Compact low-field NMR spectroscopy and chemometrics: A tool box for quality control of raw rubber

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A B S T R A C T

Styrene-butadiene rubber (SBR) is a major source material for the fabrication of elastomer products. Depending on its origin, differences are observed between SBR samples by tabletop NMR spectroscopy that relate to the constitution of the macromolecular chains. This study reports experimental results from the analysis of 108 SBR samples by low-field ^{1}H and ^{13}C NMR spectroscopy at 1 T in combination with partial least squares regression to develop a methodology for quality control of raw rubber. Partial least squares regression (PLS-R) models were developed for quantifying the individual monomer units present in SBR which are impossible to quantify directly because of peak overlap in a ^{1}H NMR spectrum obtained at 1 T. The spectra revealed differences between samples from the same and different manufacturing batches of the same and different manufacturers in a qualitative and quantitative fashion. The range of samples included regular and oil-extended solution and emulsion polymerized SBR. Referring to high-field spectra acquired at 9.4 T the peaks in the low-field ^{13}C NMR spectra could be assigned for determining the rubber microstructure, and the content of different repeat units could be quantified by partial least squares regression. Over 12 repeatable measurements the standard deviation in mass % was 0.03%, 0.06%, 0.05%, 0.33% and 0.37% for the contents of styrene, 1,2-butadiene, 1,4-butadiene, *trans*-1,4-butadiene and *cis*-1,4-butadiene units, respectively. Among 7 different sampling points in a delivery, the standard deviation was 0.51% for 1,2-butadiene, 0.88% for styrene, 0.56% for 1,4-butadiene unit, 0.42% for *trans*-1,4-butadiene and 0.68% for *cis*-1,4-butadiene units. The root-mean-square error of prediction (RMSEP) for styrene, 1,2-butadiene, 1,4-butadiene, and *trans*-1,4-butadiene was 0.15, 0.29, 0.29, and 0.28 with R^2 values of 0.93, 0.92, 0.92, and 0.95, respectively, demonstrating the potential of low-field NMR spectroscopy with compact instruments for quality control of raw rubber when used in combination with effective data analysis procedures such as chemometrics.

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1. Introduction

Different sources, synthesis procedures, and processing methods impart differences in the rubber composition, which affect chemical and physical properties of rubber and rubbery materials [1-2]. Styrene-butadiene rubber (SBR) produced by anionic polymerization in solution (S-SBR) and by free radical polymerization in emulsions (E-SBR) differs in the chain statistics due to different synthetic procedures and subsequently can exhibit differences in physical and chemical properties [3-4].

The different grades of SBR are determined foremost by the concentrations of its four repeat units consisting of styrene, 1,2-butadiene, *cis*-1,4-butadiene and *trans*-1,4-butadiene. The concentration of styrene in SBR copolymers ranges from a few percent up to 50%. With increasing styrene content tensile strength, hardness, and traction properties improve while an increase in 1,2-butadiene content decreases the elongation at break and the tear strength [5].

To improve the rheological and mechanical properties in a cost effective way SBR is extended with oil. Aromatic and paraffinic oils modify the microstructure of the rubber and affect the chemical and mechanical properties [6].

To process SBR into high end products and to recycle waste SBR, it is essential to quantify at least the chain composition, i. e. the content in the different repeat units [7]. An even more detailed characterization would include the block length statistics. High-field NMR spectroscopy [8-9], infra-red (IR) [10], near IR spectroscopy [11], pyrolysis-FTIR and TGA [12] are different analytical techniques used for qualitative and quantitative compositional

Abbreviations

1 T	One Tesla
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser enhancement
DEPT	Distortionless enhancement by polarization transfer
ATR	Attenuated total reflectance
E-SBR	Emulsion polymerized styrene-butadiene rubber
S-SBR	Solution polymerized styrene-butadiene rubber
SBR	Styrene-butadiene rubber
THF	Tetrahydrofuran
FT-IR	Fourier transform infra-red
PLS-R	Partial least-squares regression
RMSEC	Root mean square error of calibration
RMSECV	Root mean square error of cross validation
RMSEP	Root mean square error of prediction

analysis of rubber. The coupling of pyrolysis-gas chromatography (Py-GC) with mass spectrometry [13] is an efficient method for polymer analysis. It can be used without any further sample pre-treatment, which is a potential source of error in any analytical procedure. Py-GC provides information about various rubber blends but not about the chain composition unless it is combined with other techniques such as IR spectroscopy. Also, the oligomers produced by pyrolysis may not accurately represent the composition of the original polymer. Measurements with IR spectroscopy in the attenuated total reflection (ATR) mode are easy to conduct with good repeatability. However, IR spectroscopy is not an absolute method and requires reference calibration with other analytical techniques [10].

NMR spectroscopy is an absolute analytical method. It provides quantitative concentrations of chemical groups without prior calibration [14]. For reasons of sensitivity and spectral dispersion high magnetic fields are employed in most laboratories. High-field NMR spectrometers are equipped with superconducting magnets that require cryogenic cooling. Moreover, the wealth and complexity of different NMR experiments demands operation by professionals. Therefore, despite its outstanding analytical power, NMR spectroscopy is not the prime analytical method when samples need to be analyzed routinely, at low-cost and fast at the chemical workbench in laboratories and industries where high-field and large-scale analytical instrumentation is unavailable.

On the other hand, a new generation of compact NMR spectrometers [15-16] with permanent magnets [17] at field strengths of 1–2 T provides similar information as high-field spectrometers albeit a lower sensitivity and spectral dispersion. They can be used at the chemical workbench on demand for chemical analysis, reaction monitoring [18], quality control [19], and process control [20] in a working environment.

One-dimensional ^{1}H NMR spectra of SBR provide information about the chain composition in terms of styrene, 1,2- and 1,4-butadiene content [21]. One-dimensional ^{13}C NMR spectra provide additional information about *cis*- and *trans*-1,4-butadiene units which cannot be obtained with ^{1}H NMR spectroscopy due to peak overlap even at high magnetic field. The distributions of different repeat units can be quantified from ^{13}C NMR spectra even at 1 T in terms of diads and triads through the couplings of chemical groups in different repeat units [22].

Resonance overlap is an issue at low-field, which hampers the analysis of ^{1}H NMR spectra more so than at high-field, where the spectral dispersion is larger. Then chemometric methods can be engaged to sort the spectral fingerprints [23]. For example, chemometric methods have been employed to analyze high-field spectra from metabolites, proteins and polymers with severe signal overlap [24-26]. Recently, also low-field ^{1}H NMR spectra were analyzed by chemometric methods to determine the conversion of vegetable oil to bio-diesel in real time [27]. Other applications concern beef authentication [28], oil adulteration [29] and ground roast coffees [30]. In this work the partial least squares regression (PLS-R) method is employed [31]. The data matrices involved in the regression are X (independent, predictors) and Y (dependent, responses). The PLS-R model can be represented as $Y = f(X)$ to explain the variations in the Y-variables on variations in the X-variables. It extracts a set of latent variables $\boldsymbol{T}$ (x-scores) and $\boldsymbol{U}$ (y-scores) from $\boldsymbol{X}$ factors and $\boldsymbol{Y}$ responses, respectively. The extracted latent variables find the maximum covariance between $\boldsymbol{X}$ and $\boldsymbol{Y}$. The $\boldsymbol{T}$ variables are used to predict the $\boldsymbol{U}$ variables, which are further used to predict unknown responses. In the present study the X-variables are the NMR spectra and the Y-variables are the monomer concentrations.

This methodology is used in the following for the first time to determine differences in raw rubber samples obtained from the same and different lots of the same and different manufacturing batches from the same and different manufacturers in a qualitative and a quantitative fashion from NMR spectra measured at 1 T with a compact spectrometer. Note, that a lot is a production batch, which is subdivided typically into 25 kg bales from which samples are drawn for analysis. The contents of styrene, 1,2-butadiene, *trans*- and *cis*-1,4-butadiene repeat units were determined from ^{1}H and ^{13}C NMR spectra by partial least squares regression (PLS-R) referring to NMR spectra measured at a high field of 9.4 T. The regression model was then employed to predict the concentrations of repeat units from unknown samples. Differences between S-SBR and E-SBR were observed with ^{1}H and ^{13}C NMR spectroscopy by following the chemical signatures of different chemical groups. As the peaks in the ^{13}C NMR spectra at 1 T were difficult to assign to the chemical groups of S-SBR and E-SBR due to low sensitivity and low natural abundance of carbon, high-field spectra served as reference. In addition to SBR without oil, oil-extended SBR was studied with ^{1}H NMR spectroscopy using the PLS-R model. The experiments were repeated over longer time to assess the reproducibility of measurement with the available instrument. The inhomogeneity of rubber within a bale was determined by analyzing the content of repeat units from samples drawn from different spots of the same bale, the inhomogeneity of a lot was analyzed with samples drawn from different bales, and the consistency of product quality between different lots was analyzed by comparing the spectra of samples drawn from different lots of the same manufacturer. These differences between spectra recorded with a compact 1 T spectrometer and analyzed with chemometrics demonstrate a promising potential of low-field NMR spectroscopy for use in quality control of raw rubber.

2. Materials and methods

2.1. Materials

2.1.1. Samples

Different raw rubber samples were obtained from the same and different lots of same and different manufacturing industries involving different synthetic procedures. Details of all samples are provided in Table S1 of the supporting information. All samples were received in boxes; therefore they are named with respect to their boxes.