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Penetration testing and thermal behavior of bitumen 35/50 and modified bitumen 13/40

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Abstract. Physical properties of pure bitumen 35/50 and polymer-modified bitumen 13/40 are studied using needle penetration test and differential scanning calorimetry (DSC). In particular, the mechanical response under indentation conditions is achieved as a function of different loads and temperatures. Our results show that lower temperature susceptibility is associated to larger loads but its change is rather small for the tested bitumens. A pure bitumen 35/50 exhibits a single glass transition temperature for different heating rate whereas modified bitumen 13/40 presents two T_g for different heating rate.

1 Introduction

Over the last decades, bitumen heterogeneous viscoelastic materials are subject of a large number of studies ranging from basic research to applications [1,2]. Bitumen is a black or brown highly viscous liquid or semi-solid material present in most crude oils and in some natural deposits [1]. It is mostly composed of hydrocarbons with a small amount of structurally analogous heterocyclic species. Bitumen may typically contain 83–86% of carbon (up to 150 carbon atoms), 9–10% hydrogen, 1–5% sulfur, less than 1% each of nitrogen and oxygen and minor amounts of metals such as vanadium and nickel [3,4]. In addition, bitumen is a colloidal system, where the highest molecular weight components, namely the asphaltene and the lower molecular weight components, the maltenes (aromatics, saturates and resins) are dissolved in the saturated hydrocarbon mixture and heteroatomic content is in this order $S < A < R < As$ [5–8]. The use of bitumen in paving applications has generated a particular interest toward the comprehension of its rheological properties, because of its importance in the manufacture and quality of bituminous pavements. As a matter of fact, the development of the early colloidal model was based on rheological observations. Long before that, users of bitumen observed the strong effect of temperature on its consistency. But due to its highly viscous character at room temperature, giving rise to a confusing and somewhat imprecise description such as pasty or semisolid, bitumen's rheological behavior remained hard to quantify. Penetration depth is the first method, which is related to the viscous resistance of the material. Empirical relationships have been developed for newtonian materials to account for the determination of the penetration depth using a standard needle that vertically penetrates the bitumen under known conditions of loading, time and temperature [9,10]. Penetration scope can provide indirect information about the chemical constituents of bitumen and approximately the relative proportions of asphaltene (high molecular weight, responsible for strength and stiffness), resins (responsible for adhesion and ductility) and oils (low molecular weight, responsible for viscosity and fluidity) [11,12]. If the penetration is measured over a range of temperatures, the temperature susceptibility of the bitumen can be established [10,13]. Lesueur [9] has shown the benefit of using needle penetration and provided a review about the penetration test evolution since early days.

In order to understand the temperature effect, differential scanning calorimetry (DSC) has proved to be unavoidable to determine thermal behavior of bitumen. Using DSC, Claudy et al. [7,14] have related T_g to the saturates and aromatics and the endothermics only to the saturates. Chambrion et al. [15] have studied thermal behavior of bitumen 40/50 by differential scanning calorimetry and demonstrated that two glass transitions take place after cooling at constant rate. The magnitude and temperature of these transitions depend on the cooling rate. Benbouzid and Hafsi [16] have studied the thermal behavior of pure and oxidized bitumens (40/50 and 20/30, respectively) by DSC from −60 to +80 °C. They have found that the glass transition temperatures T_g of pure bitumen are higher than those of oxidized bitumen.

The aim of this work is to study static mechanical response by penetration test with different loads (100, 150, 200, 250, 300, 350 g) versus temperatures of pure

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Table 1. Penetration at 25 °C and the ring and ball softening at 5 °C of pure bitumen 35/50 and modified bitumen 13/40.

Bitumen	Standard penetration at 25 °C (1/10 mm)	Ring and ball softening at 5 °C (°C)
35/50	46.67	53.3
13/40	36.67	64.8

Table 2. The largest difference between highest and lowest depth readings following the norm NF EN 1426.

Penetration (d-mm)	0–49	50–149	150–249	250–500
Maximum difference	2	4	12	20

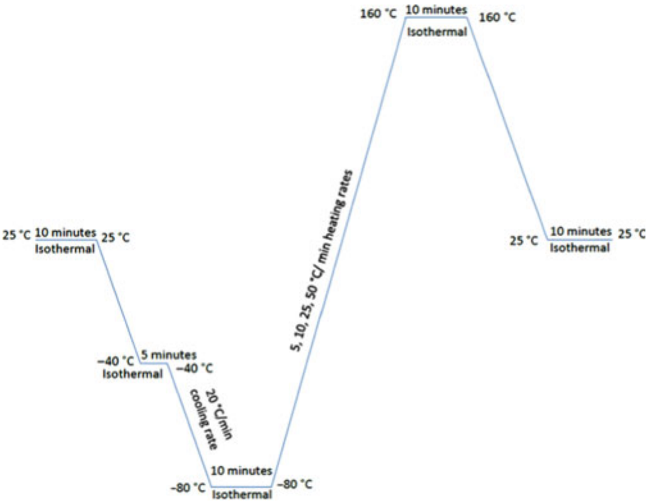

Fig. 1. (Color online) DSC program for T_g measurement.

bitumen 35/50 and modified bitumen 13/40. Despite the fact that rheology is one way to look at physical properties of bitumens using concept of complex modulus, we have chosen a mechanical approach which is based on structural mechanics. Indentation response, in a future work, would help us to determine the constitutive law by coupling the experimental response to a numerical model. In the present case, indentation testing is the best scheme to determine temperature susceptibility of studied bitumens which is dependent on load and temperature. These two parameters are both varied in this study.

This work investigates also the thermal behavior of these bitumens with a particular focus on glass transition temperature T_g. Results are discussed and compared to those of several studies from the concerned literature.

2 Material and methods

Pure bitumen of penetration grade 35/50 and modified bitumen of penetration grade 13/40 used in this study are produced by Total Company (France). Modified bitumen 13/40 is obtained by adding polymers to the pure bitumen 35/50. Table 1 summarizes penetration tests at 25 °C and 100 g load as well as the ring and ball softening at 5 °C for pure bitumen 35/50 and modified bitumen 13/40 which have been performed following norm NF EN 1426. The penetration test is a measure of the consistency or relative hardness of bitumen. Following NF EN 1426 norm, a sample of bitumen is placed in a suitable container and its temperature brought to 25 °C. A weighted needle is then brought to bear on the surface of bitumen for a given period of time. The load applied on the needle is 100 g, and the time interval is 5 s. The needle penetration into the bitumen, in units of 1/10 mm, is termed the penetration of bitumen. In our case, penetration test is undertaken using Petrotest penetrometer VG4500. Six load levels ranging from 100 to 350 g are used at different temperatures (5, 10, 15, 20, 25, 30, 35, 40 °C) and fixed penetration duration of 5 s. Prior testing, sample temperature is stabilized using a specific conditioning for about 90 min. Reproducibility of the results is checked using three replicates for each experimental run which takes less than 2 min. Needles are regularly checked for straightness, correctness of profile and cleanliness. The largest difference between highest and lowest depth readings as used in NF EN 1426 norm is illustrated in Table 2.

The glass transition temperature T_g is determined using NETZSCH DSC 04F1 Phoenix equipment. Samples are stored at room temperature for 24 h before performing the DSC analysis. In order to determine T_g, samples of about 34–37 mg are sealed in aluminum crucibles. These are heated at different rates (5, 10, 25, 50 °C/min) under a nitrogen flow rate of 20 mL/min in the sample chamber and 70 mL/min rate in the furnace chamber. The total heat is measured in a wide temperature range (−80 °C to 160 °C). Figure 1 describes the thermal protocol used in our DSC experiments.

3 Results and discussion

3.1 Penetration test

It is well known that "stiffness" of bitumen at low strains could be correlated with the penetration index and softening point of the bitumen which behavior was summarized in the well-known van der Poel nomograph [3,8].

Following the work of van der Poel, many researchers have attempted to characterize bitumen as a linear viscoelastic material, using rheological models based on springs and dashpots and continuous relaxation spectra [8,17–19]. These models required the construction of master curves for the dynamic complex modulus and phase angle. Phase angle is the phase difference between the stress and strain in an oscillatory deformation and is a measure of the viscoelastic character of the material. If phase angle equals 90°, then the binder can be considered purely viscous in nature and, vice versa, a phase angle of 0° would represent an ideal elastic solid. The ability of the binders to store deformational energy at high temperatures and to dissipate deformational energy through flow at low temperatures is called elasticity and flexibility, respectively [17]. In the construction of these master curves, the time temperature superposition principle (TTSP) or reduced variables method is employed. The TTSP described by Lesueur [9] states that the effect of increasing the loading time (or decreasing the frequency) on the mechanical properties of a material is equivalent to that of raising the temperature. This implies that the relaxation function is only shifted toward higher or lower times by a change of temperature and a material behaving this way is said to be thermorheologically simple.

However, these approaches are applicable only for relatively small strains (up to 0.1) and stresses in the linear viscoelastic range of behaviors, while the thin films of bitumen binder between the aggregate particles are subject to large stresses and strains [20]. Also in dynamic mechanical tests (rheological tests), the temperature susceptibility of binders may be evaluated by measuring various viscous and elastic parameters (e.g., storage and loss moduli, dynamic and complex viscosities) at different temperatures and frequencies [17].

In our case, we explore the well-known method of penetration test (static mechanical test) adding load change in order to extend stress and strain domains. This method could give complemental information than rheological method.

In the present study, we consider bitumen as a heterogeneous viscoelastic material subject to different loads (100, 150, 200, 250, 300, 350 g) and different temperatures (5, 10, 15, 20, 25, 30, 35, 40 °C). The main searched feature through the use of penetration testing is to determine the temperature susceptibility A which is defined as the change in the consistency parameter as a function of temperature versus load change. This technique allows us to have good evaluation of temperature susceptibility because it uses static mechanical behavior for different load change and different temperature gaps (less than softening point temperature).

Figure 2 shows the penetration response of pure bitumen 35/50 and modified bitumen 13/40 versus applied load and temperature for penetration duration of 5 s. The log plot allows us to consider simple fitting functions representing the bitumen response as a function of temperature:

$$P = \exp\left(AT + C\right), \tag{1}$$

where P is the penetration depth associated to the applied load, A is the temperature susceptibility and C is a constant.

In our case, fitting parameters (A, C) are both expected to depend on the load. Therefore, these can be further expressed as a function of load.

It turns out that fitting parameters are nicely correlated to the load using simple linear functions as illustrated in Figure 3. This is more effective for bitumen 35/50 whereas for bitumen 13/40, the linear approximation does not seem to be followed at small loads as shown in Figure 3. A is found to be negatively related to temperature whereas C increases with the increase of temperature.

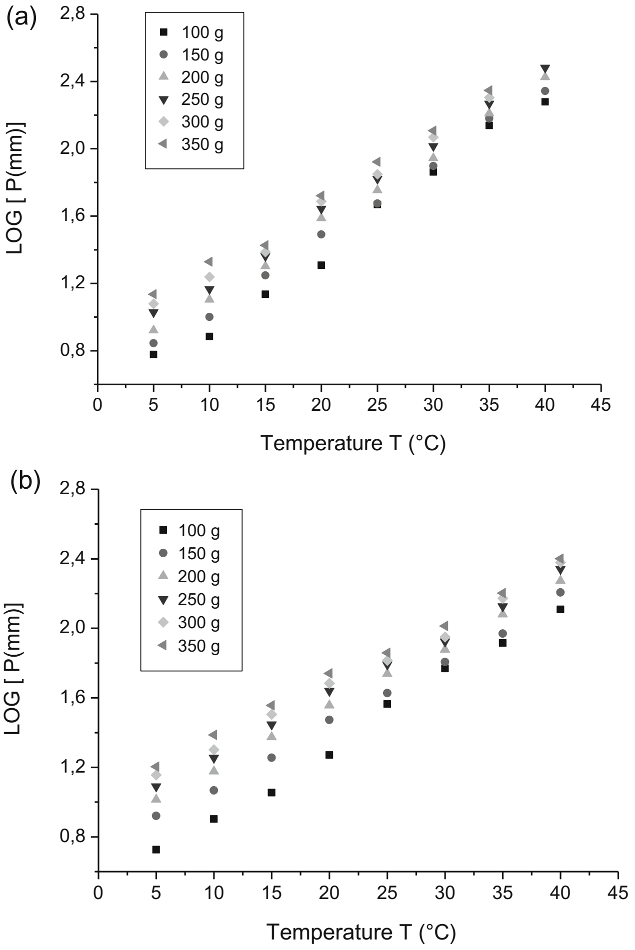

Fig. 2. Penetration diagrams versus applied load and temperature for penetration duration of 5 s of: (a) pure bitumen 35/50, (b) modified bitumen.

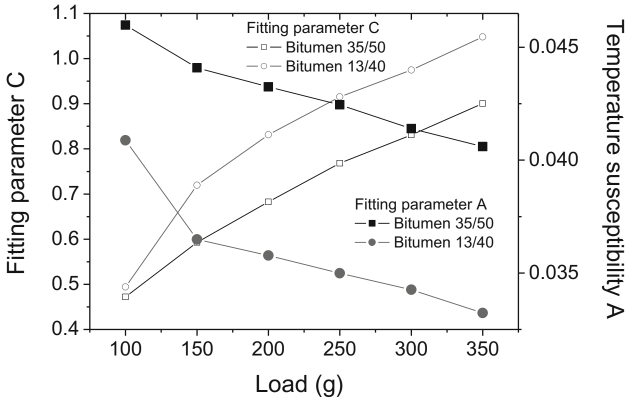

Fig. 3. Fitting parameters describing the relationship between penetration, temperature and load for the studied materials.

Applying the fitting procedure to both studied materials gives the following precise functions for bitumen 35/50:

$$P = \exp\left(\left[0.048 - 2.04 \times 10^{-5} F\right] T + 0.33 + 0.0017F\right) \tag{2}$$

and for modified bitumen 13/40:

$$P = \exp\left(\left[0.042 - 2.61 \times 10^{-5} F\right] T + 0.37 + 0.002F\right), \tag{3}$$

where F is the applied load.

It is observed that the lower temperature susceptibility A, the higher load weight with small variation of temperature susceptibility from 0.0460 (for 100 g) to 0.0406 (for 350 g) and from 0.0409 (for 100 g) to 0.0332 (for 350 g) for pure bitumen 35/50 and modified bitumen 13/40, respectively. Also, it is remarked that temperature susceptibility A for modified bitumen 13/40 at 100 g is almost equal to the value of A for pure bitumen 35/50 at 350 g. The reduction of A in modified bitumen 13/40 in comparison with that of pure bitumen 35/50 can be due to the polymer modification. Similar results have been found by Sengoz et al. [21] who attributed the reduction in temperature susceptibility to the resistance of EBA (ethylene butyl acrylate)-based polymer modified asphalt mixtures to cracking compared to SEBS (styrene-ethylenebutylene-styrene) and EVA (ethylene vinyl acetate) mixtures with the changes in temperature. Using starch (ST) and styrene-butadiene-styrene (SBS) as additives in stone matrix asphalt (SMA) mixtures (5% of ST and SBS by weight of bitumen are blended with (70/100)-paving grade asphalt), Al-Hadidy and Tan [22] have shown that temperature susceptibility is reduced by the addition of ST and SBS in the asphalt mixture. In most standard tests at 100 g during 5 s, A varies between 0.015 and 0.06, showing a considerable variation in the temperature susceptibility of bitumen from different sources [1].

Penetration indices P_{i} are calculated using the following formula [1,8,9]:

$$P_{\mathrm{i}} = \frac{20 - 500A}{50A + 1}. \tag{4}$$

Table 3 summarizes penetration index P_{i} as a function of applied loads for pure bitumen 35/50 and modified bitumen 13/40.

We observe that P_{i} lies in the range (-1.0, -0.1) and (1.3, -0.1) for pure bitumen 35/50 and modified bitumen 13/40 respectively. For pure bitumen 35/50, the largest P_{i} value (-0.10) corresponds to the largest load (350 g) whereas the smallest value ($P_{\mathrm{i}} = -0.907$) is observed for 100 g. For modified 13/40 bitumen, the largest value (1.272) corresponds to the largest load (350 g) and the lowest value (-0.144) is found for 100 g. Generally speaking, for a load value of 100 g, which represents the norm, P_{i} is a discriminating indicator for classifying bitumen rheological behavior. For example, blown bitumens have $P_{\mathrm{i}} > +1$ and straight-run bitumens have $-1 < P_{\mathrm{i}} < +1$. Only very susceptible materials such as coal tar give $P_{\mathrm{i}} < -1$. P_{i} values larger than +2 are indicative of gel bitumen whereas $P_{\mathrm{i}} < 0$ is typical of a sol type [9].

Haddadi et al. [23] have measured the penetration of a copolymer-modified bitumen for different temperatures (load is 100 g) and compared the result to that of unmodified bitumen (80/100). The authors reported a penetration index of -0.625 for the unmodified bitumen. In their study, the addition of the copolymer (ethylene vinyl acetate) has led to an increase of both hardness and penetration indices revealing a consequent improvement of temperature susceptibility of the binders.

3.2 Thermal behavior

In order to understand temperature susceptibility behaviors of pure bitumen 35/50 and modified bitumen 13/40, glass transition temperatures T_{g} for these materials have been studied.

Glass transition is the reversible change in amorphous materials or in amorphous regions of a partially crystalline material, from a viscous or rubbery state to a hard and relatively brittle glassy state and vice versa. The glass transition occurs when the characteristic time of molecular motions responsible for structural rearrangements becomes longer than the timescale of the experiment. The timescale for structural relaxation increases rapidly with decreasing temperature. The transition to the glassy state is accompanied by a sudden change in mechanical, optical and thermodynamic properties of the material. The increase in viscosity is enormous. The material becomes glassy and extremely brittle and rigid [24].

Among the available techniques for the determination of T_{g}, DSC is one of the popular ways [14–16]. In the concerned literature [18,24,25], we should also mention dynamic mechanical thermal analysis (DMTA) [18,24] and inverse gas chromatography method [25] where T_{g} is determined by constructing van't Hoff plots using *n*-pentane probes in a temperature range between −50 °C and +120 °C. T_{g} values are specified using first deviation from linearity observed in the adsorption zone of the plots. As mentioned above, we have used DSC technique to study thermal properties of our bitumens.

DSC curves (Fig. 4) depict the evolution of the glass transition temperature T_{g} as a function of the heating rates for pure bitumen 35/50 and modified bitumen 13/40. Roughly speaking, T_{g} is influenced by the presence of the saturates which do not crystallize and the aromatic fractions [9,14]. At low temperature, an increase in the heat capacity, observed as an abrupt change in the slope of the calorimetric signal and also reflected as a peak in the first-derivative curve, corresponds to the glass transition of the hydrocarbon matrix. The rheological properties of bitumens below and above T_{g} differ significantly: below T_{g}, bitumens behave like a glass, while above T_{g}, they exhibit rubbery behavior. The determination of T_{g} may thus provide a simple way to highlight main differences in the quality of bitumens regarding their final application [26]. In our case, it is observed that pure bitumen 35/50 presents one T_{g} value for different heating rate (5 °C/min, 10 °C/min, 25 °C/min, 50 °C/min), whereas modified bitumens 13/40 exhibit two T_{g} values for different heating rate. We notice also an increase of T_{g} from −23.7 °C to −20 °C for bitumen 35/50, when the heating rate increases but the difference is around 4 °C. Glass transition phenomenon has a direct dependence on time, where T_{g} position varies with heating rate. The shift of T_{g} toward higher temperatures with the decrease of the

Table 3. Penetration index P_i as a function of applied loads, for pure bitumen 35/50 and modified bitumen 13/40.

Loads (g)	100	150	200	250	300	350
P_i (bitumen 35/50)	−0.906	−0.637	−0.514	−0.392	−0.228	−0.100
P_i (bitumen 13/40)	−0.144	0.622	0.757	0.912	1.058	1.272

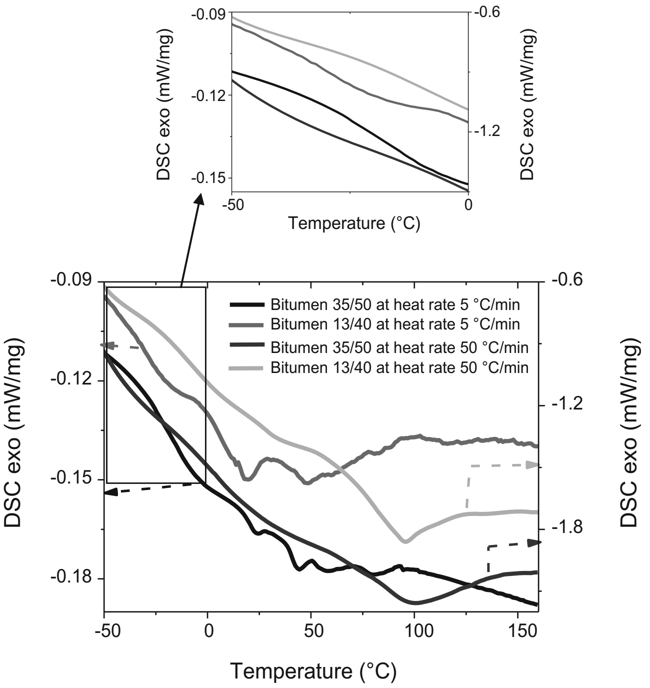

Fig. 4. DSC curves depict the evolution of the glass transition temperature as a function heating rate for pure bitumen 35/50 and modified bitumen 13/40.

heating rate can also be attributed to the reduction of the molecular mobility of the amorphous phase as a result of the effect of the physical reticulation of the crystals. Chambrion et al. [15] have studied the evolution of T_g in bitumen 40/50 versus cooling rate.

The authors [15] have found that higher T_g values are correlated to lower cooling rates. For our modified bitumen 13/40, a first T_g increase is observed within the range −29.8 °C to −25.2 °C and a second increase lies between −8 °C and −4.1 °C when the heating rate increases. Also, it is remarked that the first T_g is lower than T_g of pure bitumen 35/50 for different heating rate. The lowest T_g value of modified bitumen 13/40 in comparison with pure bitumen can be attributed to oxygen content which increases with the addition of polymers. Stangl et al. [5] have found that polymer-modified bitumen 60/90 (pure bitumen 50/70 + SBS) shows an oxygen content of 0.6%. This increase of oxygen in consequence of the allowance of SBS is explained by oxygen attaching to the double bonds of SBS, with the latter being susceptible to oxidation. Benbouzid and Hafsi [16] have determined glass transitions for pure bitumen 40/50 and oxidized bitumens 20/30 (the bitumen 20/30 is obtained by oxidization of the bitumen 40/50 at around 200 °C). The former authors have found glass transitions at −28.36 and −41.43 °C, respectively. The same authors [16] have attributed the decrease of T_g in oxidized bitumens 20/30 to oxygen reaction in bitumen 40/50 to form molecules of asphaltenes and other oxidized hydrocarbons. As the reaction advances, the size and the number of these molecules increase. As a result, the glass transition temperature is reduced. In our case, the second T_g of modified bitumen 13/40 can be attributed to the modification and chemical reactivity of polymers within bitumen.

As an attempt to relate thermal and mechanical properties, we provide a qualitative correlation between the above-mentioned effects. For both studied bitumens, a lower temperature susceptibility under 100 g loading condition is correlated to a lower T_g (−29.8 °C at 5 °C/min heating rate) for modified bitumen 13/40. A higher temperature susceptibility under the same loading conditions is positively related to a higher T_g (−23.7 °C at 5 °C/min heating rate) for bitumen 35/50. Fuentes-Auden et al. [18] have studied the influence that polymer concentration exerted on the rheological and thermal properties and microstructure of recycled polyethylene-modified bitumen. Using steady and oscillatory shear tests and dynamic mechanical thermal analysis (DMTA), respectively, and considering the temperature susceptibility as the loss tangent versus temperature slope, the authors [18] have shown that, the lower the glass transition temperature T_g, the lower the temperature susceptibility with the higher polymer concentration. In his work, Schmidt and Santucci [19] stated that for given crude source, the lower the penetration, the higher the glass transition. Assuming penetration is inversely related to the degree of polymerization, he confirmed the influence of degree of asphalt polymerization on glass transition temperature.

4 Conclusions

Needle penetration test under various temperature and load conditions as well as DSC characterization are considered to study the mechanical response and thermal behavior of pure bitumen 35/50 and modified bitumen 13/40. The following main results are obtained for our bitumen:

- Lower temperature susceptibility A is correlated to larger loads with small variation of temperature susceptibility from 0.0460 (for 100 g) to 0.0406 (for 350 g) and from 0.0409 (for 100 g) to 0.0332 (for 350 g) for pure bitumen 35/50 and modified bitumen 13/40, respectively.
- Temperature susceptibility A for modified bitumen 13/40 at 100 g is almost equal to the value of A for pure bitumen 35/50 at 350 g.

– Pure bitumen 35/50 presents one T_g at different heating rate (5 °C/min, 10 °C/min, 25 °C/min, 50 °C/min) and modified bitumens 13/40 exhibits two T_g for different heating rate.

Finally, it is observed that the use of the improved old technique (penetration test) with the adding load change could be explored for static mechanical tests and could be given more advantageous results than dynamic mechanical tests concerning thermal susceptibility.

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