A Novel Approach for the Determination of the Physicomechanical Properties of Polymers by Vibrational Spectroscopy: The Tensile Strength of Polybutadiene Rubber

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ABSTRACT: In an attempt to extend the applications of IR spectroscopy, we report here on a novel method for the determination of the tensile strength (Ts) of polybutadiene rubber (PBR). A simple linear correlation between Ts and the peak absorbance ratio was developed. The method is simple, direct, and fast and involves only the measurement of the absorbance ratio from the IR spectrum of PBR film. The results obtained by this (IR-based) method and the currently used (ASTM) method, for quality control/quality assurance purposes, were in good agreement. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2135–2139, 2001

Key words: absorbance ratio; infrared spectroscopy; polybutadiene; spectroscopy; tensile strength

INTRODUCTION

The microstructure of any material is a representation of its various macroscopic properties. Conventionally, the belief has been that it is not possible to determine macroscopic properties, such as physical or mechanical properties, from structural information. This, in our view, has mainly been due to the inherent limitations of measurement techniques. For instance, until recently, one never considered vibrational spectroscopy as a suitable technique for quantitative applications, such as the determination of composition. However, developments in instrumentation and online or hyphenated techniques have now brought about major changes in the old concepts and beliefs. Such techniques have now achieved fairly good acceptance as tools not only for quantitative information but also for nondestructive measurements, including highly absorbing/black materials (e.g., carbon fibers).[1–13]

We report here on a novel application of modern Fourier transform infrared (FTIR) spectroscopy for the determination of physicomechanical properties, such as tensile strength (Ts), izod impact strength, and flexural modulus in materials that contain C—C- and C—H-based structural units/moieties in their IR spectra. This article also supports the fact that developments in instrumentation and the availability of online computational facilities have considerably changed the scenario.[14–17]

In the light of the previous discussion, this article reports on a novel application of modern IR spectroscopy for the determination of the Ts of polybutadiene rubber (PBR).

EXPERIMENTAL

Sample

PBR samples produced in a commercial plant (with a solution polymerization process) collected

over a period of time were used in this study (data on 45 samples are reported).

Measurements of IR Spectra

The IR spectra of the samples were recorded by the casting of a film (from a solution of virgin PBR) on a NaCl window. The solvent was removed by hot-air drying. Alternately, the IR spectrum of the sample (PBR) solution in carbon disulfide was recorded with a liquid cell. Carbon disulfide was used as a reference. The absorbance was directly noted from the instrument. However, the data reported here followed the former method. The spectra were recorded on a IFS-113V FTIR spectrometer (Bruker, Germany) under vacuum with a spectral average of 32 scans (in the case of the film and without vacuum, i.e., in air in the case of solution). The instrument was modified so that the conventional source and beam splitter were replaced by a near IR (NIR) source and CaF_2 beam splitter.[12] The absorbance ratio thus obtained was used for the determination of Ts (IR).

Measurement of *Ts* by the ASTM Reference Method

The measurement of Ts of a rubber sample is a multistep and time-consuming method. The ASTM D 412 method was used for the determination of the

Table I   Recipe for the Preparation of the PBR Blend for *Ts* (std) Determination

Ingredient	Amount (g)
Polymer sample	700
Carbon black high abrasion furnace (HAF)	420
High-aromatic oil	105
Zinc oxide	21
Stearic acid	14
Vulcanizing accelerator n-tert-butyl-2-benzothiozolyl sulfanamide (NS)	3.6
Sulfur	6.0

Ts of rubber samples. The representative virgin rubber sample was mixed with several additives (the recipe of which is given in Table I). All the contents were weighed accurately and mixed thoroughly in a BR-type Banbury mixer at a temperature of $50 \pm 5°C$. The blended rubber was passed three times through 6-in. rolls at a roll gap of 5 mm. The sample was vulcanized for 35 min at 145°C, and the resulting vulcanized rubber was cooled in water for 10–15 min. The sample was cured for 72 h. The standard test molds for tensile testing were prepared, and Ts (std) was measured with a universal testing machine.
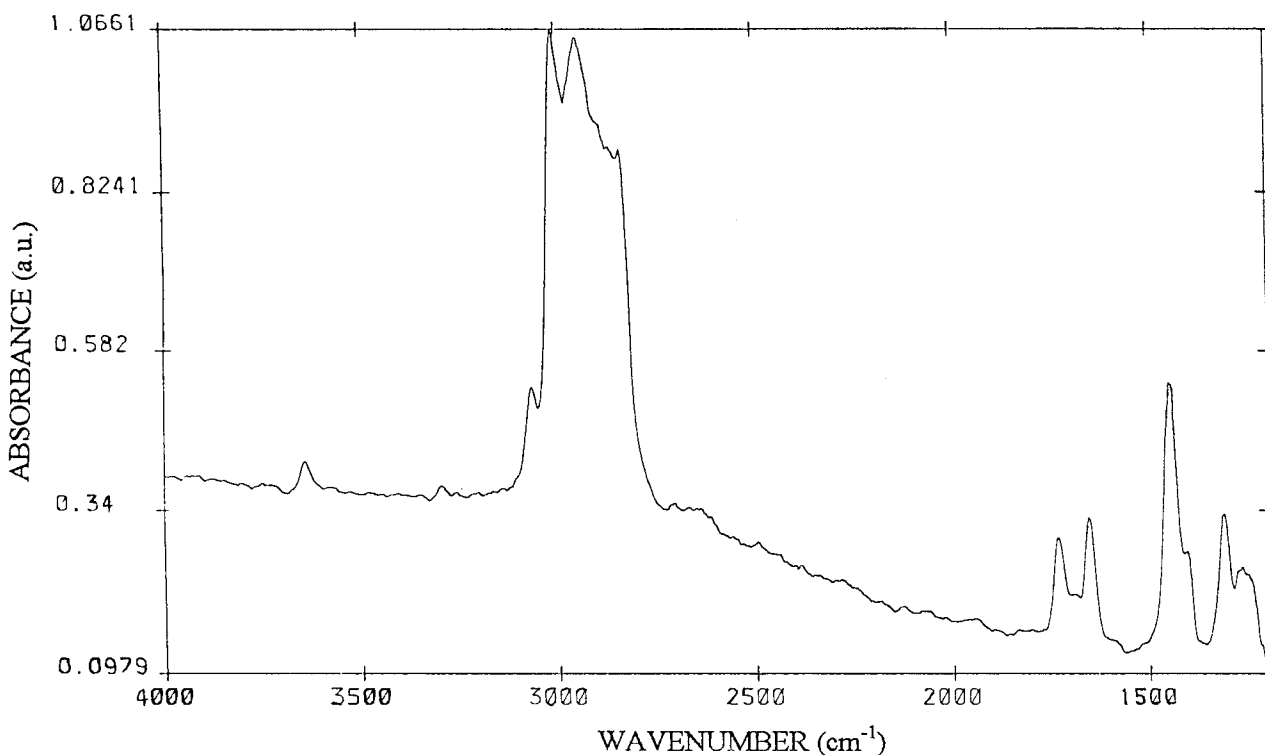

Figure 1   IR spectrum of PBR.

Table II *Ts* of PBR

Sr. Number	Absorbance Ratio	*Ts* (IR; MPa)	*Ts* (std; MPa)[a]
1	1.53	15.8	15.8 (567, 8.6)
2	1.56	16.0	16.6 (558, 8.6)
3	1.32	14.1	13.7 (514, 8.3)
4	1.30	13.9	14.5 (567, 6.7)
5	1.78	17.8	17.5 (560, 7.6)
6	1.45	15.1	15.0 (513, 8.5)
7	1.47	15.3	15.0 (513, 8.5)
8	1.56	16.0	16.0 (530, 8.5)
9	1.45	15.1	15.2 (530, 9.6)
10	1.77	17.7	17.3 (580, 9.1)
11	1.76	17.6	17.7 (575, 9.2)
12	1.75	17.5	17.6 (592, 8.5)
13	1.72	17.3	17.6 (573, 8.8)
14	1.66	16.8	16.8 (533, 8.2)
15	1.66	16.8	16.7 (579, 7.6)
16	1.68	17.0	17.0 (547, 7.9)
17	1.62	16.5	16.8 (538, 8.0)
18	1.65	16.7	16.8 (573, 7.5)
19	1.73	17.4	17.0 (547, 7.9)
20	1.74	17.5	17.3 (591, 7.7)
21	1.69	17.1	17.0 (560, 7.5)
22	1.72	17.3	17.5 (693, 8.1)
23	1.74	17.5	17.2 (585, 8.0)
24	1.70	17.1	17.0 (585, 7.8)
25	1.58	16.2	16.0 (543, 8.6)
26	1.65	16.7	16.3 (547, 8.1)
27	1.80	18.0	17.8 (599, 8.6)
28	1.82	18.1	18.0 (571, 8.7)
29	1.86	18.4	18.4 (599, 8.7)
30	1.80	18.0	18.3 (671, 7.9)
31	1.85	18.3	18.4 (647, 8.1)
32	1.84	18.3	18.2 (588, 8.6)
33	1.74	17.5	17.7 (626, 8.0)
34	1.72	17.3	17.1 (645, 7.6)
35	1.80	18.0	18.2 (624, 8.0)
36	1.74	17.5	17.6 (625, 7.9)
37	1.80	18.0	18.4 (611, 8.4)
38	1.70	17.1	17.2 (616, 7.8)
39	1.70	17.1	16.8 (646, 7.5)
40	1.72	17.3	17.5 (596, 8.3)
41	1.48	15.4	16.0 (570, 8.4)
42	1.83	18.2	19.0 (638, 7.9)
43	1.87	18.5	18.3 (603, 7.9)
44	1.90	18.7	18.1 (611, 8.0)
45	1.94	19.0	18.4 (632, 8.1)

[a] Values in parentheses correspond to the values of elongation at break (%) and modulus (MPa), respectively.

RESULTS AND DISCUSSION

The PBR samples under study consisted mainly of C—C and C—H moieties in different conforma-tions or sequences (with some impurities such as catalyst residues or additives). With the virgin PBR sample, the IR spectrum, as expected, was quite simple and consisted of bands mainly corre-sponding to different vibrational modes of C—C and C—H bonds.[18] These vibrational modes are highly variable in terms of energy absorption and sensitive to the location and neighborhood (envi-ronment) of atomic/molecular arrangements within the matrix, that is, the microstructure.

Although not much is known or reported in the published literature, our experience (based on ex-perimental results and data) on different sys-tems, including polymer blends and composites and related systems (unpublished), has been that there is, invariably, a direct and simple correla-tion between the extent of energy absorbed (i.e., band position and intensity) and physicomechani-cal properties. In the absence of any published information (except our recent work on different systems[14–17]), it is very difficult to substantiate this hypothesis except on a semiquantitative the-oretical basis as discussed later. The various properties of a material are typically governed by the atomic or molecular composition, and their typical placement, within a fixed specific space, is commonly referred to as *microstructure.* For a molecular matrix, being a dynamic system, the extent of intramolecular interaction, as expected, is dependent on the spatial freedom of molecular motions (i.e., of different bonds, viz. C—H, C—C, or H—H in this case). In other words, the extent of spatial freedom for different vibrational/rota-tional motions of different bonds is directly re-lated to the physicomechanical properties of the material. Typically, a combination of the bands corresponding to C—H bending and C—C/C=C stretching was considered for the evaluation of such properties in this study. Accordingly, absor-bance ratios of the two bands at 1450 and 1658 cm^{-1} (Fig. 1) were used to determine the *Ts* of PBR with the empirical relationship described later. The numerical values of the characteristic IR spectral features, on mathematical treatment, could be used to predict the said property. This approach is further substantiated by the fact that during the past 2 decades, considerable work has been reported in the literature, where instead of fundamental bands (as used in this work), over-tones appearing mainly in the NIR region were used extensively to predict various physical prop-erties, such as density, polymorphism, crystallin-ity, and molecular weight,[4–7,10–11,14] of various materials with C—H, C—C, and O—H moieties.

The approach is the chemometric treatment of the specific band intensities and areas at a predefined wavelength window to predict the required physical property. The NIR–chemometry approach has found applications in a wide range of areas, such as medical/clinical, chemical, and agricultural areas, to mention a few. Even international pharmacopoeia (considered to be one of the most strict agencies worldwide[19–20] in the area of pharmaceuticals) have recently accepted and incorporated NIR-based measurements for product and raw material evaluations.

The validity of this method is further substantiated by the fact that we have used this approach on different systems and on samples produced in a commercial plant over a period of time. This gave us not only confidence but helped in the evaluation of samples with a range of typical values for the comparison with the alternative standard reference method (Table II) currently accepted and used for quality control/quality assurance (QC/QA) purposes in commercial plants. As a practice, the currently used methods are not only used for QC/QA but also cross-checked at the buyer's end (a critical factor that not only determines the quality but also the price of the material). In the light of this, we report our findings on one of the systems, commercially produced PBR, for which a very simple linear correlation between Ts and the absorbance ratio was developed and found to be universal for PBR. The reason we chose PBR (a very soft solid matrix) was to demonstrate that very complicated, multistep processes (the mixing of additives, curing, molding, etc.) and time-consuming QC methods can be replaced by a fast, simple, and direct IR-based mea-

surement method, that is, the recording of the IR spectrum of PBR film (made from its solution) and the determination of the absorbance ratio of preselected bands to obtain the same information with similar precision and accuracy. We tested the method on a large number of samples produced over a period of time.

The empirical linear relationship between response (Ts) and input ($X =$ absorbance ratio) parameters was developed with standard samples data. The relationship was optimized for performance variation and is advantageous in the sense that it does not require calibration (and is also independent of the instrument used). In other words, the absorbance ratio (from the IR spectrum) is the only parameter needed for the determination of Ts. The relationship is as follows:

$$Ts = 7.9836X + 3.564 \qquad (1)$$

where $X = A_{1450}/A_{1658}$. The Ts values determined by the two methods (IR and ASTM) are given in Table II along with the absorbance ratios. The data show excellent agreement. This is also confirmed by Figure 2 (which shows a linear relationship between the two approaches). The reproducibility of the method was established by multiple spectral recording and data analysis of the same sample. Statistically, the data obtained by the two methods are quite comparable (Table III). This equation was tested on more than 100 samples (without any pretreatment) produced over a period of time in the commercial plant with Ts values in the range 13–19 MPa. It was not possible to get any samples with Ts values beyond
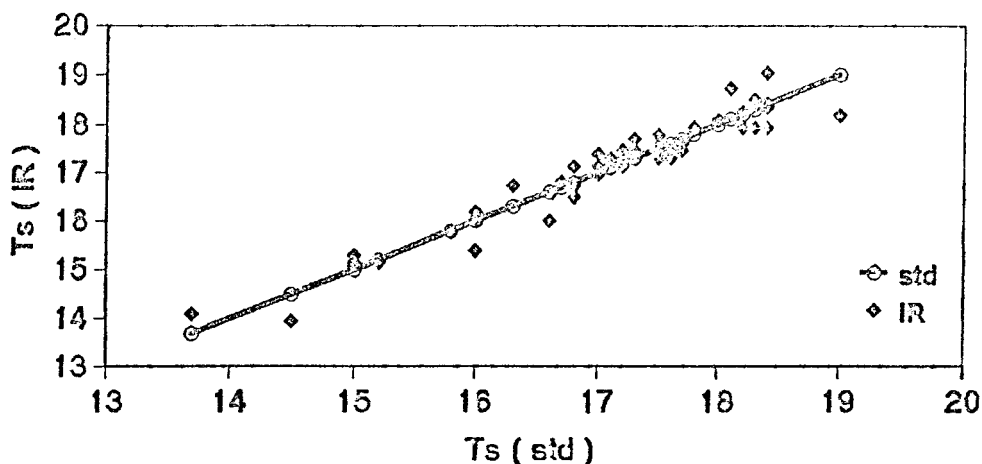

Figure 2 Ts results by standard and IR methods for PBR.

Table III   Statistical Analysis of *Ts* Data for PBR

Parameter	Value
Number of samples	45.0
Minimum deviation (%)[a]	0.0
Maximum deviation (%)[a]	5.0
[b]$\mu\ Ts_{(IR)}$	17.0
[b]$\mu\ Ts_{(std)}$	17.1
[c]SD (IR)	1.15
[c]SD (std)	1.13
σ (IR)	17.0 ± 1.15
σ (std)	17.1 ± 1.13

[a] With respect to *Ts* (std) results.
[b] μ-average.
[c] SD-standard deviation.

this range (possibly because of difficulty in production or the lack of any commercial value).

CONCLUSIONS

Apart from being a novel approach for the fast evaluation of macro properties from microstructural data, this method opens up a new direction in which IR spectroscopy can find application as a tool for nondestructive testing and evaluation. In addition, it also eliminates cost investment both in terms of recurring (chemicals, time, etc.) and capital (machines, etc.) expenditures for analysis. Normally, IR spectral measurements are done for cis content determination in rubber (another quality parameter), and adoption of this method will only require measurement over an extended wavelength range. Thus, incorporation of this method in the case of PBR will be an additional application. This makes the proposal more attractive in terms of the requirement of a new instrument, apart from the ease of measurement and other advantages mentioned previously. The obvious advantages of online *Ts* measurement (with optic-fiber-based remote spectroscopy) is another factor that will possibly make the method more attractive in terms of time saved and ease compared to offline measurements.

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