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ARTICLE

Development of a Test Method for the Estimation of SBR-BR Blend Ratio in Tyre Tread Formulation and Validating It through Robust Statistical Tools

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ABSTRACT

Blends of synthetic rubbers are widely used by rubber product manufacturing industries depending on the end use and product application. The estimation of individual rubber in blends is an important aspect to characterise the correctness of the mixing process. In tyre industry, Styrene butadiene rubber/Polybutadiene rubber (SBR/BR) blend is commonly used to achieve different performance properties, particularly for passenger car tyre. Out of the different quantitative analysis techniques to characterise the blend, one of the widely used techniques Gas Chromatography-Mass Spectrometry (GC-MS) has been used to develop and later validate a method to quantify the SBR/BR blend ratio. Through this GC-MS technique detection capability is measured, with a minimum limit of detection (LOD) of 5.17% and a limit of quantification (LOQ) of 15.67% Styrene butadiene rubber (SBR) in an SBR-BR vulcanizate. It is observed that the bias percentage is highest in case of a lower SBR content sample, i.e. 11.1% while in the case of other sets, it is varying from (–)1.4% to (+)1.5%. During the recovery study, it is observed that with increasing SBR content, recovery is also improving. All requirements for a successful method validation: Accuracy, precision, selectivity, detection capability, calibration range and robustness have been carried out in this entire work.

Keywords: Method validation; Synthetic rubber (Styrene butadiene rubber/Polybutadiene-rubber) blend; Gas chromatography/Mass spectrometry; Analytical technique; Quantitative analysis

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1. Introduction

Benchmarking of any rubber product used for a specific application provides valuable inputs for the design and development of new products. It is one of the very important and essential aspects of research and development to enhance the functionalities of an existing product or to initiate the development of a new product.

Rubber blends are commonly used by different rubber products manufacturer, to achieve the required product performance [1-3]. Commonly used rubber blends are Natural rubber/Polybutadiene rubber (NR/BR)—to achieve improved abrasion resistance [4] and chipping performance [5], Natural rubber/Solution Styrene butadiene rubber (NR/SBR) – is used to achieve optimum tack and green strength, etc. [6]. Tyre industry is also following the same rule of rubber blending to achieve different performance properties [2,7]. The most common blends in tyre industry are NR/BR or NR/SBR [2,7]. However, with the introduction of passenger radial tyre, other blends like Styrene Butadiene rubber/polybutadiene rubber (SBR/BR) with a different microstructure of SBR and BR are getting popularised [8]. Qualitative and quantitative characterisation of different rubber in blends is one of the important aspects to understand the correctness of mixing [9].

Several analytical techniques are successfully established to characterise the rubber blends in rubber compounds [9]. Maria Jose Fernandez-Berridi et al. [10] determined the blend ratio of NR/SBR using the calibration curve obtained from the peak height of NR as well as the temp of 70% weight loss vs actual NR content in the calibration standard. To determine the blend ratio of NR/SBR, Maria Jose Fernandez-Berridi et al. have used "Turbo Quant" software to estimate NR/SBR blend ratio through FTIR and results are acquired as desired. J.J. Maurer [11,12] has studied a method to estimate the composition of rubber vulcanizates by thermogravimetric analysis (TGA) in terms of polymer, oil, carbon black and ash content. In this study, to eliminate the overlap of oil and other low volatile materials over polymer, the sample has been thoroughly extracted before TGA analysis for estimation of polymer, carbon black and ash content.

However, the characterisation of SBR and BR in the SBR/BR blend is posing a challenge to analytical chemists [13]. Different authors have studied different analytical techniques to characterise SBR/BR blends [8,10,13-15].

Ghebrehiwet N Ghebremeskel et al. [16] studied the suitability of the pyrolysis GC-MS technique to estimate styrene content in SBR rubber and found that the result obtained from the FTIR technique is comparable with pyrolysis GC-MS technique. Sung-Seen Choi et al. [17] have determined the styrene content and butadiene content in cured SBR-based samples by pyrolysis GC-MS technique. Edward R Terrill et al. [18] have used Py GC-FID to determine natural rubber content, butyl rubber content and styrene butadiene rubber content in tyre inner liner. Youn Suk Lee et al. [13] have used TGA, pyrolysis GC-MS and FTIR techniques to estimate the blend ratio of NR-SBR-BR in cured rubber matrix and identified pyrolysis GC-MS technique is superior to measuring the blend ratio of SBR-BR in the cured rubber matrix rather than TGA and FTIR.

So overall, except for Lee et al. not much work has been done on SBR/BR blend ratio. Also to be noted that Lee et al. have worked on a tri-blend Natural rubber/Styrene butadiene rubber/polybutadiene rubber (NR/SBR/BR) formulation and that also not in a commodity product like tyre where there is a direct impact of SBR/BR blend ratio on physical property as well as on performance.

In this present study, to confirm the suitability of the procedure employed for its intended use, the method has been developed and validated to estimate SBR-BR blend in rubber matrix used in tyre formulation by assessing detection capability in terms of limit of detection (LOD), the limit of quantitation (LOQ), working range or calibration range, trueness, recovery, repeatability and precision through robust statistical tools [19-21]. According to ISO 17025:2017 [22] clause no 7.2.2.1, the laboratory must validate: a) non-standard method, b) laboratory-developed method, c) standard methods used outside their intended scope, d) modification of standard methods. There are two ways of doing that, one is through an inter-laboratory approach and the second one is through a single laboratory approach where methods are developed for use in a specific laboratory or when a method is not for general interest.

2. Materials

Solution styrene-butadiene rubber (SBR), NS616 with 21% styrene content is supplied from Zeon Chemicals; Japan and Nickel Catalyst-Polybutadiene rubber (BR) with 95.6% cis content from Ms. Reliance Industries Limited, Baroda, India has been used. Details of other ingredients are mentioned in **Table 1**.

3. Experimental

3.1 Sample preparation

A binary rubber blend of SBR-BR ranging from 10 to 100 phr (with an increment of 10 phr), has been prepared in a tangential mixer (Stewart Bolling, USA with two-wing rotor facility) of 1.6 litre capacity with fill factor 0.75. The detailed formulation has shown below in **Table 2**. The mixed compound has been cured at 160 °C for 30 min under 150 kg/cm^2 moulding pressure in a Hind Hydraulics curing press.

3.2 Method

Detail methodology/process flow of the analysis is shown in **Figure 1**. Cured tyre sample is getting sliced first. Cured calibration samples have been extracted for 16 hours in acetone to remove low-volatile materials [23]. After that a small specimen (0.6-1.0 mg) of the extracted sample has been kept inside the quartz tube to place inside the pyrolyzer.

Approximately 0.6 to 1.0 mg of extracted samples have been analysed in CDS 5150 pyrolyzer hyphenated with Agilent 7890B, 5977B GC-MS. A separate pyrolyzer program is made where pyroprobe temp and transfer line temperature are fixed at 750 °C and 320 °C respectively [24-26]. For the GC, the injection temperature is fixed at 350 °C with a split ratio of 600:1. HP 5MS (30 m × 0.25 mm, 0.25 µm) column has been used for the entire study. The initial oven temperature is 50 °C with a holding time of 3 min. The optimum ramp rate for better separation has been estimated at 15 °C/min up to 270 °C. MS condition in full scan mode is stated in **Table 3**.

Table 1. Details of ingredients used except rubber.

Sl no	Material	Supplier
1	Carbon Black (N234)	Birla Carbon, Uttar Pradesh, India
2	Zinc Oxide (White seal)	POCL enterprises ltd., Chennai, India
3	Stearic acid	Godrej industries ltd., Mumbai, India
4	TRAE Oil	Raj Petro industries, Chennai, India
5	N-Cyclohexyl-2-benzthiazolesulphenamide (CBS)	Shandong Derek New Materials Co Ltd, Shandong, China
6	Soluble Sulphur	The standard chemical co. Pvt. Ltd., Ambattur, India

Table 2. Recipe of calibration standard.

Ingredients	Parts Per hundred (phr)rubber
S-SBR NS616	10-100
PBR	90-0
N234	65.0
TRAE oil	10.0
ZnO	5.0
Stearic Acid	1.0
CBS	1.0
Soluble sulphur	2.0

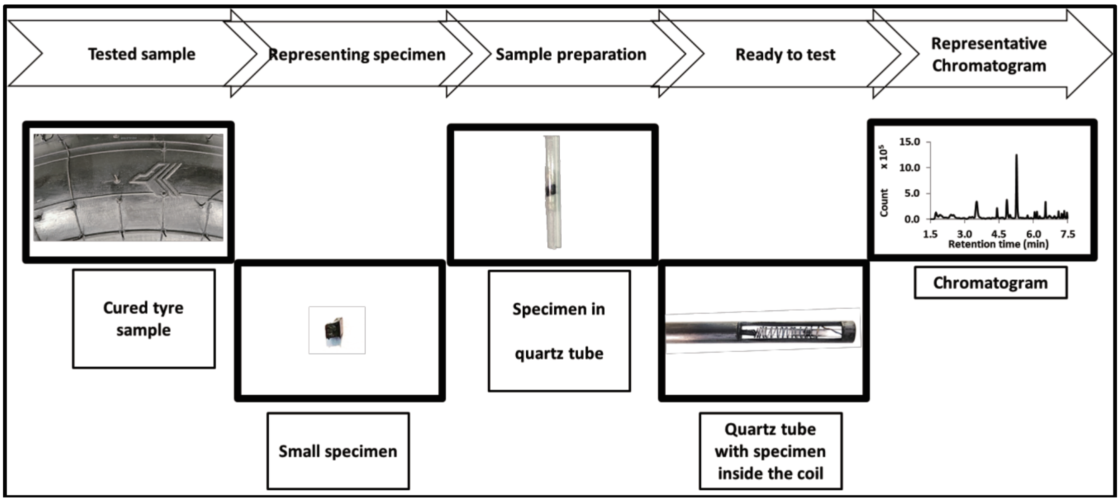


Figure 1. Process flow for the SBR/BR blend ratio determination.

Table 3. MS condition (full scan mode).

Tune	Standard spectrum auto tune
Scan range	35-550 amu
Interface temperature	280 °C
Electron impact	70 eV

4. Results

A typical chromatogram of pyrolysed SBR-BR-based compound has been depicted in **Figure 2**. Several pyrolysates have been formed on the pyrolysis of cured samples. On analysis of obtained chromatogram, the peak at 5.2 min (marked as A) is representing 4-Vinyl Cyclohexane and the peak at 6.4 min (marked as B) represents the styrene group. These two peaks are potentially used for quantitative estimation of SBR-BR blend ratio.

Styrene peak is being considered as an equivalent to Styrene butadiene rubber (SBR) and the same for Polybutadiene (BR) is 4-Vinyl Cyclohexane. The ratio of styrene content (A_x) has been measured using the following equation:

$$A_X = \frac{A_S}{A_B + A_S} \tag{1}$$

A_X: Ratio of styrene content with respect to the area for Styrene and 4-Vinyl Cyclohexane

A_B: Peak area for 4-Vinyl Cyclohexane

A_S: Peak area for styrene

4.1 Repeatability

A calibration curve between A_X (ratio of styrene

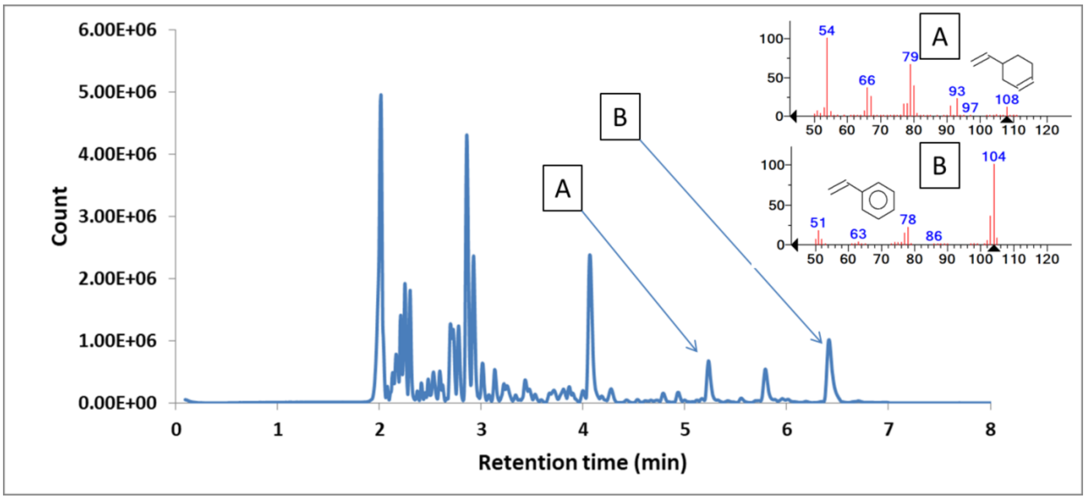


Figure 2. Typical chromatogram of pyrolysed SBR-BR-based compound.

content with respect to the area for Styrene and 4-Vinyl Cyclohexane) and PHR of SBR rubber content has been drawn (**Figure 4**). From the equation, the SBR rubber content in the sample has been calculated. To understand the stability/consistency of the developed method, twenty-five replicate tests of calibration standard samples have been analysed using the different calibration curves and results are mentioned in the following **Figure 3**.

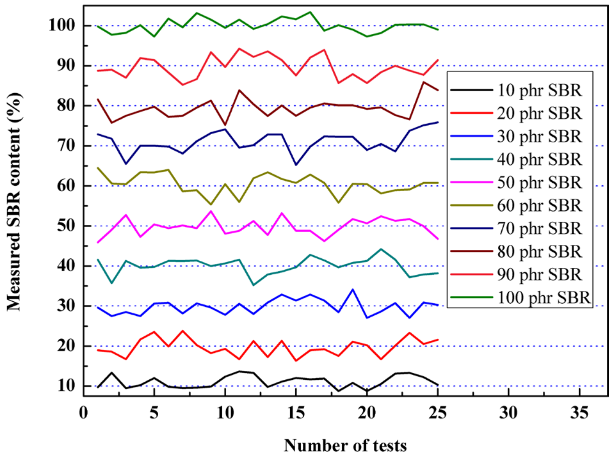


Figure 3. Repeatability of the calibration standard measured 25 times of each cured calibration standard sample contains 10 to 100 phr SBR.

It has been observed that with an increase in the PHR of SBR in the matrix, the recovery factor increases. The standard deviation of calculated SBR content drops significantly. Above 50 phr SBR content, the accuracy is noticeably high compared to the lower range, as shown in **Table 4.**

Table 4. Actual SBR in phr vs experimental results.

Actual SBR (phr)	Range of Experimental Result (phr)
10	8.7-13.7
20	16.3-23.8
30	27.1-34.1
40	35.2-44.2
50	45.9-53.7
60	55.4-64.5
70	65.2-75.9
80	75.3-85.9
90	85.2-94.3
100	97.3-103.4

4.2 Estimation of limit of detection (LOD) and limit of quantitation (LOQ)

Detection capability describes the lowest reliable concentration that can be measured by any analytical method. Limit of detection (LOD) is the lowest concentration that is possible to detect using a specific method at a specified level of confidence. If and limit of quantitation (LOQ) is up to which lowest possible level, performance is acceptable for a selective application [27]. In this method validation process LOD, LOQ, standard deviation (S) at the lowest possible concentration i.e. calibration standard sample having 10 phr SBR, has been measured. LOD and LOQ are calculated from the standard deviation at the lowest concentration using the following equations [28].

$$S = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \mu)^2} \tag{2}$$

$$LOD = 3.3 \times \frac{S}{Slope} \tag{3}$$

$$LOQ = 10 \times \frac{S}{Slope} \tag{4}$$

where,

S: Standard deviation of twenty-five replicates data of lowest calibration standard sample

x_i: i^{th} test result of lowest calibration standard sample

μ: Mean of twenty-five replicates data of lowest calibration standard sample

n: Number of replicate tests performed

Using the above formula, LOD and LOQ of the method have been found 5.17 phr and 15.67 phr respectively, which signifies that a sample containing 5.17 phr SBR can be detected with confidence and a sample containing a minimum 15.67 phr SBR can be quantified through this technique.

4.3 Estimation of working range

To develop one method and to validate it is mandatory to establish the working range. That is actually the range within which this method is suitable. By visual means and support from statistics, method working range has been established. Lower end is

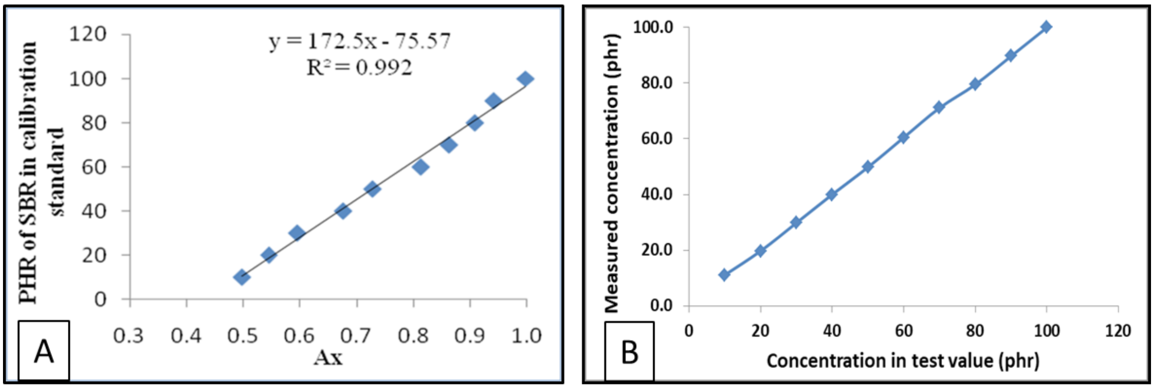


Figure 4. A) Calibration curve based on Ax (Ax: Ratio of styrene content with respect to area for Styrene and 4-Vinyl Cyclohexane) and B) the working range obtained with a measurement procedure where test sample concentration is plotted against measured concentration.

obtained from LOQ i.e. 15.67 phr and the upper end is identified as 100 phr using the measurement procedure where test sample concentration is plotted against measured concentration.

In the present study to support the working range, the linearity of response obtained from different calibration standards tested on six different days (Day 1 to Day 6) has been analysed (**Figure 5**).

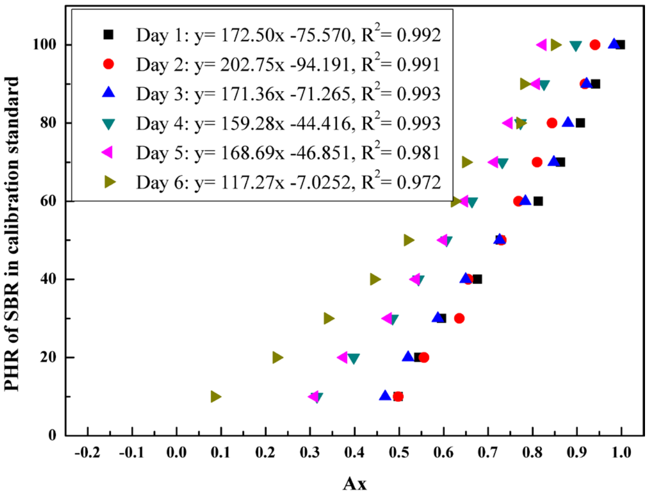


Figure 5. Linearity study from day 1 to day 6 where Ax is the ratio of styrene content with respect to area for Styrene and 4-Vinyl Cyclohexane.

From the above linearity study, it has been found that in every case the regression coefficient factor is coming to more than 0.95 which is completely acceptable for a newly developed method validation.

4.4 Trueness

Trueness is defined as the closeness of a single value to the mean of an infinite number of results (which is practically impossible). That is why in place of the mean of infinite data i.e. true value, actual SBR content in the calibration standard has been considered. The Trueness of this method has been estimated in terms of bias and precision.

Bias is defined as the closeness of the result with true value and can be estimated by three different techniques, (a) analysis of reference material (b) recovery of the analyte (c) comparison of results obtained from different techniques. In this study, the calibration standards have been considered as reference material. Bias, percent bias and recovery have been estimated and the results are mentioned in **Figures 6 and 7**.

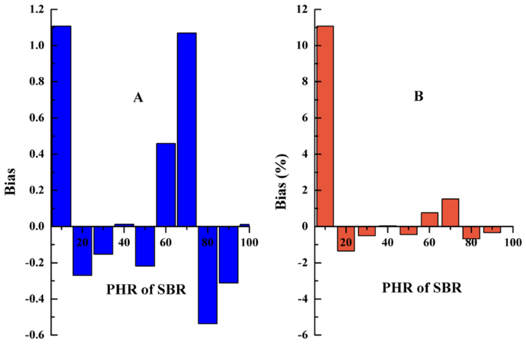
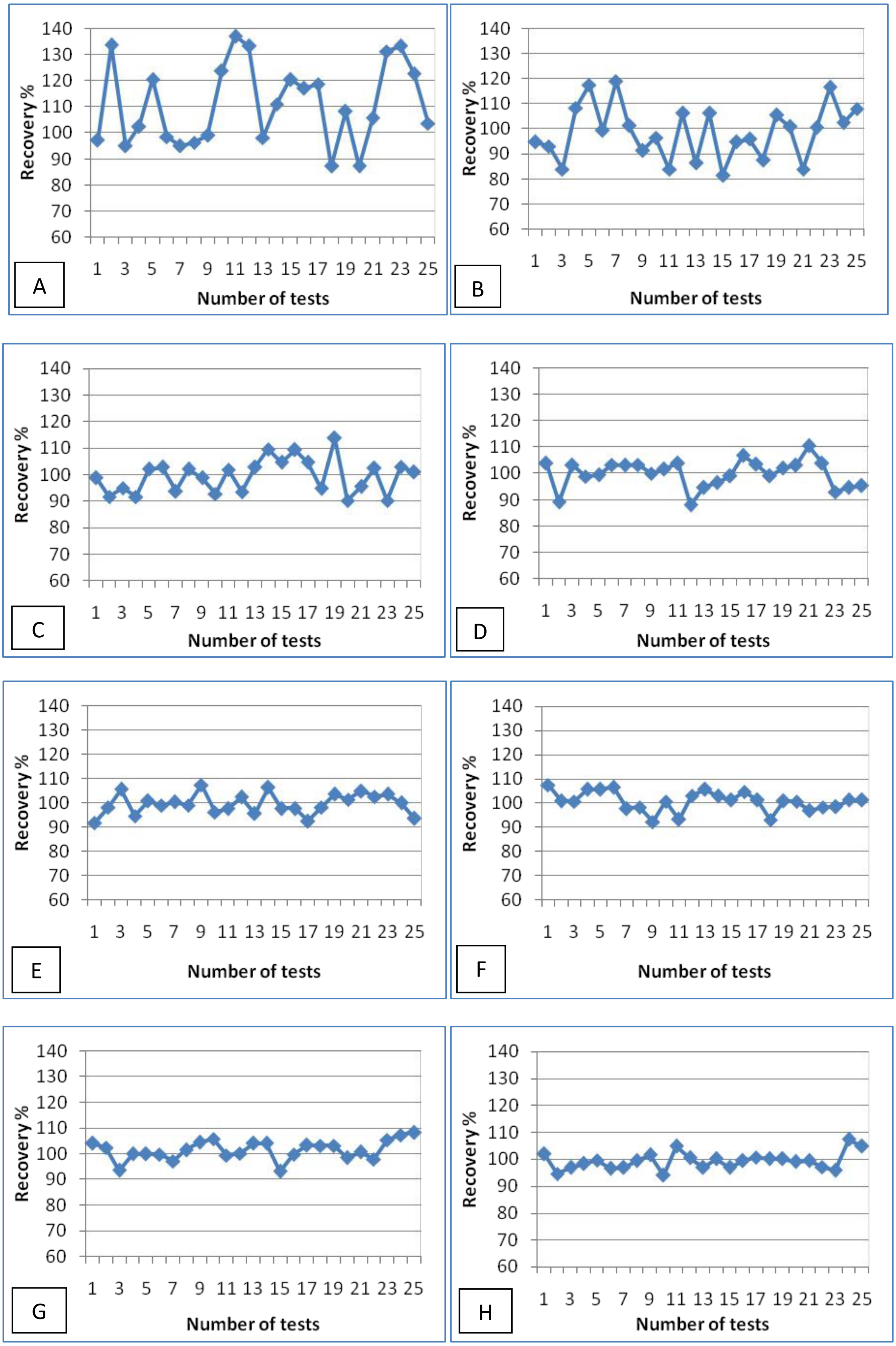


Figure 6. A) Bias and B) percent bias in different SBR/BR blend sample.


A
Recovery %
140
130
120
110
100
90
80
70
60
1 3 5 7 9 11 13 15 17 19 21 23 25
Number of tests
B
Recovery %
Number of tests
C
Recovery %
Number of tests
D
Recovery %
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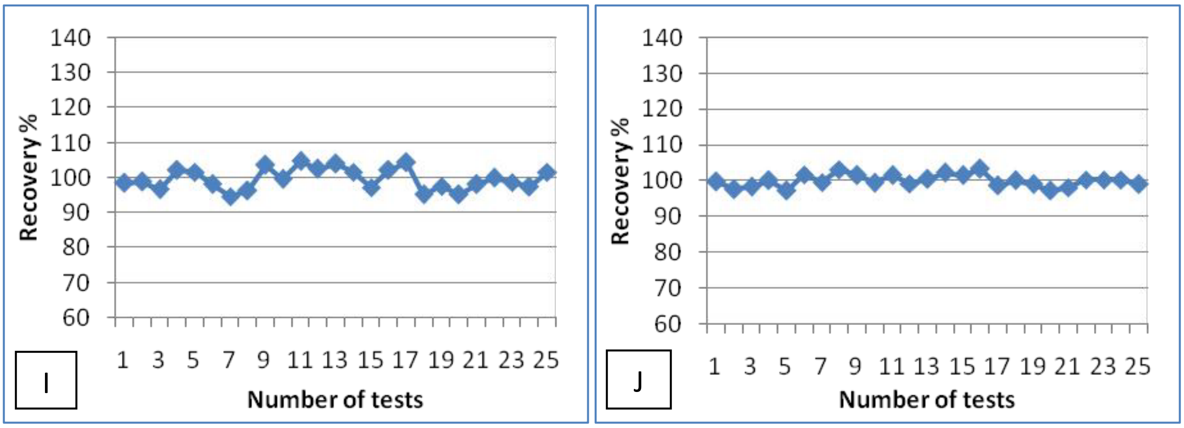

Figure 7. Recovery % of A) 10 phr, B) 20 phr to J) 100 phr SBR in BR/SBR blend.

4.5 Precision

Precision is defined as the closeness of the results obtained in different analysis. To estimate precision, repeatability and reproducibility of the analysed data are measured. Repeatability (r) has been measured using the following Equations (5) and (6) and the results are represented in **Table 5**. Since there is no validated method exists for this study so we are not able to find a sufficient lab for the estimation of repeatability through interlaboratory correlation.

$$r=2.8\times S_r \qquad (5)$$

$$S_r=\sqrt{\sum_{i=1}^{p}\frac{S_i^2}{p}} \qquad (6)$$

where,
r: Repeatability
S: Standard deviation for ith laboratory
S_r: Repeatability standard deviation
p: number of laboratories

Table 5. Repeatability limit of different SBR content.

SBR content	Repeatability limit
10 PHR	+ 4.41
20 PHR	+ 6.13
30 PHR	+ 5.46
40 PHR	+ 6.01
50 PHR	+ 6.04
60 PHR	+ 7.00
70 PHR	+ 7.49
80 PHR	+ 7.20
90 PHR	+ 7.73
100 PHR	+ 4.80

5. Discussion

During any statistical analysis of a newly developed method or an existing method, it is most important that the standard deviation of consecutive analysis must reflect the precision of the particular test sample. So, sufficient numbers of replicate tests are required to have an appropriate standard deviation. Here, in the present study twenty-five replicate tests have been performed. And the standard deviation obtained from those replicate tests is being utilized to obtain the limit of detection (LOD) and limit of quantitation (LOQ) for the estimation of the SBR/BR blend ratio in the cured synthetic rubber matrix.

The working range of a method defines an interval where results can be obtained with a tolerable uncertainty. Generally, LOQ is nothing but the lower end of the working range. The upper end is the limit value until which results are produced without any major deviation or anomalies. In some of the cases upper end can be defined as the beginning of the plateau. In this present study linearity and the proposed calibration procedure, are both taken into account. Certain standard steps are followed while determining the working range a) the machine is perfectly calibrated based on the standard process, b) different samples with different concentrations are taken covering the entire range of interest, c) samples with known concentrations have been taken and taken for the entire measurement procedure. The method working range has been established from 15.67 phr to 100 phr as stated in the result part.

To support the working range linearity of response from six consecutive days has been analysed. It is interesting that a similar trend has been observed in all the 6 days analysis for the stated concentration range of the calibration standards. The inference, that we can draw from here is the linear trend line and repeatable analysis. Both of which are important tools regarding the quality of sample analysis. The assessment of this working range is further supported by precision and bias studies, providing that these studies cover concentration throughout the entire working range.

With the increase in SBR content in the synthetic rubber blend standard deviation of calculated SBR content reduces, as a result recovery and recovery % have been increased. The accuracy is perceptibly high in the case of blends with more than 50 phr SBR content.

Case studies

Three known tread components are taken from tyre cut section for the determination of the BR/SBR blend ratio. A calibration curve is drawn from the ten different known standard compounds. The regression coefficient (R^2) value is obtained above 0.95. That graph is further used for unknown blend ratio calculation. For verification of this method, we have analysed our regular tyre Type 1 and found the blend ratio as 43:10:47, from formulation actual blend ratio is 40:11.5:48.5. We have also estimated polymer blend ratio of one of our regular tyre Type 2 compounds as 30:42:28, where actual blend ratio from the formulation is 30:40:30. We have also taken another pattern tyre Type 3 and reported the blend ratio as 30:42:28, where actual blend ratio was 30:45:25. In all three cases error percentage is well under acceptable range (**Table 6**).

Table 6. Blend ratio of NR/SBR/BR.

Sample-Id	NR		SBR		BR	
	Expt. (phr)	Actual (phr)	Expt. (phr)	Actual (phr)	Expt. (phr)	Actual (phr)
JK tyre: Type 1	43	40	10	11.5	47	48.5
JK tyre: Type 2	30	30	42	40	28	30
JK tyre: Type 3	30	30	42	45	28	25

6. Conclusions

During the development and validation of the test method, it has been observed that the regression coefficient factor (R^2) in linear calibration is always higher than 0.950, which signifies that there is linear correlation exists between the factor A_x (Styrene to styrene-butadiene ratio) and SBR content in the matrix throughout the range of 10 phr to 100 phr. From the trueness and bias study, it is observed that the deviation in reported value to actual value is maximum (10%) in the lowest concentration. Recovery sets of samples are always lying between 80% to 140%. In the case of 10 PHR SBR content, recovery varies from 87%-137%, whereas in the case of 20, 30 and 40 PHR SBR content it was found that the percentage recovery lies between 80 to 120. In the case of SBR content higher than 50 PHR, recovery is reclining between 90% to 110%. The deviations in recorded value to actual value are maximum in the case of lowest concertation whereas for higher concentration, the observed deviation is getting minimized. Repeatability of the sets of samples found always within ±10. Through this technique up to 5.17% SBR in an SBR-BR vulcanizate can be detected and quantified up to 15.67%, i.e. the LOQ of the present study. The above-stated criteria are met when we have analysed some of our known tyre samples.

Above kind of study is very much practicable for the benchmark analysis of the tyre sample which can help one compound/material expert develop a new product. In future we may concentrate to understand/quantitatively predicting the NR percentage of below 10 phr (basically low concentration) in NR/SBR/BR blend tyre sample.

Author Contributions

Tirthankar Bhandary is basically the primary responsible person for this entire work.

Dr. Hirak Satpathi is responsible for the data interpretation and structuring the manuscript.

Mrs. Aratrika Banerjee is responsible for the characterization of the rubber compound.

Mr. Koushik Pal is responsible for the sample preparation of the rubber compound.

Dr. Abhijit Pal is responsible for assisting in data interpretation.

Dr. Barun Kumar Samui is responsible for assisting in data interpretation.

Dr. Saikat Das Gupta is responsible for the financial and moral support.

Dr. Rabindra Mukhopadhyay is responsible for the financial and moral support.

Conflict of Interest

We declare that this manuscript or its content in some other form has not been published elsewhere and is not under consideration by any other journal at the time of submission. All authors have approved the manuscript and agree with submission to Organic Polymer Material Research journal. The authors have no conflict of interest to declare.

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