

Polyacrylonitrile Determination in Acrylonitrile–Butadiene Rubber

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ABSTRACT: Acrylonitrile content from copolymer of acrylonitrile–butadiene has been studied combining vibrational spectroscopy and a nuclear technique. On the basis of the results obtained, it has been proven that these techniques can clearly be an asset to determine acrylonitrile content in rubber materials without prior separation and in a nondestructive fast and simple manner. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 187–190, 1997

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INTRODUCTION

Acrylonitrile–dienes (ACN–dienes) copolymers are part of a larger classification of products often referred to as special-purpose rubbers, primarily because they exhibit a high degree of resistance to attack by oils both at normal and elevated temperature.^{1–12} Oil resistance is the most important property of nitrile rubbers and is the reason for their extensive use. Nitrile rubber is available in several grades of oil resistance based on the acrylonitrile content of the polymer, ranging from about 18 to 50%, thus giving the rubber compounder a wide choice from which the optimum combination of properties desired for any given application is selected. However, not all manufacturers identify their product to distinguish one kind from the other. Therefore, it is of interest to clearly define the ACN content using a ground sample or a thin film for indicating whether or

not the material formulation/processing has changed.

This study describes a method by which the quantitative determination of ACN in nitrile–butadiene rubber (NBR) is performed both quickly and accurately. Using infrared (IR) spectroscopy and a nuclear technique, the speed of this determination is increased, making of this analysis a routine method.

The purpose of this work was to determine if ACN can be determined from an acrylonitrile–butadiene copolymer rubber (NBR) sample containing additives.

EXPERIMENTAL

In this article, we present a method by which the quantitative determination of acrylonitrile (ACN) content of a rubber product may be obtained with methods based on vibrational examination to measure the ratio of ACN to butadiene and from the nitrogen content of the sample with the use of (d, p) and (d, α) nuclear reactions for nitrogen

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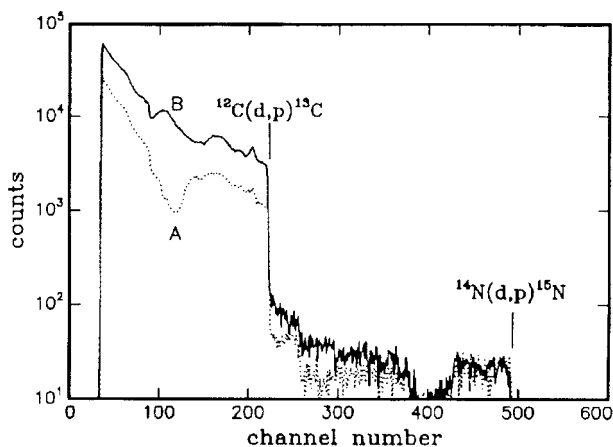


Figure 1 Representative energy spectra of charged particles obtained from 3.0 MeV deuteron bombardment of (A) Kaptan (polypyromellitimide) 50- μm foil, and (B) Chemigum-N30 thick sample.

determination in organic matter. A nuclear reaction is associated with a strong interaction between the incident particles (projectiles) and the nuclei of the sample atoms; this usually takes place with a liberation ($Q > 0$) or absorption ($Q < 0$) of energy.

With the use of a data manipulator, the isolation of the spectrum of ACN from the copolymer nitrile-butadiene without additives (CHEMIGUM-N30) was obtained. Here, the DIFF command takes the difference of two spectra. If a common band is defined by start and end in the command line, the DIFFerence routine also normalizes the data for varying band intensities, a condition which occurs with varying sample thicknesses or concentrations. Automatic factor determination is done by choosing a common band in the spectra and entering the start and end wave numbers that encompass the band. The DIFFerence calculations are performed in absorbance. Thereby, the ACN content was obtained. This value was then compared with the quantitative determination using the (d, p) and (d, α) reactions. The agreement between data reported in spectroscopy and results obtained with nuclear reactions were generally good.

In this study, four standard Chemigum-N30 were used to prepare the Beer-Lambert plot of absorbance ratios versus concentrations to demonstrate the procedure and deviations.

In order to determine an unknown concentration of ACN in the rubber samples with additives, the determination follows the nuclear analysis procedure.

Vibrational spectroscopy was carried out on a Perkin-Elmer Model 283B IR-Spectrophotometer. A film of NBR without additives was cast from chloroform onto a KBr window. To obtain the vibrational spectra of a single component, no prior separation technique was necessary. A sample of purity butadiene was used as a reference. Spectral data for the ACN was then revealed by normalizing the intensity of a common band at 965 cm^{-1} . Then it was possible to determine the ACN content of Chemigum-N30 from a vibrational spectrum. The spectra of Chemigum-N30 show characteristic peaks, but none at all for the largest and most sensitive peak in the $-\text{C}=\text{C}-$ at 965 cm^{-1} . The absence of this absorption band indicates excessive aging or oxidation.

Rubber and plastic products have a plasticizer added in order to make them more pliable or softer. One type of common plasticizing material is di-2-ethylhexylphthalate, more commonly known as dioctyl phthalate or DOP. Sometimes a spray silicone as a lubricant is used, but it is allegedly absorbed into the material and is not visible. However, silicone oil can attack NBR. The amount of plasticizer in the NBR is added in limited amounts so that no extreme attack occurs, just control of properties. For NBR samples, the additives absorb very strongly, making it practically impossible to observe vibrational spectra. To overcome this problem, we employed a nuclear technique. Nuclear reaction analysis of NBR samples (1, 2, and 3), as well as the reference material Chemigum-N30 and a 50- μm Kaptan foil ($\text{H}_{10}\text{C}_{22}\text{N}_2\text{O}_5$, polypyromellitimide), were carried out under vacuum conditions using a 3.0 MeV deuteron beam, based on $^{14}\text{N}(d, p)^{15}\text{N}$, and $^{14}\text{N}(d, \alpha)^{12}\text{C}$ reactions for nitrogen content determination.

These $Q > 0$ reactions permit having the events associated with nitrogen (p 's and α 's), separated on the high-energy end of the energy spectra obtained from a pulse height analysis of charged particles arriving to a (conventional) surface barrier detector electronic arrangement. This detector arrangement permits us to identify and count the number of proton and alpha particles associated with nitrogen, providing pulses that are arranged (according to their height) by a multichannel analyzer. In this way, an energy spectrum is generated, which displays the number of events (charged particles) that arrive to the detector as a function of their energy (channel). The deuteron beam was produced by the Tandem Van de Graaff accelerator of the National Institute of Nuclear

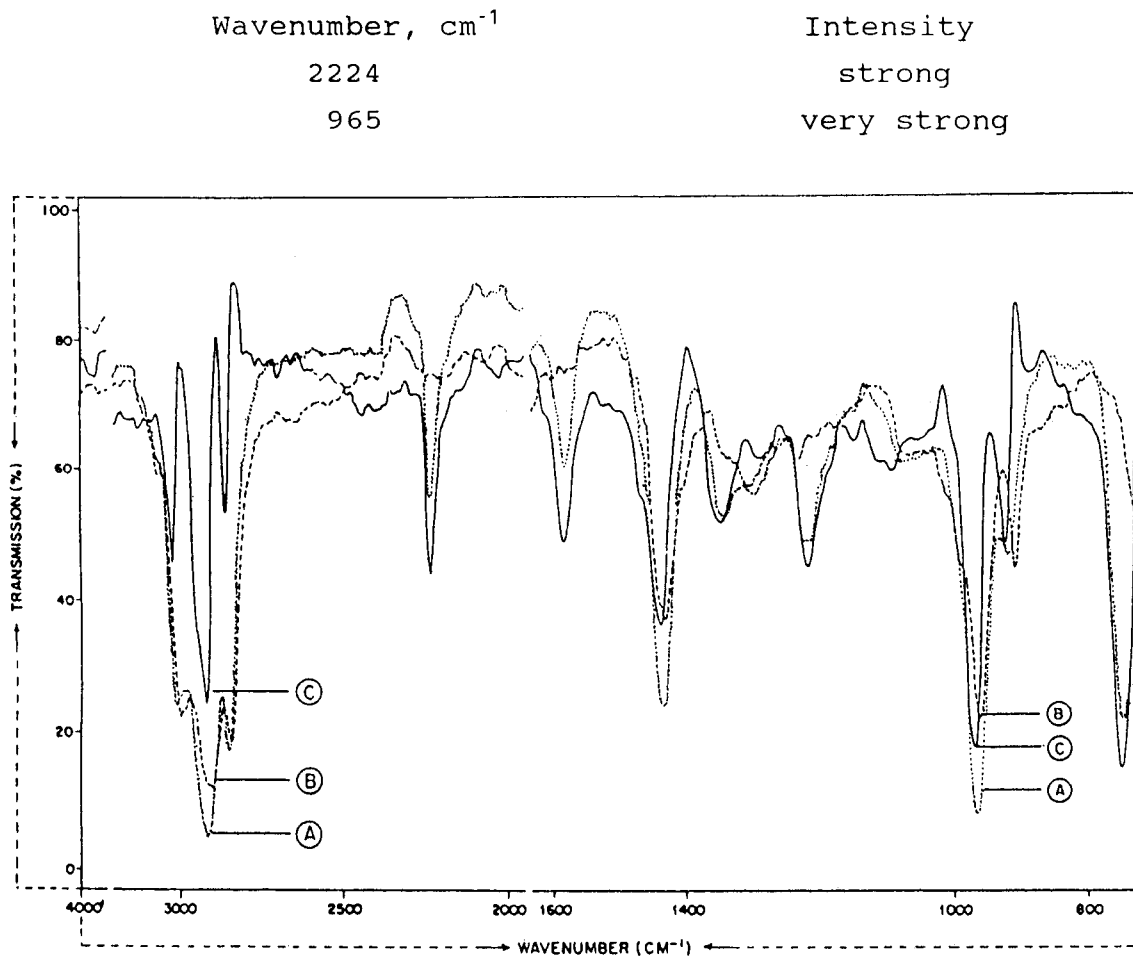


Figure 2 Computer difference IR spectrum of Chemigum-N30: (A) Chemigum-N30 without additives of ACN concentration known, (B) sample of pure butadiene used as an IR reference, and (C) IR spectrum of the extracted ACN from Chemigum-N30.

Research, taking about 30 min for each irradiation in order to have a 2.5% statistical uncertainty in the number of counts due to nitrogen reactions. The samples, slices of nearly 3 mm thick, and a

Table I Individual Comparison Between the Vibrational Spectroscopy and (*d, p*), (*d, α*) Methods for Determination of Relative Nitrile Content in Nitrile-Butadiene Rubber (NBR)

Kind of NBR	From Vibrational Spectroscopy (%)	From Reactions in ^{14}N (%)
Chemigum-N30	40.1 ± 2.0	40.0 ± 0.442
1		11.8 ± 0.442
2		12.1 ± 0.430
3		13.1 ± 0.460

few centimeters square each, were set to approximately 3×10^{-5} mbar pressure in a vacuum chamber, which housed a silicon surface barrier detector positioned at 140 degrees in relation to the beam direction. Reference materials (Kapton and thick Chemigum-N30) were irradiated under the same conditions in order to normalize nitrogen content, taking appropriate ratios between counts due to nitrogen (high-energy interval) with an interval mainly associated with pulses due to ^{12}C , $^{12}\text{C}(\textit{d, p})^{13}\text{C}$ edge. Representative energy spectra are shown in Figure 1(A,B).

RESULTS AND DISCUSSION

ACN content of a NBR without additives may be obtained from methods on vibrational spectroscopy.

copy to measure the ratio of ACN to butadiene. The IR scan must be such that the C=C and CN peaks, respectively, at about 960–965 and 2220–2230 cm^{-1} , are both fully within the boundaries of detectability. Therefore, the C=C and CN IR absorption peaks related to the spectra^{11,12} from Chemigum-N30 are shown in Figure 2(A).

The spectrum of the known polymer (polybutadiene) was then scanned [Fig. 2(B)]. To find the difference between the two spectra, it was first necessary to normalize the data for the varying band intensities caused by different thickness of the two sample films. The DIFFERENCE program is used to subtract the absorbance spectrum of the known component from the Chemigum-N30. Spectral data for the new spectrum [Fig. 2(C)], such as the ACN, was then obtained. The percentage of the ACN content from Chemigum-N30 was obtained as a function of the ratio of the absorbance of the 965 cm^{-1} band. Vibrational spectra show the NBR content as 40.1% ACN, the amount needed to qualify a NBR as higher nitrile. However, its nominal ACN content is given as 40.0%. Results obtained by this method have been verified to be consistent with the $\pm 2\%$ variation. On the other hand, the ACN content of a NBR with additives (samples 1, 2, and 3) may be obtained from the nitrogen content of the sample if no other nitrogen-containing materials are present. Here, the evaluation process was performed for both, without and with additives, measuring the quantity of nitrogen with two well-established nuclear reactions.^{13,14} Samples 1, 2, and 3 were low in ACN as compared to Chemigum-N30.

A strong positive correlation was demonstrated between the ACN/nitrogen ratios obtained with the vibrational spectroscopy and the nuclear method. This circumstance made possible to measure average nitrogen content from NBR with additives. The corresponding values (Table I) indicate that the nitrogen content was approximately the same in all samples. However, these materials are referred to as low-nitrile types. These values differ compared to reference material that contain

at least 40.0% ACN. The net results of the particular NBR involved are (samples 1, 2, and 3) a low-nitrile NBR compared with material known (Chemigum-N30).

This article attempts to explore some of these issues and to offer guidance on how nuclear analytical techniques may be applied in a standardized way, thus helping to ensure that the results reported by the two different techniques will be compatible and comparable with each other. Nuclear analytical techniques are sufficient in themselves to provide a complete answer to a urgent demand. They have unique properties that enable them to determine many of the important bulk constituents of solid.

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