Analysis of Mechanical Performance of Bitumen Modified with Waste Plastic and Rubber Additives by Rheology and Self Diffusion NMR Experiments

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Article info

Abstract

In this study, the mechanical and physico-chemical properties of a new kind of modified bitumen are presented. The bituminous binders have been modified in order to understand the effect on the structural properties of several compounds such as a Polymer elastomer as Styrene Butadiene Rubber (SBR), Polymer thermoplastic polypropylene (PP) and a waste plastic (Waste PP). Laboratory tests have been focused on the characterization of bitumen modified with single product and their binary combinations compared with pristine binder as a reference. Characterization has been conducted by using conventional as well as advanced methods on bitumens. Fundamental rheological tests, based on dynamic shear rheometer in the temperature range from -30 °C to +160 °C have been performed and the structure of a bitumens and modified bitumens has been analysed by the mobility of the oily maltene by self-diffusion Pulsed field gradient spin-echo (PGSE) FT-NMR experiments.

1. Introduction

Bituminous binders are organic materials whose binding and hardening properties are caused by the temperature-related change of adhesion and cohesion of their molecules [1, 2]. Bitumen is commonly modelled as a colloid, with maltenes as the continuous phase and micelles of asphaltenes stabilized by associated resins as the dispersed phase [3, 4]. Following the analogy with reversed micelles in water-oil microemulsions where the stabilization of the polar domains is of pivotal importance for determining both the structure and the properties of the overall aggregates [5, 6, 7], in the same way in bitumens the composition and the colloidal structure [8] influence its physical and rheological properties [9, 10, 11]. These binders are commonly used in the pavement constructions to meet the raising requirements of the surface durability of the roads. A wide range in viscoelasticity values

is essential to achieve long-lasting road surface, as it ensures consistency of rheological state of bitumen in extreme service temperatures [12]. The rheological weakness of the conventional bitumen has generated an increasing interest in the use of polymer modified binders to enhance the conventional bitumen properties [13]. A limited number of polymers has been used as modifying agents due to their high cost. In fact, due to the high cost of these polymers the amount needed to improve pavement performance should be as small as possible. The main modifiers applied to improve the viscoelasticity of bitumen are long chained hydrocarbon polymers. Moreover, elastomers increase the elasticity of the bitumen at high temperature and reduce the stiffness at low temperature. Linear and radial styrene–butadiene–styrene (SBS) copolymers are the most used ones. In the bitumen, SBS forms a highly elastic network that disappears above 100 °C and reforms when cooled.

Nowadays the use of polymers reclaimed from waste plastic (bottles, glasses, etc…) is one of the hot topics in the field of bitumen modification.

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In this regard waste plastic represents the biggest polymer sources. As reported in [14] 8300 million of Metric Tons (MT) of virgin plastic have been produced to date. Approximatively 6300 MT had been generated in 2015, around 9% of which had been recycled, 12% was incinerated and 79% was accumulated in landfills or in the natural environment. The use of recycled plastic is the only way to avoid environmental pollution which is, together with climate changes, the biggest problem that human being has to overcome.

In this work a Polypropylene, abbreviated as PP, polymer obtained from waste plastic was used as a bitumen modifier in comparison with a typically used polymer styrene-butadiene-rubber (SBR).

PP is a recyclable thermoplastic polymer widely used in many different products. PP is rugged and resistant to different chemical solvents, acids, and bases. PP's resin identification code is 5, and it is recyclable.

2. Materials

The bitumen used in this study has been produced in Kazakhstan and it was supplied by Kazakhstan Highway Research Institute (Almaty, Kazakhstan). It has a 50/70 penetration grade. The bitumen was modified with Polymer elastomer (SBR), Polymer thermoplastic (PP) and a Waste polypropylene plastic (WPP).

SBR: Styrene/Butadiene-rubber was furnished by CMS SPA (Mangone, Italy);

PP: Polypropylene was furnished by Sigma Aldrich (Mangone, Italy);

WPP: waste Polypropylene was furnished by Calabria Maceri (Rende Italy), label WPP;

Waste PP was pulverized by milling in order to homogenize the sample.

2.1. Sample preparation

The first step was to prepare the polymer modified bitumen, by using a high shear mixing homogenizer (IKEA model). Firstly, bitumen was heated up to 180±5 °C until it fully flowed and then three blends with SBR (0.5% of the weight of the base bitumen, wt.%), WPP and PP (1% of the weight of the base bitumen) were prepared gradually added the polymers to the melted bitumen under a speed shear mixer of 600 to 800 rpm. The mixtures were stirred by a mechanical stirrer at 180 °C for 1 h while the rotation speed was 600 rpm so that the blends became essentially homogenous.

Table 1
Sample Labels

Sample	Sample ID
Pristine Bitumen	PB
Bit. + 0.5% SBR	SBR
Bit. + 1% Waste PP	WPP
Bit. + 1% PP	PP
Bit. + 1% WPP + 0.5% SBR	WPP/SBR
Bit. + 1% PP + 0.5% SBR	PP/SBR

The PP/SBR WPP/SBR modified bitumens were prepared adding 0.5 wt.% of SBR and 1wt.% of Polypropylene by using the same procedure for the bitumen modified by single polymer. After mixing, the resulting blends were poured into a small sealed can and then stored in a dark chamber at a constant temperature of 25 °C to retain the obtained morphology.

All the prepared mixtures are listed and labelled in Table 1. The following labels will be adopted for the samples throughout the text.

2.2. Rheological measurement

Rheological measurement has been conducted using a shear stress-controlled rheometer SR5000 (Rheometrics, USA) equipped with a plate geometry (gap 2 mm, diameter 25 mm). The temperature has been controlled by Peltier system (±0.1 °C).

All the experiments have been performed during heating. The rheological behaviour at different temperatures has been investigated by a time cure test at 1 Hz with a heating ramp rate of 1 °C/min. The small amplitude dynamic tests provided information on the linear viscoelastic behaviour of materials through the determination of the complex shear modulus [15].

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

or in terms of complex viscosity,

$$\eta^* = \frac{G^*(\omega)}{\omega}$$

where $G'(\omega)$ is the in phase (or storage) component, $G''(\omega)$ is the out-of-phase (or loss) component, and i is the imaginary unit of the complex number. $G'(\omega)$ is a measure of the reversible, elastic energy, while $G''(\omega)$ represents the irreversible viscous dissipation of the mechanical energy.

The dependence of these quantities on the oscillating frequency gives rise to the so-called mechanical spectrum, allowing the quantitative rheological characterization of studied materials. The applied stress amplitude for the viscoelastic measurements has been reduced until the linear response regime has been reached. This analysis has been made by performing stress sweep tests in all investigated temperature range.

2.3. Nuclear Magnetic Resonance (NMR) characterization

NMR spectroscopy is one of efficient and reliable technique for the characterization of complex materials such as bitumen. ^{1}H and ^{13}C NMR spectra are commonly used in solution for the characterization of synthetic/natural products, while the use of anisotropic media allows to investigate the structural and conformational behaviour of flexible molecules [16, 17, 18].

Dynamic NMR measurements like determination of self-diffusion coefficients provide information about molecular dynamics and spatial dimensions of aggregates and cavities. In this work, measurements of the self-diffusion coefficients were carried out on the samples analysed to investigate their mobility and microstructure.

NMR measurements were carried out using a Bruker 300 spectrometer under certain operating conditions, in particular in a temperature. The NMR spectra were derived from Free Induction Decay (FID) through the Fourier transform. In the pulsed NMR experiment the pulse width was equal to $\pi/2$ while the number of scans used was equal to 8. Experimental measurements of the self-diffusion coefficient (D) directly were made using a Diff30 NMR probe. The sequence that was used is the PFG-STE (Pulsed Field Gradient Stimulated-Echo) because the transverse relaxation time (T_2) is much shorter than the longitudinal relaxation time (T_1) [19, 20]. This sequence consists of three pulses 90 rf ($\pi/2$-τ_1-$\pi/2$-τ_m-$\pi/2$) and two gradient pulses which are applied after the first and third pulse rf. The echo was identified at time $\tau = 2\tau_1 + \tau_m$, while the amplitude attenuation of the ECO was decrypted from the following equation:

$$I(2\tau_1 + \tau_m) = I_0 e^{-\left[\frac{\tau_m}{T_1} + \frac{2\tau_1}{T_2} + (\gamma g \delta)^2 D\left(\Delta - \frac{\delta}{3}\right)\right]}$$

where D is the self-diffusion coefficient. The experimental NMR parameters that were used to study the samples are: the gradient length pulse, δ, diffusion delay time, Δ, while the gradient amplitude, g. The number of scans is 8, this increases as the number of repetitions increases. The standard deviation of the fitting is very low and on the repeatability of measurements, the uncertainties in D fall within ~3%.

3. Results and discussion

In the present work, 50/70 penetration grade bitumen was modified by Polymer thermoplastic (PP), Plastic waste (waste PP) and SBR. Firstly, the penetration depth (PN) and the softening point (R&B) were determined with standardized tests (Table 2).

A good correlation exists between bitumen hardness and polymer content for each of the investigated bitumen. As can be seen from Table 2 all the additives induce a shifting in the viscoelastic-sol transition temperature (TR) of about 20 °C higher than the neat bitumen. In particular, the best polymer modification was observed in presence of SBR. Temperature-sweep experiments have also been exploited to have some information on the structural changes induced by temperature, trying to better define a TR range. In fact, in this experiment, the evolution of the storage modulus is continuously monitored during a temperature ramp, at a constant heating rate (1 °C/min) and at a frequency of 1 Hz.

In Fig. 1 the Dynamic Temperature Ramp Test of all investigated blends are shown in the temperature range 25–100 °C. At high temperatures the elastic modulus $G'(\omega)$ have a non-linear behaviour approaching to the viscoelastic to liquid transition (60 and 80 °C for neat and modified bitumens respectively). The starting point of the non-linear region of $G'(\omega)$ can be considered as the beginning of the TR region. The whole transition process from viscoelastic to liquid regime ends when $G'(\omega)$ modulus is no longer detectable and consequently the loss tangent tan δ diverges at about 80 °C for the polymer modified bitumens. Tan δ increases with increasing temperature, evidencing a reduction in material consistency. In fact, the prevalent liquid-like behaviour is enhanced by the temperature increase. In Fig. 2 the tan δ of the investigated blends are shown at low temperatures. Phase angle values at low temperature are quite scattered, due to instrumental problems related to the high material consistency.

Table 2
Penetration depth (PN) Softening point and
Transition temperature of prepared blends

Sample ID	PN (1/10 mm)	R&B (°C)	Transition temperature (°C)
PB	64	47.2	65.9
SBR	48	63.6	88.7
WPP	53	56.4	81.5
PP	51	59.4	84.5
WPP/SBR	55	58.6	83.5
PP/SBR	54	57.2	82.2

In principle, to prevent the cracking phenomena, a system is required to keep a viscous character. Herein, it is worth to note that between 0 °C and 30 °C, the tan δ trends of WPP, WPP/SBR, PP/SBR and SBR overlap. The pure bitumen (B) shows higher tan δ values, while PP has a more rigid behaviour (lowest tan δ). These results are interesting in terms of mechanical properties because:
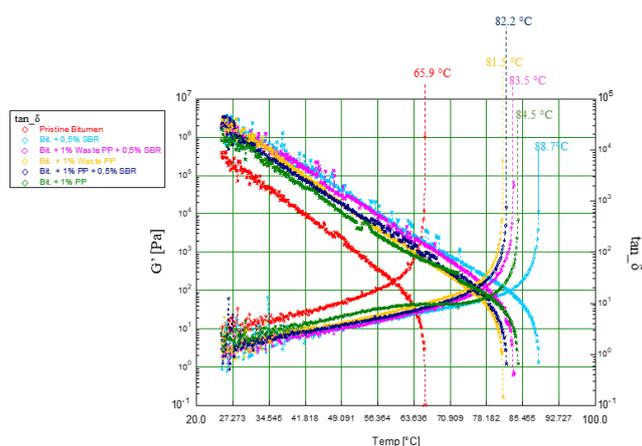
Fig. 1. Dynamic temperature ramp test (TimeCure) at high temperature (25 to 130 °C).
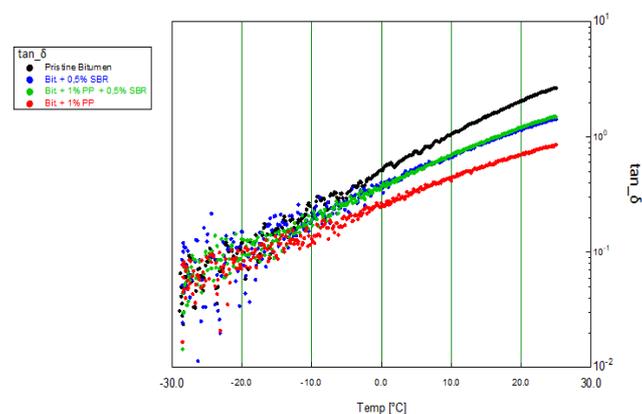

Fig. 2. Dynamic temperature ramp test (TimeCure) at low temperature (-30 °C to 25 °C).

a) it is evident that even only WPP polymer improves the rheological properties at low temperatures limiting the "solid effect".

b) the PP modified bitumen show higher rigidity of the system exposing the binder to possible cracking phenomena.

Fourier transform NMR self-diffusion provides insight into the bitumen microstructure by determining the long-range mobility of the mixture components. Detection of motion over long distances, compared with typical micelles (some nm), provides a sensitive probe for the aggregate state [20, 21]. Unfortunately, because of the short transverse relaxation times of asphaltenes protons, asphaltenes molecules self-diffusion values cannot be detected and consequently the measured self-diffusion coefficients can be related to the maltenes phase. Here self-diffusion coefficients of oil protons at 100 and 120 °C are reported in Figs. 3 and 4 respectively.

The self-diffusion is due to the mobility of the observed molecules and is hindered by the obstruction they meet during their motion. The data can be considered as a fingerprint of the structure where the motion occurs. The observed data are really interesting. The highest self-diffusion values are found for the PP and PB bitumens. The WPP, SBR WPP/SBR PP/SBR affect the mobility of the maltene reducing the diffusion. The data confirm what observed by rheology where PP modified bitumen shows a mechanical behaviour different from the bitumens doped by the other polymers. WPP, SBR WPP/SBR PP/SBR seem to absorb the light part of the maltenes trapping them in their network. As a consequence, maltenes phase is enriched by the heavy oil part. The mobility is therefore reduced. The PP does not interact with oily part of the maltenes and consequently the self-diffusion is comparable to the pure bitumen. This analysis takes into account that the percentage of asphaltenes is the same and therefore the obstruction factor can be neglected for all samples.
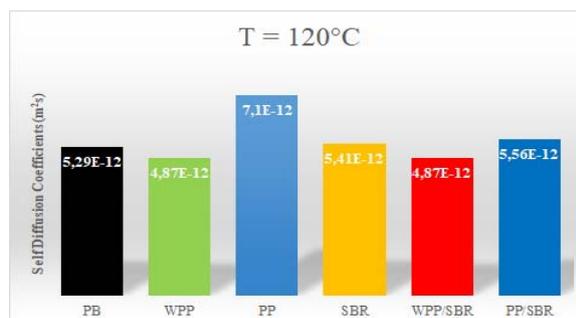

Fig. 3. NMR characterization at 120 °C.

Fig. 4. NMR characterization at 100 °C.

4. Conclusions

A bitumen system modified with waste plastic (WPP) was investigated and compared to other polymer modifiers. It has been shown that the addition of WPP enhances bitumen mechanical performance at high and low temperatures. This investigation also showed that the WPP can be considered a useful polymer in the road construction. In fact, even though the pure reference has lightly higher temperature transition, WPP shows similar values. Additionally, the effects at low temperature are practically equal confirming the goodness of its use as polymer for the bitumen modification.

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