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Low temperature rheology of polyphosphoric acid (PPA) added bitumen

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HIGHLIGHTS

- The effects of polyphosphoric acid (PPA) on bitumens from different sources were investigated.
- Dynamic Mechanical Analysis (DMA) at low temperatures was adopted.
- PPA shifts, towards lower values, the bitumen glass transition.
- PPA seems to improve low temperature bitumen behavior.
- Experimental results suggest the existence of an optimal PPA concentration.

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ABSTRACT

In the present work a laboratory evaluation of the low-temperature rheological properties of neat and polyphosphoric acid (PPA) modified bitumens by using a Dynamic Mechanical Analyzer (DMA) is presented. Fundamental rheological properties were evaluated in controlled kinematic conditions and the results obtained were compared with traditional procedures such as the Fraass breaking point. The results show that the effect of polyphosphoric acid addition at low temperature is strongly dependent on bitumen composition (i.e. wax and asphaltene content), nevertheless it seems that PPA is able to decrease the glass transition temperature (T_g) and to increase the stiffness, improving the low temperature performance of the modified materials.

1. Introduction

Bitumen is a primary engineering material, often employed as a binder in road construction and roofing systems, thanks to its thermoplastic nature, water resistance and adhesion to many other materials. It is characterized by rheological properties strongly dependent on temperature, governed by the chemical-physical interactions of their individual constituents [1].

During the last few years the research into bituminous materials has focused on low and high temperature performance, because the mechanical properties of bituminous binders play an important role in the performance of the corresponding asphalt mix [2]. Bitumen has to be hard enough at high temperature to avoid permanent deformation of the pavement (rutting) and soft enough at low temperatures to avoid fractures due to a lack of flexibility (cracking) [3,4]. It is usually difficult to obtain materials that could work properly in a wide temperature range, therefore there is a different paving grade, suitable for specific applications. As a consequence, nowadays, there are many types of bitumens with different mechanical properties, also owing to the different sources that affect their composition, and, therefore, their rheological properties.

Depending on the source, bitumen can be rich in waxes or almost wax free and the presence of these components can improve the sensitiveness to cracking or create plastic deformations after the laying of asphalts. At high temperature waxes act as a plasticizer, reducing viscosity, whereas at low temperature, owing to crystallization phenomena, they increase the stiffness making the bitumen more susceptible to cracking.

Moreover, properties of bitumen containing wax are also affected by ageing processes such as chemical ageing and physical hardening (also referred to as steric hardening). The former occurs either during asphalt mix preparation at high temperature (short ageing) or during the service life of the material (long term ageing) and is due to chemical modifications; the latter occurs with time

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and it is a heat reversible phenomenon potentially due to the strengthening of the asphaltene network with time. Both of them yield, as a final consequence, to material hardening which is particularly evident at low temperatures [3,5].

In order to widen the operative temperature range and reduce the ageing issues, many additives, such as polymers and acids, are currently used as bitumen modifiers; among them polyphosphoric acid seems particularly interesting [3] because, in small amounts, it can improve bitumen rheological properties in a significant way both for high and low temperatures [5].

Edwards et al. (2006) [5] observed a slight reduction of both glass transition temperature (T_g) and complex shear modulus when adding up to 1% PPA to different 160/220 bitumens obtaining a higher stiffness at intermediate and high temperatures.

Nevertheless, the PPA added bitumens showed an increased sensitivity to permanent deformation, when compared with a mixture without additive [5], evidencing potential breaking problems.

Even though there is great interest in PPA addition for commercial applications, data on rheological behavior of added bitumen at low temperature are still scarce. In the present paper the rheological behavior of different PPA added bitumens was investigated by Dynamic Mechanical Analysis (DMA) aiming at a better understanding of the effects of different PPA levels on bitumen behavior at low temperature ($\leqslant$5 °C).

2. Materials and methods

2.1. Materials

Four plain bitumens from three different sources (Venezuela, Saudi Arabia and Russia) were used in this study. Venezuelan (N) and one Saudi Arabian (C) binders were 70/100 penetration grade bitumens, while the others, from Saudi Arabia (P) and Russia (M), were 50/70 penetration grade bitumens.

Polyphosphoric acid, 83.3% P_2O_5, or otherwise stated 115% H_3PO_4 equivalent [6], was provided by ICL Performance Product LP (St. Louis, MO, USA).

Asphaltenes were isolated from bitumens according to the procedure described by Altgelt and Boduszynski [7]. Bitumen (2–3 g) is dissolved in a volume of toluene numerically (in ml) equal to the weight of the sample. A volume of pentane equal to forty times the toluene is added. The mixture is shaken and then kept in the dark during precipitation for 2 h with occasional shaking. Asphaltenes are collected on a Buchner funnel filter (16–40 μm pore size), washed with pentane until filtrate is colorless, dried and weighed. The separated asphaltenes were further purified by repeating the precipitation procedure. Obtained values are reported in Tables 1 and 2.

Separation of wax from bitumen was carried out according to the European Standard Method EN 12606-1. This method is based on DIN 52015, a German method used for determining the paraffin wax content of bitumen and bituminous. The test is carried out on two portions, each of 25 g of bitumen. A specified distillation process is used to obtain the distillate from the bitumen. The wax is obtained by dissolving the distillate in a diethyl ether/ethanol (50/50, v/v) solvent and crystallizing at a temperature of −20 °C.

2.2. Sample preparation

The proper amount of PPA was added to bitumen, at 120 °C, to reach a level of 0.5, 1, 1.5% by weight. After mixing, the system was heated up to 160 °C (ARE, Velp Scientifica, Italy) and maintained at this temperature, under stirring conditions at 600 rpm (RW 20 Digital, IKA, Germany), for 30 min in a closed beaker to avoid any oxidation process. Afterwards, the resulting bitumen was poured into a small sealed can and then stored in a dark chamber kept at 25 °C to retain the obtained morphology. Samples ID are reported in Tables 1 and 2 for the 50/70 and for 70/100 penetration grade bitumen respectively and they will be used throughout the text.

Specimens for rheological tests were prepared by pouring the molten bitumen in a Teflon mould (10×5×3 mm) and cooling the system at 4 °C, for 4 min, and then at −18 °C, for 30 s, to allow the material solidification. Afterwards the sample was removed from the mould and kept at 4 °C for the last 6 h before testing.

2.3. Material characterization

The rheological tests were carried out with a Dynamic Mechanical Analyzer (TTDMA, Triton Technology, UK), equipped with a liquid nitrogen cooling system, in a 3-Point Bending configuration.

Temperature ramp tests (time cure) were carried out at 1 Hz frequency in linear viscoelastic conditions previously determined by strain sweep tests at different temperatures. The samples were initially kept a −30 °C for 4 min, to obtain uniform temperature conditions, and then heated up to 5 °C with a 1 °C/min thermal ramp. During the tests a periodic sinusoidal displacement was applied to the sample and the resulting sinusoidal force was measured in terms of amplitude and phase angle [8]. The resulting dynamic modulus can be split into two components: the storage modulus, E', being the in-phase part, is a measure of the reversible, elastic energy, whereas the loss modulus, E'', being the out-of-phase component, represents the irreversible viscous dissipation of the mechanical energy. The damping factor or loss tangent, tan(δ), is defined as the ratio of loss to storage modulus and, by definition, is a measure of the dissipated energy compared with the stored one; the complex modulus E^* is obtained by combining loss and storage modulus:

$$E^* = \sqrt{(E')^2 + (E'')^2} \quad (1)$$

Typical technological tests were, also, used to characterize the bitumen.

Table 1
Empirical and rheological characteristics of modified and unmodified bitumens having a penetration grade 70/100 (sample N from Venezuela and sample C from Saudi Arabia).

Sample ID	PPA (w/w%)	FRAASS (°C)	Penetration (mm)	R&B T (°C)	x_A (w/w)	Wax content (w/w)	T_g (°C)	E^* (1 Hz, −30 °C) (MPa)
N0	0	−13	81	46.3	0.105	0.008	−9.5 ± 0.7	17.2 ± 0.2
N0.5	0.5	−8	69	51.3			−9 ± 1	25.5 ± 0.2
N1	1	−16	57	56.0			−10.5 ± 0.7	36 ± 3
N1.5	1.5	−11	51	60.2			−7.0 ± 0.5	23 ± 1
C0	0	−6	81	47.5	0.076	0.064	−8.0 ± 0.1	19 ± 2
C0.5	0.5	−4	77	50.2			−6.5 ± 0.6	27 ± 3
C1	1	−4	74	52.1			−16.0 ± 0.1	46.7 ± 0.2
C1.5	1.5	−4	73	52.6			−12 ± 1	45 ± 7

Table 2
Empirical and rheological characteristics of modified and unmodified bitumens having a penetration grade 50/70 (sample M from Russia and sample P from Saudi Arabia).

Sample ID	PPA (w/w%)	FRAASS (°C)	Penetration (mm)	R&B T (°C)	x_A (w/w)	Wax content (w/w)	T_g (°C)	E^* (1 Hz, −30 °C) (MPa)
M0	0	−6	5.7	51.3	0.110	0.05	−24.5 ± 0.7	54.30 ± 0.02
M0.5	0.5	−6	4.9	57.1			−21.5 ± 0.7	60.6 ± 0.1
M1	1	−7	3.8	63.9			−11.5 ± 0.7	543 ± 5
M1.5	1.5	−9	3.1	72.4			−7.0 ± 0.5	66.0 ± 0.2
P0	0	−4	6.1	48.3	0.091	0.044	−1 ± 0.1	7.2 ± 0.1
P0.5	0.5	−4	6.0	50.9			−15.5 ± 0.7	7.03 ± 0.02
P1	1	−4	5.9	52.1			−13 ± 1	62.10 ± 0.02
P1.5	1.5	−4	5.8	54.9			1.05 ± 0.1	10.6 ± 0.5