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Epoxidized natural rubber — Determination of epoxidation and ring opening level by NMR spectrometry

Caoutchouc naturel époxydé — Détermination de l'époxydation et du niveau d'ouverture des anneaux par spectrométrie RMN

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Contents

Page

Foreword

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This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Epoxidized natural rubber (ENR) is one of the modified rubbers derived from natural rubber (NR). The modification process is done by introducing oxygen atom to the unsaturated molecule of NR. This chemical reaction produces an oxirane or epoxide compound that consists of a three-membered ether in a cyclic form. A few grades of ENR are currently available depending on the extent of modification such as ENR 25 (25 mole% epoxide) and ENR 50 (50 mole% epoxide).

ENR is used in many applications which include tyres, bearings and adhesives. Epoxidation and ring opening level are very important parameters to check ENR quality. Various techniques are available for quantification of the epoxidation level, such as elemental analysis (carbon, hydrogen and oxygen), infrared spectroscopy (IR), proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance spectroscopy (NMR), as well as the chemical titrimetric technique.

This document specifies a quantitative method, using proton (^{1}H) nuclear magnetic resonance spectrometry, for the determination of epoxidation and ring opening level of raw ENR. This test method is an important document to support ISO 24483, as these parameters are included as specifications for ENR. This work will benefit the market to specify a measurement method for the epoxidation and ring-opening level of ENR.

Epoxidized natural rubber — Determination of epoxidation and ring opening level by NMR spectrometry

1 Scope

This document specifies a quantitative method, using proton (^{1}H) nuclear magnetic resonance (NMR) spectrometry, for the determination of epoxidation and ring opening level of raw epoxidized natural rubber (ENR). This method applies to ENR of all grades available commercially.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
epoxidized natural rubber
ENR
natural rubber which has been chemically treated and modified through the addition of oxygen atom onto the double bond structure of the *cis*-1,4-polyisoprene to form three-membered ether (C-O-C) in a cyclic form by a process known as epoxidation reaction

[SOURCE: ISO 24483:2023, 3.1]

3.2
epoxidation level
level and/or degree of the epoxy groups (C-O-C) in the NR structure

[SOURCE: ISO 24483:2023, 3.4]

3.3
ring opening level
level and/or degree of ring opening due to the formation of secondary by product from uncontrolled condition of epoxidation reaction in the natural rubber structure

[SOURCE: ISO 24483:2023, 3.5]

3.4
ENR 25
epoxidized natural rubber with 25 mol % epoxidation

3.5
ENR 50
epoxidized natural rubber with 50 mol % epoxidation

4 Principle

^{1}H NMR technique is used to identify and quantify selectively the hydrogen atoms which are characteristic for both NR and ENR. The raw ENR is dissolved in appropriate solvent and the dissolved part is measured using NMR. Epoxidation and ring opening level are determined by taking the integration area of the proton from the epoxy group and the proton from the ring opening products, respectively, to the total integration areas of the proton from natural rubber, epoxy group and ring opening products.

5 Reagents

5.1 Deuterated chloroform, $CDCl_3$, containing 0,03 % by mass fraction of tetramethylsilane (TMS) as internal standard. The purity of the $CDCl_3$ shall be ≥99,8 %.

6 Apparatus

6.1 Analytical balance, accurate to 0,1 mg.

6.2 Sample vial.

6.3 NMR sample tube.

6.4 Pasteur pipette.

6.5 NMR spectrometer, Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer with resonance frequency of more than 100 MHz, preferably with the following acquisition parameters:

— probe: ^{1}H;

— degree pulse: 45°;

— pulse delay: 5 s;

— number of scans: 256.

6.6 Data system, using an acquisition and a data processing software.

7 Procedure

7.1 Sample preparation

7.1.1 Weigh about 25 mg to 30 mg ENR sample and put into a sample vial (6.2).

7.1.2 Add about 2 ml of $CDCl_3$ into a specimen vial and shake for a few times.

7.1.3 Leave the sample to dissolve in the dark for 16 h to 24 h.

7.1.4 Transfer about 1 ml of the liquid sample into the NMR sample tube (6.3) using a Pasteur pipette (6.4). Cap the tube and shake for a few times.

Try to eliminate the solid in 7.1.4 as it will cause the NMR peak to broaden and might affect the result.

7.2 NMR measurement

7.2.1 Place the NMR sample tube into the spinner and analyse the sample using the specified acquisition parameters.

7.2.2 Acquire the free induction decay (FID) signal and apply a Fourier transform to obtain the spectrum. See Figure A.1 and Figure A.2.

7.2.3 Adjust the resonance of the reference peak to 0,00 ppm for TMS.

7.2.4 Correct the baseline of the spectrum. Integrate the spectrum and record the following areas:

— I_1 the methine proton area of NR, from 5,3 ppm to 5,0 ppm;

— I_2 the methine proton area of epoxy group of ENR, from 2,9 ppm to 2,6 ppm;

— I_3 the furan proton area of ENR, from 3,8 ppm to 4,0 ppm;

— I_4 the hydroxyl proton area of ENR, from 3,3 ppm to 3,5 ppm.

8 Calculation

Calculate the percentage of epoxidation and ring opening levels, within one decimal, using Formulae (1) and (2).

$$E = \frac{I_2}{I_1 + I_2 + I_3 + I_4} \times 100 \quad (1)$$

$$O_r = \frac{I_3 + I_4}{I_1 + I_2 + I_3 + I_4} \times 100 \quad (2)$$

where

E is the epoxidation level, in %;

O_r is the ring opening level, in %;

I_1 is the methine proton area of NR;

I_2 is the methine proton area of epoxy group of ENR;

I_3 is the furan proton area of ENR;

I_4 is the hydroxyl proton area of ENR.

9 Precision

See Annex B.

10 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 5260:2023;

b) all details necessary for the complete identification of the product tested;

c) the method of sampling used;

d) the values of I_1, I_2, I_3, I_4, epoxidation level E and ring opening level O_r;

e) any unusual features noted during the determination;

f) any operation not included in this document, or any operation regarded as optional such as the NMR parameters in (6.5) if different from the specified one;

g) the date of the test.