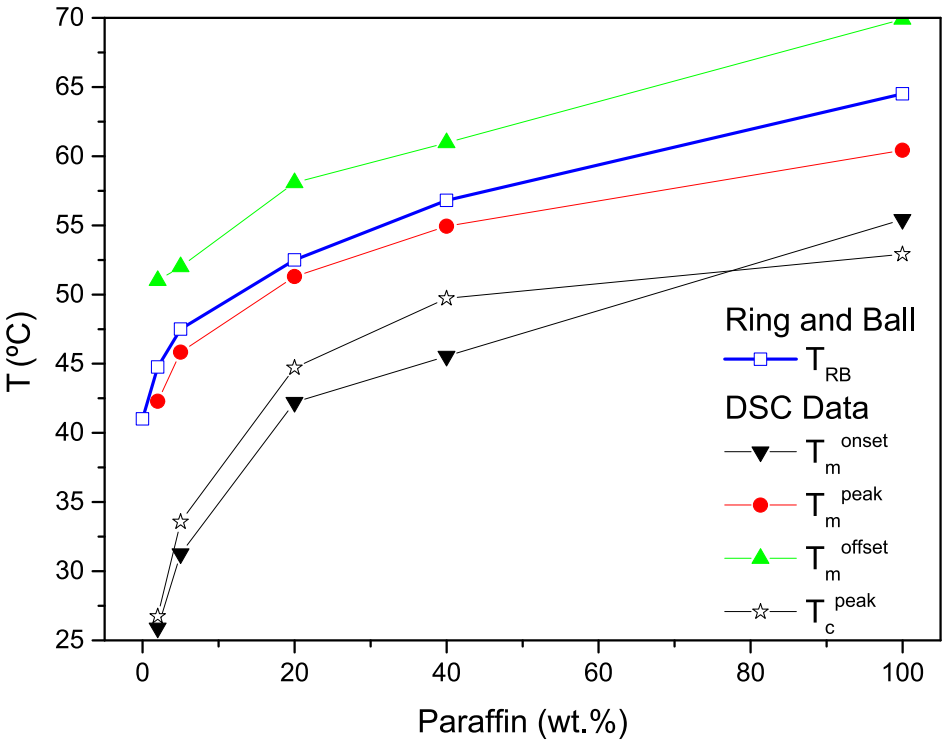

Fig. 6. Effect of paraffin concentration on the Ring and Ball softening point (T_{RB}), and crystallization (T_c^{peak}) and melting temperatures (T_m^{onset}, T_m^{peak} and T_m^{offset}) from DSC measurements.

mesophasic phase of the paraffin wax, that marks its softening, happens at much higher temperatures leading to the delay of the drop of the viscoelastic moduli [34]. By contrast, the decrease of T_g^{MDSC} of the bitumen phase with paraffin wax concentration points out a modification in the amorphous bitumen phase, pointing out a partial compatibility between both compounds [3,4].

3.3.2. *Thermo-rheological behaviour at intermediate and high temperatures*

At temperatures above the bitumen β-relaxation (mechanical glass transition), a decay of elastic and viscous moduli takes place for BP40, leading to the mentioned intermediate rheological behaviour between pristine compounds (Fig. 2). However, even though bitumen is the major component of the mixture, the thermomechanical response is much closer to that of paraffin wax. Thus, for example, by analysing the crossover temperature that marks the transition from the predominant elastic to viscous behaviour, BP40 tends to reach the value to the paraffin wax, pointing out a major influence of this compound in the bulk rheological properties.

A more detailed analysis of the evolution of the linear viscoelastic properties with temperature and concentration is presented in Fig. 3. This figure reveals that bitumen/paraffin blends show a concentration-dependant behaviour where two distinctive rheological responses are clearly distinguished. Then, at low paraffin content (<20 wt%) the evolution of G' and G" with temperature resembles that of neat bitumen, which is characterised by a progressive decrease of both moduli as temperature rises [1,14]. However, this thermomechanical response evolves to a sigmoidal-type profile, as paraffin concentrating rises (Fig. 3). This behaviour has been previously reported for commercial wax-modified bitumens for road paving applications and points out a two-step relaxation process of the bituminous and paraffin-rich phases [5,12,21].

At higher paraffin wax contents (>20 wt%), the sigmoidal shape is so pronounced that the rheological behaviour is qualitatively similar to that of the neat paraffin, where two distinctive decay regimes are noticed at low and high temperature. It is important to note that the intermediate mesophase region, disclosed as a flattening in the slope in the paraffin wax, is no longer observable for these samples.

Consequently, these outcomes seem to indicate notable microstructural changes and a phase inversion with concentration, from a continuous bitumen-rich phase to paraffin-rich phase, approximately at a threshold concentration of 20 wt%.

3.4. *Microstructure evolution with paraffin wax concentration*

From the previous results, it can be deduced that bitumen/paraffin blends are multiphasic systems where both phases contribute in a different way to the bulk properties, depending on the testing temperature and the developed continuous phase. Therefore, the thermomechanical response of the blends is expected to follow a sort of superposition mechanisms related to both phases. Then, both phases partially maintain their individual character and specific transitions, but also undergo associations and interactions that leads to the modification of the macroscopic behaviour [12].

Regarding the paraffin-rich phase, the strong temperature-triggered softening is related to phase change transitions. Thus, as commented in section 3.1, the transition from the glassy crystalline behaviour to the isotropic flow region happens in a wide temperature interval and passes through an intermediate mesophase region, where solid-to-solid transitions of the paraffin chains occurs [15,17,18]. Consequently, in all blends, the drop in the viscoelastic moduli with temperature takes place in multistage and overlapping process where paraffin-rich phase exerts a major influence. Then, as temperature increases, crystalline paraffin chains undergo a first softening stage due to the transition to rotator phases and, next, they go through the melting process that yields a sudden loss of the consistency [1]. The rheological transition to rotator phases is only clearly apparent for pristine paraffin whereas blends undergo a less pronounced softening in this interval. Then, the melting of the crystalline fraction seems to be the dominant factor (Fig. 3). The onset and offset temperatures for the melting process, presented in Fig. 6, have been calculated from the inflection points of the heating

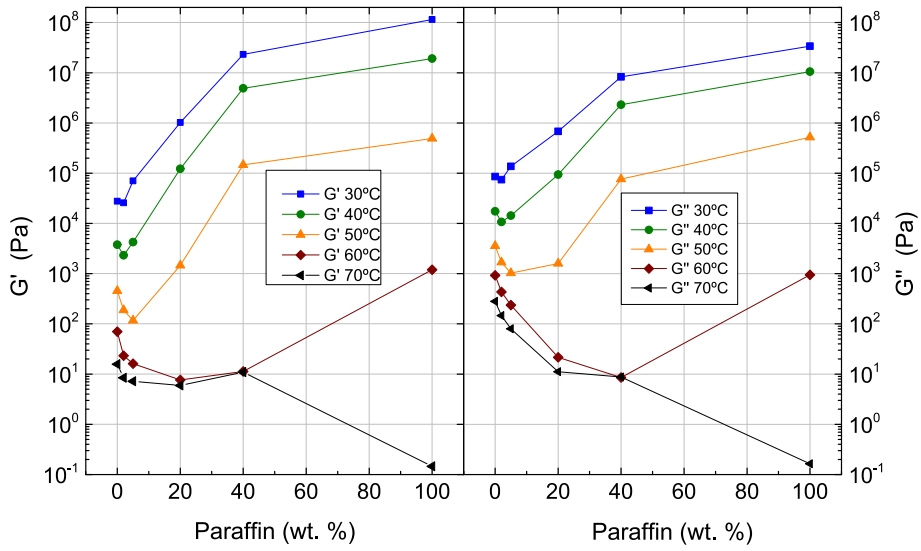

Fig. 7. Evolution of elastic (G') and viscous (G'') moduli, at 10 rad/s, with paraffin wax concentration.

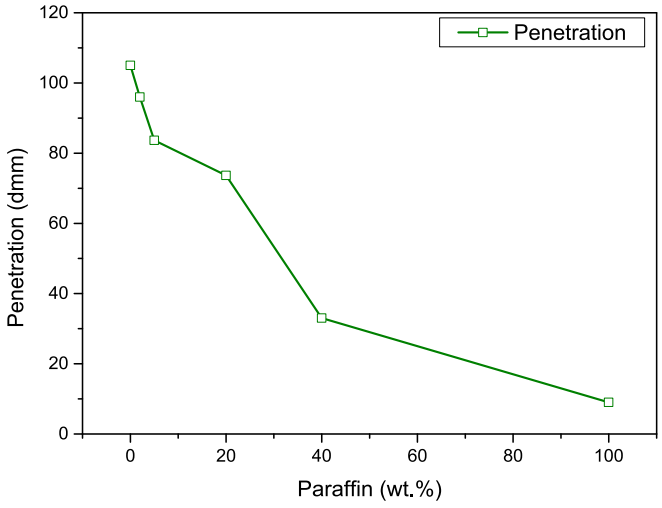

Fig. 8. Evolution of penetration of blends with paraffin wax concentration.

scan, and mark the beginning and the end of this transition. It is important to note that, the melting interval is shifted to lower temperatures as paraffin concentration decreases, a fact that clearly affects the rheological behaviour as explained next.

The isochronal evolution of G' and G'' with paraffin wax concentration, at selected temperatures (from 30 to 70 °C), is shown in Fig. 7, and points out that the physical state and microstructural distribution of the paraffin phase exert a major role in the rheological behaviour in this temperature range.

Thus, at 70 °C, above the melting interval (see T_m^{offset} in Fig. 6), paraffin wax yields a decrease in both viscoelastic moduli, because behaves as low viscosity liquid. By contrast, at low temperature (30 °C), below the melting interval of the crystalline fraction of the paraffin (from T_m^{onset} to T_m^{offset} in Fig. 6), the addition of paraffin rises G' and G'' in the whole concentration interval. This effect is in line with the evolution of the penetration with paraffin wax concentration, as portrayed in Fig. 8.

As penetration can be considered a measurement of the consistency at 25 °C, the reported decrease with concentration indicates a similar stiffening effect. This is consistent with the presence of a highly-crystalline paraffin-rich phase which is much harder than the bituminous phase [12].

At higher temperatures (40–60 °C, see Fig. 7), within the melting interval, the tendency changes. Then, after a slight decrease at low paraffin content, as concentration increases a sharp increase of several orders of magnitude is clearly observed. In general, the decrease of the viscoelastic moduli at low paraffin content is attributed to the presence of softer disperse paraffin domains, due to largest drop of the melting temperature interval (Fig. 6). On the contrary, as paraffin concentration increases, and the melting temperature range is shifter to higher values, paraffin phase is progressively stiffer, leading to the observed rise of both moduli.

On the other hand, Fig. 7 also points out a different evolution of thermomechanical properties at low and high wax concentration. This is attributed to microstructural changes, caused by a phase inversion from a continuous bituminous-rich phase to a continuous paraffin-rich phase. Therefore, at low paraffin content (<20 wt%), the progressive decrease of the viscoelastic moduli with temperature is consistent with the development of a continuous bituminous-rich phase where disperse paraffin-rich phase acts as filler. By contrast, at high concentration (>20 wt%) the notable rise of several orders of magnitude in the viscoelastic moduli with paraffin concentration and the sharp drop with temperature is associated with the formation of a continuous paraffin-rich phase.

Another common bitumen characterization parameter, that provide valuable structural information for the high temperature performance of the binder, is the ring and ball-softening point. Thus, as can be seen in Fig. 7, this parameter is strongly correlated with the melting process of the paraffin-rich phase and points out that the major softening happens at temperatures just above the DSC melting peak temperature, in line with the reported rheological data. In addition, once again, a change in the slope at a 20 wt% paraffin content is indicative of the previously commented phase inversion.

Cross polarized light micrographs, taken at 25 °C, allows for the visualization of paraffin wax crystal microstructure in the blends, since birefringent anisotropic crystals appear bright while amorphous paraffin chains and bituminous phase remain dark under polarized light. Then, Fig. 9 shows the evolution of the microstructure with paraffin concentration and confirms the reported phase inversion.

As observed in Fig. 9E, neat paraffin wax presents large needle-like crystals, developing a highly interconnected three dimensional network structure, in agreement with what was previously reported for macrocrystalline waxes [5,21,30]. This microstructure of paraffin crystals is still apparent for the blend BP40, but with smaller, finer and less developed crystals. By contrast, at low paraffin concentration (BP2 and BP5), a bitumen-rich phase is clearly noticed, where disc-like paraffin

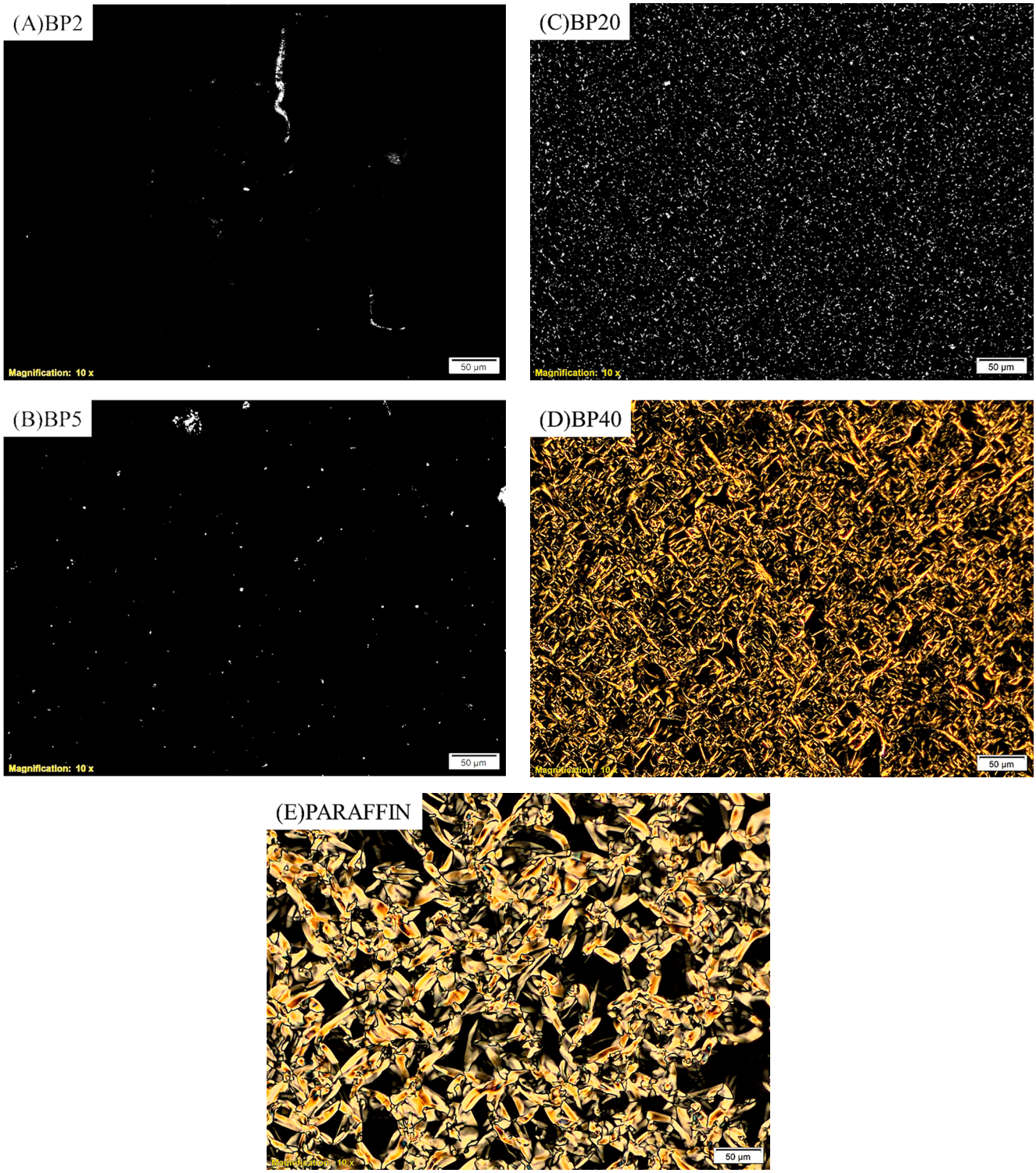

Fig. 9. Cross-polarized micrographs, at 25 °C, of bitumen/paraffin blends and neat paraffin wax.

crystals appear evenly distributed. Finally, BP20 presents an intermediate morphology where irregular flake-like crystals are apparent. However, for this sample, as the dark regions correspond to both bituminous fraction and amorphous paraffin, it is not clear which phase forms the continuous matrix.

3.5. Miscibility and thermal behaviour

It has been shown that both paraffin wax and bitumen maintain their own identity in the blend with separated relaxation and transitions. However, a number of experimental evidences point out a partial miscibility between phases. As regards the bituminous phase, the non-reversing component of the heating MDSC scan may help to shed some light on this issue. Thus, Fig. 5B and Table 1 show the presence of the thermal events associated to the bituminous phase, mentioned in section 3.2, for all blends. However, while the low temperature cold crystallization is always discernible, the endothermic background is overlapped with the phase transitions of the paraffin wax, especially the

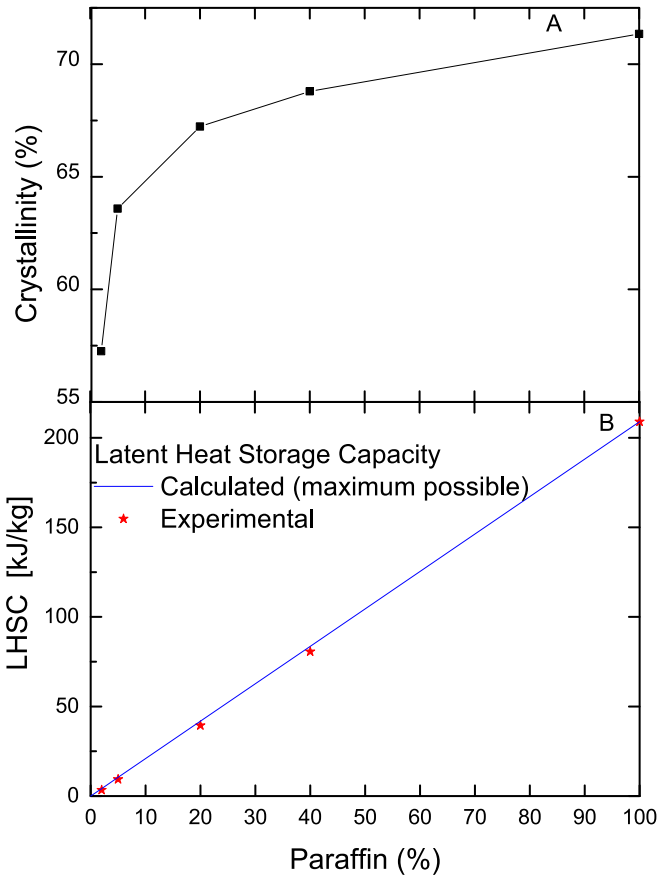

Fig. 10. (A) Evolution of the maximum crystallinity and (B) Latent Heat Storage Capacity, LHSC, of the blends, as a function of paraffin wax concentration.

melting of the crystalline fraction [2,31,34]. Therefore, even though it is clear that bitumen-rich phase is preserved in the blend, it presents some modifications. Thus, both the glass transition and cold crystallization temperatures (T_g^{MDSC} and T_{cc}^{MDSC} in Table 1) are shifted to lower values as paraffin concentration increases, a fact that points out a composition change in bitumen amorphous phases, probably due to mutual diffusion between paraffin wax and bitumen phases [30]. On the one hand, amorphous paraffin wax molecules which present a much lower estimated glass transition temperature (<100 °C out the experimental range), may migrate into the amorphous bitumen phases lowering the T_g^{MDSC} [36]. In addition, some crystallisable maltenic molecules, mainly waxes and saturates, naturally present in bitumen, could also diffuse to the paraffin-rich phase [33]. This result is in agreement with the modification of the crystalline phase of the paraffin, as shown by the decrease of the melting temperature, inversely proportional to paraffin concentration, reported in Fig. 6. Moreover, this outcome is associated with a reduced quality and dimension of the crystals, which is clearly observed in cross-polarised micrographs (Fig. 9) [5].

In addition, it has been calculated the maximum degree of crystallinity of the paraffin phase of blends by comparison with heat of fusion perfectly crystalline polyethylene (293 J/g) and weighted by its mass fraction (Fig. 10A).

According to this, it is clear that the paraffin crystallinity is proportionally reduced by the presence of larger amounts of bitumen, which is in line with the lowering of melting and crystallization temperatures and confirm the partial compatibility. Furthermore, once again, the phase inversion is also reflected by the change in the slope in Fig. 10, at a paraffin concentration of 20 wt%.

Finally, as these blends may serve as a basis for the formulation of thermal storage materials, it is important to note that, despite the wide concentration range analysed, the degree of crystallinity is not modified in a large extent, especially for high paraffin contents. Consequently, this is considered a very positive result since a high fraction of crystallinity means a large capacity to store thermal energy, for applications such as solar thermal collection or thermoregulation of buildings. In this regard, the so-called Latent Heat Storage Capacity (LHSC) is defined from the enthalpy of phase change per kg of the blend and portrayed in Fig. 10B. According to this, all experimental values of LHSC are very close to those calculated for a blend where paraffin maintains its prior crystalline state, due to the mentioned slight crystallinity decrease. In addition, it is worth mentioning that the storage capacity of the blends, at high PCM concentration, are in line with other form-stable phase change materials for thermal energy storage reported in the bibliography [37]. As a result, from both thermal and rheological perspectives, bitumen/wax mixtures are promising base materials for the development of new and cost-effective formulations for energy storage and related applications. Then the results would be of interest for the design of novel bitumen-based membranes for outdoors solar energy harvesting and for indoors thermoregulation of buildings.

4. Conclusions

Bitumen/paraffin wax blends are multiphasic system, where paraffin-rich and bituminous-rich phases form independent domains at a microscale level, showing a certain degree of compatibility. Then, the bulk rheological response is strongly dependent on composition, developed microstructure and temperature. The thermorheological properties and cross-polarised optical microscopy point out two distinct microstructures and a phase inversion at around 20 wt% paraffin content. Then, at low paraffin content, the disperse paraffin-rich phase acts as filler that reinforces the continuous bitumen matrix, until the melting transition is reached in heating tests. Above the critical concentration of the phase inversion, the continuous paraffin-rich phase controls the rheological response.

In general, both compounds in the blends retain their own identity and show their individual transitions and relaxations, but with a modification in intensity and temperature of the events. Thus, the paraffin phase undergoes a characteristic α-relaxation associated to the interfacial regions of the crystalline domains, a transition from the highly ordered crystalline region to a mesophasic phase (rotator phases), and the melting towards the isotropic state. The bitumen-rich phase of blends presents a more complex behaviour where amorphous regions, mesophases and ordered phases go through various temperature dependent transitions that may overlap with melting process of the crystalline paraffin. Then, a wide low temperature glass transition of maltenic amorphous domains is followed by a cold crystallization process of supercooled molecules capable of crystallizing, and overlapped with a wide endothermic melting of multiple ordered structures.

In general, the reported partial compatibility and miscibility allows both phases to maintain their basic morphological structure and, consequently, their physical characteristics. Finally, even though the crystalline fraction of the paraffin phase is slightly reduced, the resulting blends still keep a high crystallinity and, therefore, retrain a large enough latent heat to be used for thermal energy storage, thermoregulation and similar applications.

However, this is only a preliminary study about compatibility and phase behaviour,r and therefore, the reported bled formulations need to be improved in future studies for market-oriented products. Then, additional global stiffness is desirable to formulate a form-stable material able to resist in-service stresses and to avoid PCM leakage. In addition, an analysis and enhancement of thermal conductivity is required to be applied to recover waste heat and for solar energy harvesting.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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