

# ROAD BITUMENS STUDIED USING SOLID STATE NMR SPECTROSCOPY

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## 1. Introduction

The performance of an asphalt mixture used for road pavements depends upon its susceptibility to changes in its physical and chemical properties with time, temperature, and exposure to moisture [1]. This is determined by the ratio and physical and chemical properties of components used for its preparation – bitumen which is used as a binder, aggregates, and other additives which are expected to improve its properties, e.g. crumb rubber. Crumb rubber can replace part of the aggregates in the asphalt mixture, i.e. it is added directly to the asphalt mixture (dry process) or it is blended with bitumen first forming bitumen-rubber and then used for the preparation of the asphalt mixture (wet process) [2]. In general asphalt mixtures prepared by the wet process exhibit better and more reliable performance than those prepared by the dry process. This could be caused by the poorly-controlled and not fully understood process of swelling of rubber particles during asphalt mixture preparation, laying and compaction [2].

Bitumen consists of approximately 25 wt.% of aromatic hydrocarbons and 75 wt.% of aliphatic hydrocarbons containing minor elements in bonded form, and from the thermodynamical point of view it is a very viscous liquid at room temperature [3].

The aim of the research presented in this paper was to detect changes in the environment of <sup>13</sup>C and <sup>1</sup>H nuclei in the structure of commercial road bitumen and crumb rubber, having undergone the standard procedure used for asphalt mixture preparation, using <sup>13</sup>C and <sup>1</sup>H NMR experiments.

## 2. Experimental

Two samples were studied: commercial road bitumen 50/70, produced by the company TOTAL Polska Sp. z o.o. (sample A) and bitumen extracted from a piece of compacted asphalt mixture which was prepared with addition of crumb rubber using the standard dry process (sample B).

<sup>13</sup>C and <sup>1</sup>H NMR experiments were performed on a Varian 400 NMR spectrometer operating at 100.54 MHz and 399.82 MHz respectively, using a 4 mm rotor and a magic angle spinning (MAS) rate of 10 kHz. The measurements were carried out at room temperature. <sup>13</sup>C NMR spectra were acquired with 90° pulse duration of 2 μs with high power

proton decoupling during acquisition, delay times of 1.5 and 150 s, and averaging over 480 scans.  $^1\text{H}$  NMR spectra were acquired with  $90^\circ$  pulse duration of  $3.4\ \mu\text{s}$ , delay time of 7 s, and averaging over 64 scans.

### 3. Results and Discussion

The  $^1\text{H}$  NMR spectra of static solid samples are broad and featureless (typically 100 kHz wide) due to the strong dipolar couplings between the protons. Spinning the sample at an angle of  $54.7^\circ$  with respect to the external magnetic field (magic angle spinning technique – MAS) has the effect of averaging anisotropic interactions, but if the MAS rate is smaller than the width of the unaveraged spectrum the averaging is only partial. In the case of so-called “inhomogeneous” interactions (chemical shift anisotropy and heteronuclear interactions), sharp center bands at the isotropic chemical shift and spinning sidebands separated by multiples of the rotation frequency are observed in the spectra [6]. In the case of “homogeneous” interactions (homonuclear dipolar coupling), the centerbands and spinning sidebands have a finite width which decreases slowly with increasing MAS rate [6]. The strength of dipolar interaction is characterized by the dipolar coupling constant, which is directly proportional to the inverse cube of the distance between the protons [7].

As can be seen in Fig. 1 the  $^1\text{H}$  MAS NMR spectra of both samples display broad spectral features - center band and spinning sidebands. The  $^1\text{H}$  MAS NMR spectrum of sample A displays a peak at the chemical shift of 1 ppm, which can be assigned to alkyl protons, and shoulders at 4 and 7.3 ppm produced by protons in  $-\text{NCH}$  groups and aromatic protons [5] respectively, and four spinning sidebands.

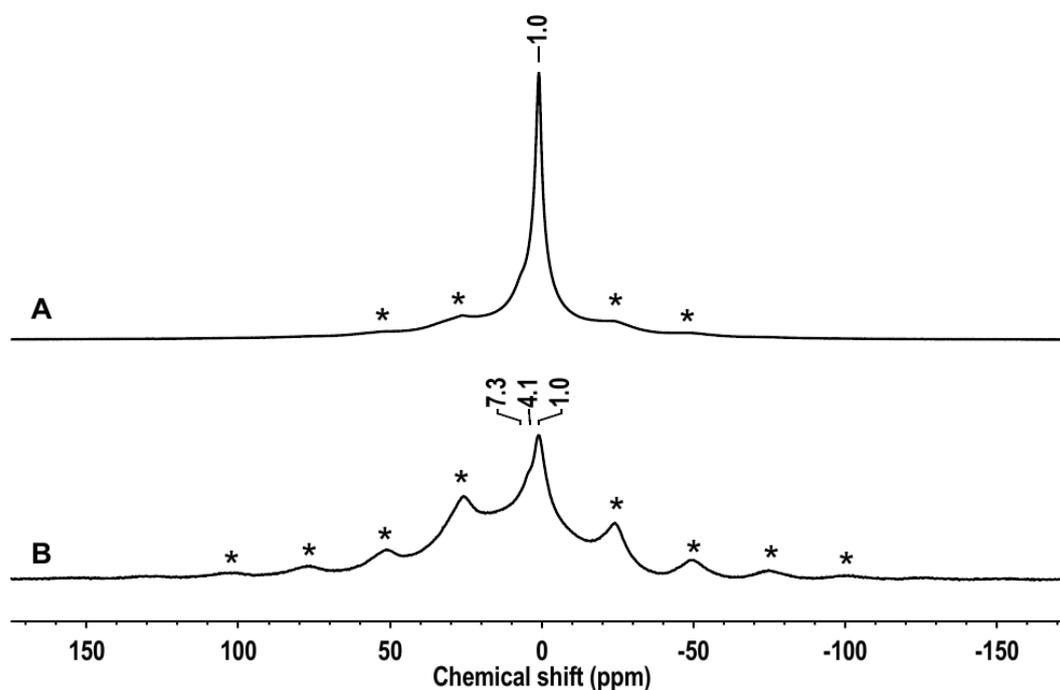


Fig. 1:  $^1\text{H}$  MAS NMR spectra of sample A (A) and sample B (B) measured at room temperature with MAS rate of 10 kHz (spinning sidebands are denoted by asterisks).

The signals in the  $^1\text{H}$  MAS NMR spectrum of sample B can be assigned to the same proton species, although the range in which spinning sidebands appear is considerably larger,

and at least eight spinning sidebands can be distinguished. This indicates a stronger homonuclear dipolar interaction than in sample A due to shorter distances between hydrogen nuclei in the dense and rigid bitumen structure.

$^{13}\text{C}$  MAS NMR spectra of bitumens display broad lines of aromatic carbons in the range of 100-160 ppm and better resolved lines of aliphatic carbons in the range of 0-90 ppm [1]. Crumb rubber produces  $^{13}\text{C}$  MAS NMR spectrum [4] with seven relatively narrow lines in the same ranges as  $^{13}\text{C}$  MAS NMR spectra of bitumens, which are assigned to carbons in natural and synthetic rubber.

The  $^{13}\text{C}$  MAS NMR spectrum of sample A recorded with a delay time of 150 s displays four signals in the aliphatic region, which can be assigned to carbons in  $\text{CH}_3$  and  $\text{CH}_2$  groups, while the broad signal in the 100-160 ppm region is produced by aromatic carbons (Fig. 2). The  $^{13}\text{C}$  MAS NMR spectrum of sample B recorded with a delay time of 150 s (Fig. 2) displays only two broad signals – one in the aromatic and the other in the aliphatic regions, which arise from broad and strongly overlapping signals. In order to obtain qualitative information on carbon mobility the  $^{13}\text{C}$  MAS NMR spectra were recorded for both samples with a delay time of 1.5 s. Shorter delay time suppresses the signal of more rigid carbons in the aromatic region and enhances more mobile aliphatic carbons (not shown). The signals of crumb rubber are not observed, probably due to very large signal broadening caused by very strong interaction between rubber chains and bitumen and the relatively small amount of crumb rubber in the asphalt mixture. Moreover, the destruction of the rubber structure during asphalt mixture preparation cannot be excluded.

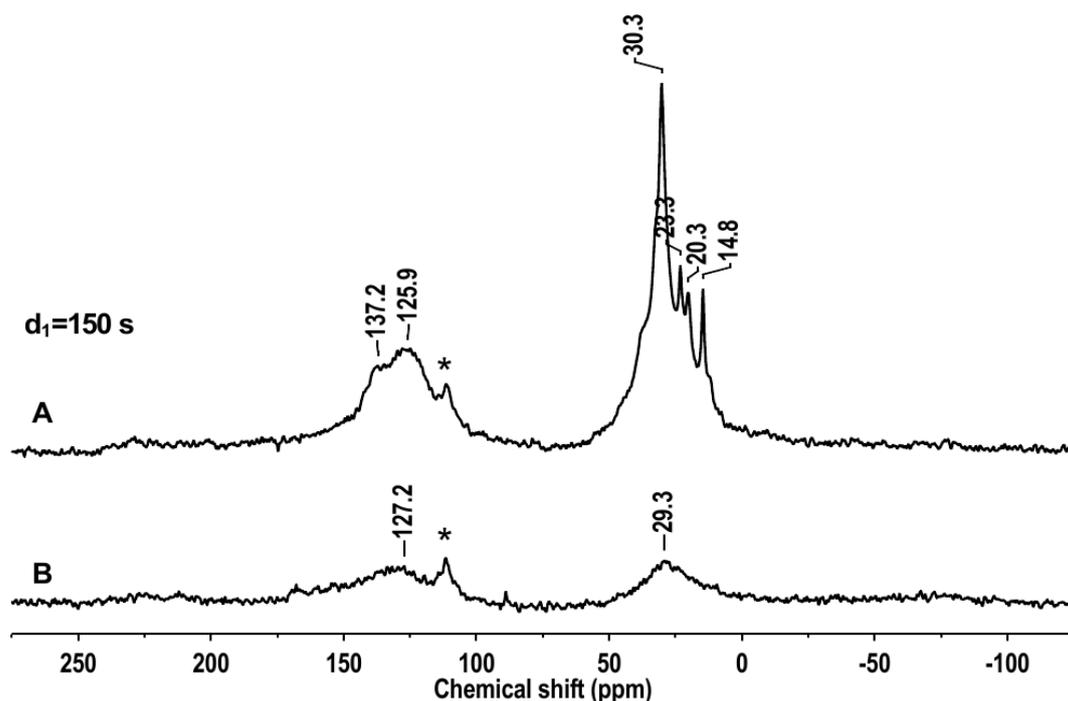


Fig.2:  $^{13}\text{C}$  MAS NMR spectra of sample A and sample B recorded with a delay time of 150 s at room temperature and MAS rate of 10 kHz (rotor signal is denoted by asterisk).

The total area beneath the spectrum is smaller probably due to the fact that part of carbons can have a spin-lattice relaxation time considerably longer than the delay time used for recording of this spectrum, and they cannot be observed in the spectrum. From this we can deduce that sample B has a more rigid, solid-like structure.

#### 4. Conclusions

$^{13}\text{C}$  and  $^1\text{H}$  MAS NMR can detect changes in the structure of commercial road bitumen which has undergone the standard procedure of preparation of asphalt mixture with addition of crumb rubber using the dry process. The line broadening in the  $^{13}\text{C}$  MAS NMR spectrum of processed bitumen, and stronger homonuclear dipolar interaction inferred from the wider range of spinning sidebands in  $^1\text{H}$  MAS NMR spectrum, indicate that bitumen in the resulting asphalt mixture is solid-like material in contrast to as-supplied commercial bitumen, which can be considered as a very viscous liquid. The NMR signals of crumb rubber in the processed bitumen were not observed.

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