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Determination of the Composition of Ethylene–Propylene–Rubbers Using ^{13}C -NMR Spectroscopy

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SYNOPSIS

A detailed ^{13}C -NMR procedure has been developed to analyze ethylene–propylene–rubbers (EPM). Special attention has been paid to instrumental and spectral parameters and calculation methods. By applying this procedure, it is possible to obtain consistent and reproducible molecular composition results on EPM, independent of the measuring laboratory and the calculation method. The procedure has been tested in eight industrial laboratories. Using this procedure, the composition of a set of 10 EPM standards has been defined. These standards will be used for worldwide infrared calibration purposes (ASTM D-3900).

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INTRODUCTION

Ethylene–propylene–rubbers (EPM) and ethylene–propylene–diene–rubbers (EPDM) are very important elastomeric products and extensive research has been carried out into the structure and properties of these materials. Special attention has been given to establish the molecular composition of EPM/EPDM, because it is an important basic property related to the green strength of both the pure polymer and the compound, their extrusion characteristics, and a variety of properties of the cured material.

EPM/EPDM suppliers use different test methods to characterize polymers. To get truly comparable results, these tests require standardization. Some years ago, the joint European EPM/EPDM suppliers began such an effort, under the coordination of the European Section of the International Institute of Synthetic Rubber Producers (IISRP/ES), evaluating several procedures of characterization of EPM/EPDM.

The most commonly used method to determine the molecular composition of EPM/EPDM, and the only one recognized by the American Society of Testing of Materials (ASTM), is the infrared

method ASTM D-3900. In this procedure, infrared, being a relative technique, was calibrated using absolute data obtained by analysis of radioactive carbon-tagged monomers.

However, the results obtained by applying this method were the subject of considerable debate. To check on and improve the accuracy of the existing infrared method, ^{13}C -nuclear magnetic resonance spectrometry has been used in a round robin organized by the IISRP to determine the molecular composition of a set of EPM standards.

The initial differences between data obtained from different laboratories underlined the necessity to develop a NMR procedure that would give reproducible and consistent results whenever and wherever it was used. The purpose of the IISRP effort was to identify and eliminate every cause of deviation by standardizing the various parts of ^{13}C -NMR analysis: sample preparation, data acquisition, spectral interpretation, and calculation methods.

The procedure developed was tested by four European laboratories (IISRP European Section group: DSM, Enichem Elastomeri, Exxon Chemical Europe, and Hüls AG) and four U.S. laboratories (ASTM D 11.11 group: Copolymer, DuPont, Exxon Chemical America, and Uniroyal) on a set of 10 EPM samples: four new commercial EPM and six original ASTM standards.

Table I EPM Standards

VISTALON 404	E/P rubber produced by Exxon Chemical
VISTALON 805	E/P rubber produced by Exxon Chemical
BUNA AP301	E/P rubber produced by Hüls AG
DUTRAL-CO038	E/P rubber produced by EniChem Elastomeri
ASTM 1-6	E/P rubber standards supplied by ASTM

EXPERIMENTAL

EPM Standard Set

The series of EPM that have been designated as standards includes four commercial polymers and the six ASTM standards, 1–6, as referenced in ASTM D-3900. The list of standards is compiled in Table I. The four new commercial materials have been added to the list of the existing ASTM stan-

dards to allow correction for possible degradation of the already old set of ASTM standards.

Sample Preparation

Approximately 0.375 g of the polymer sample is weighed into a 10 mm NMR tube and 2.5 mL of 1,2-dideutero-1,1,2,2-tetrachloroethane is added as a lock solvent, so that a concentration of 15 wt-vol % is reached $[(\text{g/mL}) \times 100]$. Preferably, degassed solvent is used. To dissolve the polymers, samples are heated at the analysis temperature of 120–125°C for 24 h, with appropriate mixing to homogenize the solution.

DATA ACQUISITION

Equipment

^{13}C -NMR spectra have been acquired on NMR spectrometers equipped with a 10 mm ^{13}C -NMR probe and a variable temperature unit. The following

Table II ^{13}C -NMR Assignment of EPM (Solvent TCE- d_2 , Temperature 120°C, Reference TMS)⁶

Peak No.	Carbon Type ⁷	Chemical Shift	Sequence ⁶	Integration Limits
1	$S_{\alpha\alpha}$	48.1 ÷ 45.3	$S_{\alpha\alpha}$	48.50–44.50
2	$S_{\alpha\gamma}$	38.8	$r\text{-}S_{\alpha\gamma}$	40.00–36.50
3	$S_{\alpha\delta}$	38.4	$r\text{-}S_{\alpha\delta}$	
4	$S_{\alpha\gamma}$	37.96	$m\text{-}S_{\alpha\gamma} + m\text{-}S_{\alpha\gamma}$	
5	$S_{\alpha\delta}$	37.58	$m\text{-}S_{\alpha\delta} + m\text{-}S_{\alpha\delta}$	36.20–34.30
6	$S_{\alpha\beta}$	35.7	$r\text{-}S_{\alpha\beta}$	
7	$S_{\alpha\beta}$	34.9	$m\text{-}S_{\alpha\beta} + m\text{-}S_{\alpha\beta}$	
8	$T_{\gamma\gamma}$	33.9	$T_{\gamma\gamma}$	34.29–32.80
9	$T_{\gamma\delta}$	33.6	$T_{\gamma\delta}$	
10	$T_{\delta\delta}$	33.3	$T_{\delta\delta}$	
11	$T_{\beta\gamma}$	31.2	$T_{\beta\gamma}(m) + T_{\beta\gamma}(r)$	31.91–30.61
12	$T_{\beta\delta}$	30.9	$T_{\beta\delta}(m)$	
13	$S_{\gamma\gamma}$	30.8	$S_{\gamma\gamma} + T_{\beta\delta}(r)^a$	
14	$S_{\gamma\delta}$	30.4	$S_{\gamma\delta}$	30.61–30.23
15	$S_{\delta\delta}$	30.0	$S_{\delta\delta}$	30.23–29.32
16	$T_{\beta\beta}$	28.8 ÷ 28.5	$T_{\beta\beta}(mm) + T_{\beta\beta}(mr + rr)$	29.15–28.22
17	$S_{\beta\gamma}$	27.85	$S_{\beta\gamma}$	28.22–27.63
18	$S_{\beta\delta}$	27.45 ÷ 26.30	$S_{\beta\delta}$	27.63–26.63
19	$S_{\beta\beta}$	24.9, (24.7; 24.6)	$S_{\beta\beta}$	25.60–23.95
20	$P_{\beta\beta}$	22.0 ÷ 21.3	$P_{\beta\beta}(mm)$	22.50–19.00
21	$P_{\beta\gamma}$	21.3 ÷ 20.6	$P_{\beta\beta}(mr) + P_{\beta\gamma}(m) + P_{\beta\delta}(m)$	
22	$P_{\gamma\gamma}$	20.6 ÷ 19.5	$P_{\beta\beta}(rr) + P_{\beta\gamma}(r) + P_{\beta\delta}(r) + P_{\gamma\gamma}$	

^a $S_{\gamma\gamma}$ is obtained by the formula $[(S_{\beta\delta} - S_{\gamma\delta})/2]$.⁶

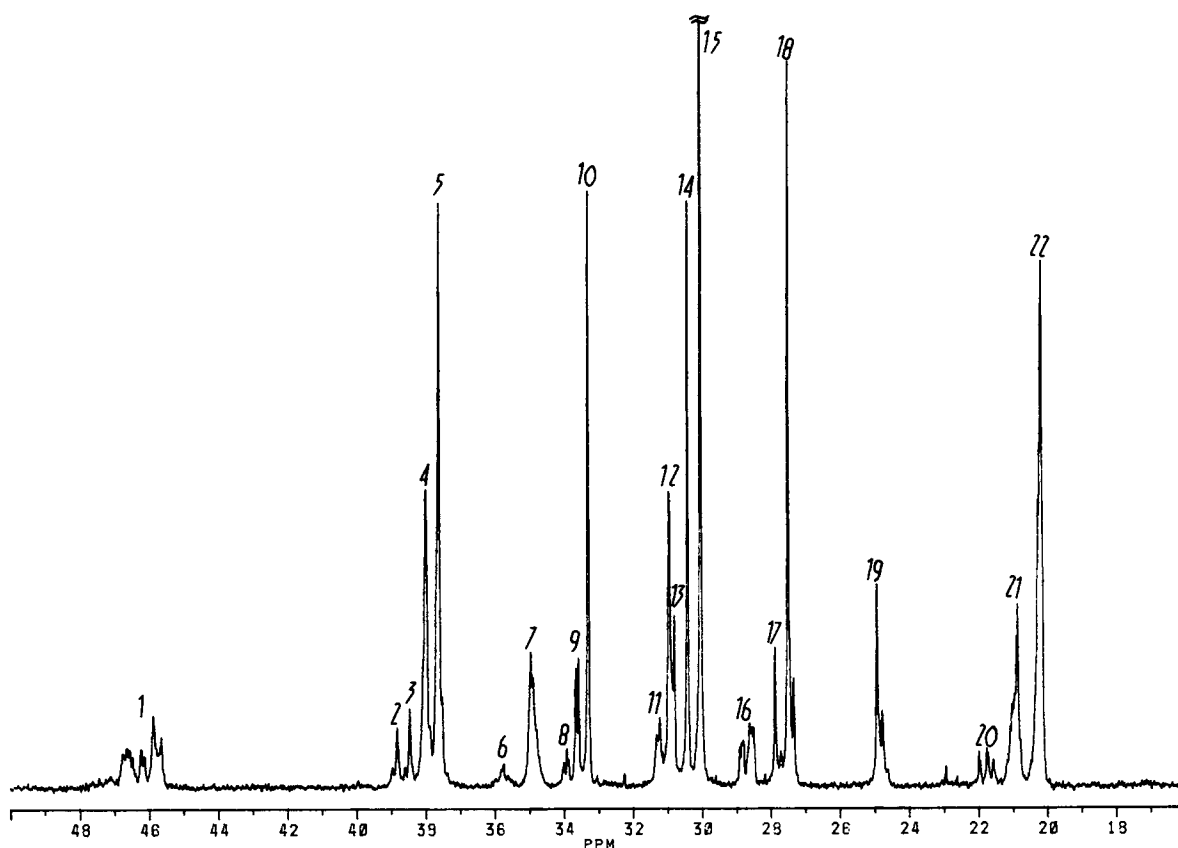


Figure 1 The ^{13}C -NMR spectrum of an ethylene-propylene-rubber.

types of equipment have been used, with three instruments at 75 MHz and one at 90 MHz:

- Lab 1: Varian Unity 300
- Lab 2: Varian VXR-300
- Lab 3: AC-300 Bruker
- Lab 4: AM-360 Bruker.

Instrumental Parameters

^{13}C -NMR can be used for quantitative analysis under two conditions:

- The delay time between pulses must at least equal five times the longest spin lattice relaxation time T_1 , to avoid saturation problems which would attenuate signals. The methyl carbon of the propylene units has been shown to relax the slowest of all the carbon atoms present. At 125°C and 25 MHz, the T_1 is approximately 2.3 s.¹ At 125°C and 50 MHz, the T_1 is approximately 3 s.² Because magnets at higher field have been used, the pulse repetition time has been fixed at 20 s.

- Gated decoupling must be used, to avoid problems related to differences in nuclear Overhauser enhancement (NOE). For many polyolefins, the NOE factor has been shown to be nearly full and constant for all the carbons.^{3,4}

Additionally, for quantitative purposes, it is important to obtain a good signal-to-noise ratio (S/N) because the integration of varying degrees of instrumental noise can affect peak areas and, consequently, the final results (S/N is defined as 2.5 times the signal intensity of the 30.0 ppm peak [S_{30}] divided by the peak-to-peak noise in the region from 50 to 70 ppm⁵).

To meet these conditions, the following instrumental parameters were used by the different labs involved in the round-robin test. As was observed, deviation from these parameters could lead to significant differences in results:

- | | |
|----------------------------|---------------|
| a. Pulse angle | 90°C |
| b. Pulse repetition | 20 s |
| c. Temperature of analysis | 120–125°C |
| d. Data points | At least 32 K |

e. Digital resolution	At least 0.5 Hz/point
f. Sweep width	130 ppm
g. Acquisition mode	Quadrature detection
h. To avoid the NOE effect	
Bruker instruments	Program: INVGATE Decoupling: CPD/ WALTZ
Varian instruments	Decoupling mode: NNY Decoupling modulation mode: WALTZ
i. Number of scans	At least 3000 in order to achieve a good signal-to-noise ratio ($S/N > 500$)
l. Line-broadening factor	=1.0 Hz.

SPECTRAL INTERPRETATION

Chemical Shift Assignments

The chemical shift assignments of E/P rubbers are well known from the literature: Cheng's 1984 proposal, reported in Table II and Figure 1, has been followed.⁶ The terminology for carbons is that proposed by Carman and Wilkes for E/P spectra: primary, secondary, and tertiary carbons are labeled, respectively, *P*, *S*, and *T*. In addition, the two Greek letters in the subscripts define the position of the carbon relative to the nearest tertiary carbons in the chain.⁷

CALCULATIONS

Integration Limits

A typical ¹³C-NMR spectrum of an EPM is given in Figure 1. Well-defined integration limits have been used to minimize the influence of the instrumental noise on the integrations (Table II).

Calculation of the Monomer Concentration

Through combination of the integral areas in different ways, it is possible to set up several methods to determine the monomer concentration. Four different calculation methods that were used in the different laboratories involved have been explored. These methods, explained in Table III, are using different kinds of chemical information. In method 1, all the carbons in the spectrum are used. In methods 2 (Ref. 6a) and 4 (Ref. 8b), only the secondary

Table III Calculation Methods

Method 1:

S = all secondary carbons

T = all tertiary carbons

P = all primary carbons

$$\text{Mol \% ethylene} = [(S + T - 2 \times P)/(S + T)] \times 100$$

$$\text{Mol \% propylene} = 100 - \text{mol \% ethylene}$$

Method 2 (Ref. 6a):

$$P' = S_{\alpha\alpha} + 0.5 \times (S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})$$

$$E' = 0.5 \times [S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + 0.5 \times (S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})]$$

$$\text{Mol \% propylene} = [P'/(E' + P')] \times 100$$

$$\text{Mol \% ethylene} = [E'/(E' + P')] \times 100$$

Method 3 (Ref. 8a):

$$N_0 = \text{total no. methylenes} = (S_{\alpha\alpha} + S_{\alpha\beta} + 3 \times S_{\beta\beta} + 2 \times S_{\beta\gamma} + 5 \times S_{\gamma\gamma} + 3 \times S_{\gamma\delta} + S_{\delta\delta}) \quad (1)$$

$$N_1 = \text{total no. of methyls} = (P_{\beta\beta} + P_{\beta\gamma} + P_{\gamma\gamma}) \quad (2)$$

$$\text{Mol \% ethylene} = [(N_0 - N_1)/(N_0 + N_1)] \times 100$$

$$\text{Mol \% propylene} = [2 \times N_1/(N_0 + N_1)] \times 100$$

Method 4 (Ref. 8b):

n_0 = number-average sequence length of uninterrupted methylenes

$$n_0 = \frac{(S_{\alpha\alpha} + S_{\alpha\beta} + 3 \times S_{\beta\beta} + 2 \times S_{\beta\gamma} + 5 \times S_{\gamma\gamma} + 3 \times S_{\gamma\delta} + S_{\delta\delta})}{(S_{\alpha\alpha} + 0.5 \times S_{\alpha\beta} + S_{\beta\beta} + 0.5 \times S_{\beta\gamma} + S_{\gamma\gamma} + 0.5 \times S_{\gamma\delta})}$$

$$\text{Mol \% propylene} = [2/(1 + n_0)] \times 100$$

$$\text{Mol \% ethylene} = 100 - \text{mol \% propylene}$$

carbons are taken into account, while in method 3 (Ref. 8a), in addition, also primary carbons are used.

RESULTS

Each European laboratory measured the four commercial samples twice and determined the molecular compositions using all four calculation methods. The mol percentages obtained in these ways have been converted to weight percentages.

In the different subtables of Table IV, the results obtained by the same laboratory on the same polymer are given horizontally and the results from the different laboratories, using the same calculation methods, are given vertically. In most cases, the spread between data coming from different labora-

Table IV ^{13}C -NMR Determination of Ethylene Content in Commercial EPM Standards (Wt % Ethylene)

IISRP Labs	Wt % Ethylene Calculation Methods					Intralab Spread
	1	2	3	4		
<u>Vistalon 404</u>						
Lab 1	(a)	43.93	43.84	43.54	44.02	0.48
	(b)	—	—	—	—	
Lab 2	(a)	45.55	44.7	44.6	45.1	0.95
	(b)	44.85	45.55	44.75	45.65	0.9
Lab 3	(a)	44.55	44.42	43.94	44.65	0.71
	(b)	44.88	45.10	44.32	45.21	0.89
Lab 4	(a)	44.78	45.1	45.02	45.2	0.42
	(b)	45.21	45.53	45.9	45.7	0.69
Interlab spread		1.62	1.71	2.36	1.68	
<u>Buna AP301</u>						
Lab 1	(a)	51.9	51.67	51.76	52.12	0.45
	(b)	—	—	—	—	
Lab 2	(a)	53.6	52.05	52.8	52.3	1.55
	(b)	53.25	52.75	52.8	52.95	0.5
Lab 3	(a)	52.85	52.52	52.66	52.68	0.33
	(b)	52.1	51.65	52.05	51.84	0.45
Lab 4	(a)	53.5	52.9	53.3	53.2	0.6
	(b)	52.8	52.6	53.2	52.9	0.6
Interlab spread		1.7	1.25	1.54	1.36	
<u>Dutral-CO038</u>						
Lab 1	(a)	69.18	69.09	68.9	69.46	0.56
	(b)	—	—	—	—	
Lab 2	(a)	69.7	69.5	69.15	69.7	0.55
	(b)	69.75	70.05	69.75	69.8	0.3
Lab 3	(a)	69.56	69.48	69.17	69.62	0.45
	(b)	69.22	69.66	69.0	69.78	0.78
Lab 4	(a)	69.3	69.3	69.7	69.3	0.4
	(b)	69.2	70.0	69.5	69.6	0.8
Interlab spread		0.5	0.96	0.85	0.5	
<u>Vistalon 805</u>						
Lab 1	(a)	77.13	76.9	77.01	77.1	0.23
	(b)	—	—	—	—	
Lab 2	(a)	77.65	77.35	77.15	77.75	0.6
	(b)	77.5	77.7	77.1	77.55	0.6
Lab 3	(a)	77.87	77.35	77.72	77.85	0.5
	(b)	77.33	77.38	77.22	77.28	0.56
Lab 4	(a)	77.44	77.82	77.93	77.44	0.49
	(b)	77.63	77.76	77.89	77.7	0.26
Interlab spread		0.7	0.92	0.92	0.75	

Table V European Round Robin : Weight % Ethylene Composition Range of Commercial Samples

	Vistalon 404	Buna AP 301	Dutral-CO038	Vistalon 805
Min	43.54	51.67	68.90	77.01
Max	45.90	53.30	70.00	77.93
Average ^a	44.84	52.60	69.48	77.48
Spread	2.36	1.63	1.10	0.92
Relative precision at 2 σ	2.71	2.12	0.85	0.75

^a Average from all data in tables.

tories is larger than is the spread between data obtained by different calculation methods in the same laboratory.

So, by using the specified procedure, the intralab consistency has increased dramatically. But there are still some interlab differences (instruments, equipment calibrations, operators, local conditions, etc.), which, however, have also been minimized strongly. One of the contributing factors for intralab and interlab differences is the variation in spectral and integral phases, which, through the various combinations of peak areas, affects the final results in different ways. It was observed, in fact, that the spread in composition becomes larger if spectrum and/or integral phases are not correct.

Because all the spectra were collected avoiding NOE and any problems related to relaxation times, all methods were considered to have the same level of precision and all results were given equal importance. The final result for each standard was calculated by averaging the results of the four laboratories and the four calculation methods.

If all the results are taken as unique measurements, then the relative precision at 2 σ is at the

maximum 2.7%, which is well below the value accepted for LLDPE analysis.² An overview of the results is presented in Table V.

While the European group analyzed the four commercial EPM samples, the ASTM D 11.11 group adopted the same procedure to determine the monomer concentration of the six ASTM standards. To further check on the procedure, two European laboratories (labs 2 and 3) also analyzed the ASTM samples and the U.S. group analyzed Buna AP301 and Dutral-C0038. The average values are summarized in Table VI.

For both series of standards, very similar results are obtained by the two groups. However, for the ASTM standards, the results are clearly and consistently different from those originally given in ASTM procedure D-3900, which calls for a revision of that method.

To come to a revised D-3900 procedure, the IISRP group and the ASTM group decided to merge their efforts and proposed the newly analyzed set as new standards for the infrared procedure. As a consequence, 10 standards are now available to calibrate ASTM D-3900:

Table VI Intercontinental Round Robin : Wt % Ethylene

Sample	Original Values ASTM D3900	IISRP European Section Average Value	ASTM D 11.11 Average Value	New Assigned Value
Vistalon 404		44.8	—	44.8
Buna AP301		52.6	51.8	52.6
Dutral-CO038		69.5	69.4	69.5
Vistalon 805		77.5	—	77.5
ASTM 1	37	40.5 ^a	40.1	40.1
ASTM 2	48	52.4 ^a	52.4	52.4
ASTM 3	55	58.3 ^a	58.6	58.6
ASTM 4	63	66.0 ^a	66.8	66.8
ASTM 5	69	70.6 ^a	70.8	70.8
ASTM 6	79	78.3 ^a	78.6	78.6

^a Data from only two laboratories.

- Four IISRP standards, with concentrations defined by the IISRP group.
- Six ASTM standards, with revised concentrations defined by the ASTM group.

CONCLUSIONS

Using the ^{13}C -NMR procedure outlined in this work, it is possible to obtain consistent and reproducible molecular composition results on EPM, independent of the measuring laboratory and the calculation method. This has been demonstrated for a set of 10 EPM standards that will be used for worldwide infrared calibration purposes.

The International Institute of Synthetic Rubber producers, Inc. (IISRP), is an international not-for-profit trade association with about 50 corporate members who produce more than 90% of the world supply of synthetic rubber. Among the purposes of the IISRP are the promotion of the interests of the synthetic rubber manufacturers and the public in manufacturing, engineering, safety, environmental control, transportation, and international trade. The institute exists, among other reasons, to provide a forum for information exchange relating to technology and industry innovation and the gathering and dissemination of information concerning the synthetic rubber industry. The European members of the IISRP are Advanced Elastomer Systems N.V./S.A., Bayer AG, DSM Elastomers Europe B.V., DuPont de Nemours International S.A., Efremov Synthetic Rubber Enterprise, Enichem Elastomeri SRL, Exxon Chemical Europe Marketing Inc., Goodyear Chemicals Europe, Hüls AG, Karbochem Division of Sen-trachem. Ltd., Michelin et Cie, Petrochim N.V., Repsol

Quimica S.A., Shell International Chemical Co. Ltd., Syntheskauchuk, and Zeon Chemicals Europe Ltd. The authors wish to thank all members of the IISRP working group for their contributions: Dr. J. Noordermeer, Dr. K. De Vries, and Mr. J. Beulen (DSM—Geleen [N]), Mr. T. Andreotti (Enichem Elastomeri—Ferrara [I]), Dr. J.-R. Schauder and Mr. J.-J. Muls (Exxon Chemical Europe—Machelen [B]), and Dr. H.-J. Metternich (Hüls AG—Marl [D]). Special thanks to Dr. C. B. Friedersdorf (Exxon Chemical America) and the other members of the ASTM D11.11 group.

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Received December 14, 1994

Accepted January 4, 1995