Rheological performance and NMR structure investigation of ultrasound crumb rubber modified bitumen

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ABSTRACT

Rutting and fatigue cracking are the major distresses for road pavement performances [1-2]. In addition approximately 9 to 10 kg of rubber from tyres per inhabitant and year are currently discarded in the industrialized societies . Thus, the introduction of crumb rubber (CR) in the production of asphalt rubber (AR) mixes for road pavements should be considered as a sustainable technology to transform an unwanted residue into a new bituminous mixture highly resistant to fatigue and fracture [3]. As an asphalt additive, the wasted rubber needs to be devulcanized (UCRM). In this work base bitumens interacted with neat crumb and ultrasound devulcanized crumb rubber to produce AR mixes. By means of nuclear magnetic resonance and Rheology dynamic experiments we investigated the influence of ultrasound treated crumb rubber modifier on the morpho-structure and rheological properties of bitumen binder. Ultrasounds cause the partial devulcanization of the CR resulting into enhanced mechanical properties in a wide range of temperatures.

Keywords: green building, crumb rubber, asphalt, bitumen, ultarsounds

1 INTRODUCTION

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 for building industry. Due to their high cost, a limited number of polymers have been used as modifying agents [4]. The use of exhausted vehicle tires in pavement construction has been going on for the last three decades [5-8]. The characteristics of crumb rubber depend on the rubber type, asphalt composition, and size of rubber crumbs, as well as time and temperature of devulcanization reaction. These factors affect significantly pavement performances [9-11]. Initially, when devulcanized crumb rubber is blended with bitumen at high temperatures the interaction between UCRM and bitumen is a non-chemical reaction where the rubber particles are swollen by absorption of the bitumen's aromatic oils [12]. Absorption of bitumen components by the rubber inevitably depletes the bitumen of the absorbed components and consequently modifies its properties making it stiffer and more brittle [13], until a complete dissolution of rubber polymer macromolecules occurs. Furthermore, preliminary results (data not shown) report that CR and UCRM have stability problems (sedimentation/dissolution) . The challenge is to subject the rubber to a devulcanization regime that will produce a substance capable of greatest swelling but still maintaining enough cross links to prevent the rubber from dissolving in bitumen. In this frame, ultrasonic energy may be a valuable method [14] to partially break C-S and S-S bonds trying to convert rubber waste to a efficient usable material, environmental friendly also. In the present study, we focused on the understanding of the chemical-physics interactions between partially ultrasound devulcanized crumb rubber and bitumen. To reach this goal we performed dynamic rheological and nuclear magnetic resonance experiments in a wide range of temperatures.

2 EXPERIMENTAL

2.1 Materials and Samples

For the present study, plain bitumen sources are from Saudi Arabia and Russia and were already characterized [1]. According to the supplier (Bagigi srl, 33030 Coseano/UD – Italy), the crumb rubber used in this work was obtained by mechanical means and constituted by truck (DTRB) and car (DCRB) tyres. These materials were supplied both untreated and already partially ultrasound devulcanized by means of a unknown procedure for copyright reasons, that allowed to devulcanize only the surface of the rubber particles. In collaboration with StarAsphalt S.p.A., (S.P. Piana Loc. Garga, 87010 - Saracena (CS) – Italy), the supplied crumb rubber was sieved in order to use only the fraction that have 1mm dimension. Materials were then washed with toluene and dried at 135 ºC. Its solubility and density were determined according respectively to ASTM D 6814-02 and AG:PT/T144. A 10.0% w/w of crumb rubber was added to the base bitumen for the preparation of all samples.

2.2 Rheological Measurements

A SR5 rheometer (Rheometric Scientific, USA) has been used to make rheological tests. This is a shear stress

controlled instrument which is equipped with a parallel plate geometry (gap 2 mm, Φ 25 and 8 mm) and a Peltier system for temperature control in the range +20 / +100°C (±0.1°C) .Dynamic tests, have been performed in linear conditions where the measured material functions are independent on the amplitude of the applied load and are only function of microstructure [15]. Samples are subjected to oscillatory small deformations (or stresses) to maintain linear viscoelastic conditions and the resulting meauserd dynamic modulus can be split in two components: the storage modulus, G′, the in-phase part, is a measure of the reversible elastic energy, whilst the loss modulus, G″, the out-of-phase component, 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 [15]. The loss tangent, tan δ, is a measure of the of the energy lost to energy stored ratio in a deformation cycle.

$$\tan\delta = \frac{G''(\omega)}{G'(\omega)} \tag{1}$$

Temperature sweep tests were performed at 1 Hz frequency and increasing temperature from +25 to +100°C at 1 °C/min step rate and applying the proper stress values to guarantee linear viscoelastic conditions within the investigated temperature range. Temperature sweep tests were also performed decreasing temperature from +20 to -30°C at 1 °C/min step rate.

2.3 NMR measurements and Inverse Laplace Transform

For the ^{1}H spin-spin relaxation measurements, a homemade NMR instrument has been used. It operates at a proton frequency of 15 MHz. Measurements have been performed at temperatures from +120 to +25 °C with an error of ± 0.1°C (Eurotherm Temperature Controller). A classic Carr-Purcell pulse sequence has been used to record the echo decay[16]. In a basic NMR concept, at equilibrium, nuclei are distributed among the energy levels according to a Boltzmann distribution. The absorption of radiofrequency energy disrupts this distribution, then the nuclear spin system returns to equilibrium with its surroundings (the "lattice") by a first-order relaxation process characterized by a time T_1 called the spin-lattice relaxation time. To account for processes that cause the nuclear spins to come to equilibrium with each other, a second time T_2 is required. The T_2 is called the spin-spin relaxation time, because the relaxation is concerned with the exchange of energy between spins via a flip-flop type mechanism. Usually the T2 relaxation time varies all over the sample because of the sample heterogeneity or surface relaxation differences, then a multi-exponential attenuation of the registered signal envelope should be observed. Hence, if inside the sample a continuous distribution of relaxation times exists, the amplitude of the nth echo in the echo train is given by:

$$A_n = A_0 \int_0^\infty P(T_2) e^{-2\pi/T_2} dT_2 \tag{2}$$

A_n is the amplitude of the nth echo in the echo train and A_0 is a constant. $P(T_2)$ is the Inverse Laplace transform (ILT) of the unknown function that fit the plot of the echo amplitudes. Hence $P(T_2)$ can be understood as a distribution of rate constants, strictly, a probability density function, PDF. The ILT can give the answers required where it needs to face the inverse problem of estimating the desired function from noisy experiments.

3 RESULTS AND DISCUSSION

Figure 1 illustrates the plot of tan δ at different temperatures for all of the compared samples.

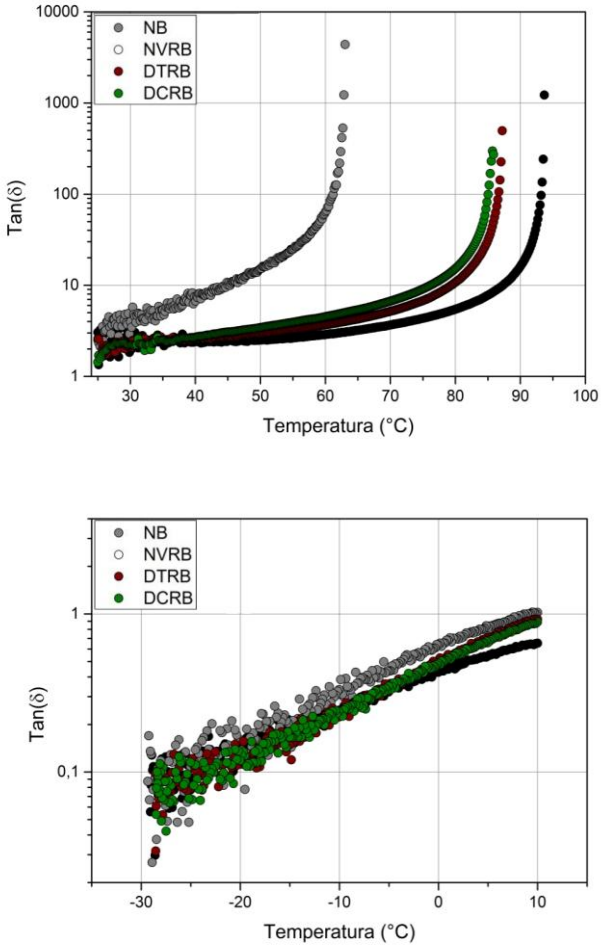

Figure 1: Plots of tan δ vs temperature for neat bitumen (NB), Not Devulcanized rubberized bitumen (NVRB), Partially Devulcanized Truck rubberized bitumen, (DTRB), Partially Devulcanized Car rubberized bitumen, (DCRB).

The not devulcanized sample (NVRB) shows higher transition temperature (93.8 °C), while the neat bitumen (NB) presents the lowest transition temperature (62.9 ° C). The ultrasound partially de-vulcanized samples have transition temperatures close each other (DTRB 87.4 °C – DCRB 85.9 °C). From the trends of tan δ it can be observed that NB shows a viscous behavior if compared to the other samples. The samples DTRB, DCRB and NVRB show similar rheological behaviors, but the partially devulcanized samples are characterized by values of dynamic viscosity slightly greater than the sample not devulcanized.

At high temperatures, the measurements indicate that, DTRB and DCRB have a higher transition temperature than the neat bitumen and, having a higher elastic modulus, are able to "recover" a possible further applied deformation.

At low temperatures the samples that contain partially devulcanized rubber have greater tan δ and lower elastic modulus, therefore they better dissipate the applied stress. In a NMR basic concept, the spin-spin relaxation time (T_2) is proportional to the molecular mobility of a material. As a result higher mobility corresponds to longer T_2 times. Hence, the proton T_2 time was measured in the temperature range between +120 °C and +30 °C. Inverse Laplace Transform (ILT) to the measured echo envelope, shown in Figure 2, give us the T_2 distribution as a function of temperature. Hence for bituminous materials, shorter T_2 times distributions correspond to more rigid fractions (asphaltene), whereas longer spin-spin relaxation times should correspond to the maltene fraction [2]. Intermediate T_2 times should represent resins, which are expected to have an intermediate mobility between asphaltenes and maltenes [2]. Figure 2(A) shows T_2 distribution for neat bitumen and just as expected we found essentially two distributions corresponding to the asphaltene and maltene fractions. Figure 2(B) illustrates the T_2 distributions of the sample containing the not devulcanized CR and one may appreciate the presence of a third T_2 distribution missing in the reported data of the neat bitumen (2A) that falls at shorter times for all the temperatures. This peak can be attributed to the partly separated CR. In addition this T_2 distribution seems to be less affected by temperature and to form rubber-aggregates unlinked to the bitumen-aggregates. On the other hand ultrasound partially treated crumb rubber modifier shows a different behaviour, Figure 2(C). Except for 30 and 40 °C, the T_2 distribution due to the rubber-aggregates is not so distinguishable from the bitumen-aggregates. The partially devulcanized rubber seems to somehow correlate to the maltene-asphaltene aggregates of the bitumen.

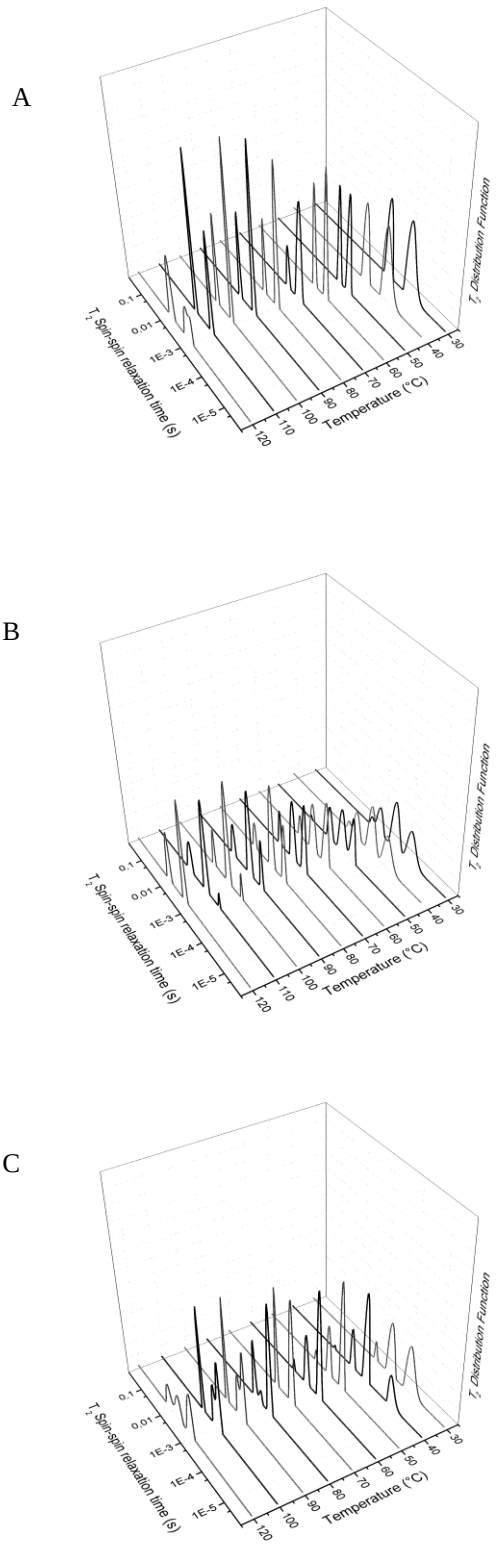

Figure 2: T_2 time distribution along temperatures. A) Neat Bitumen. B) bitumen+10% w/w not devulcanized crumb rubber. C) bitumen+10% w/w partially devulcanized crumb rubber.

4 CONCLUSIONS

The ultrasound partially devulcanized crumb rubber is a technology that may enable homogeneity, stability and improve properties of bitumen binder. In the present work we used partially devulcanized wasted truck (DTRB) and car (DCRB) tyres as bitumen modifiers .The result is a higher performance of the bituminous binder with unique properties that are consistent. Partially ultrasound devucanized crumb rubber is ideally suited for hot climates. It enhances the key properties of asphalt mixes, i.e. deformation resistance and fatigue life. These improvements are the result of three crucial physical changes which the polymer makes in the conventional binder structure: reduces temperature susceptibility, increases stiffness modulus and enhances elasticity.

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