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Quantitative Analysis of Natural Rubber, Polybutadiene Rubber and Styrene/Butadiene Rubber Blends by Infra-Red Spectroscopy*

V. K. Kaushik and Y. N. Sharma

Research Centre, Indian Petrochemicals Corporation Limited, Baroda 391 346 (Gujarat), India

SUMMARY

Infra-red spectra of natural rubber (NR), polybutadiene rubber (PBR) and styrene butadiene rubber (SBR) have been studied for the estimation of these polymers in ternary rubber blends. A study of different infra-red active bands suggests that the bands at 1316 Cm^{-1}, 1379 Cm^{-1} and 1493 Cm^{-1} are most appropriate for quantitative purpose. A detailed analysis of observed data has been made and based on this analysis, formulae for the estimation of these rubbers have been deduced.

INTRODUCTION

Unlike the estimation of two elastomers in a blend (1-2), estimation of constituents in ternary rubber blend is a difficult task where the absorbance of two will change in the presence of third polymer. This complexicity is observed because of the following reasons - (a) The absorbance frequencies are quite close in these polymers hence, the base line changes with different compositions and (b) In some cases even the shape of absorption band changes. An example of this is shown in Fig 1. SBR absorbs infra-red radiations at 700 Cm^{-1} and 760 Cm^{-1} while PBR shows the absorption at 740 Cm^{-1}. A composition variation of 10%-90% in the mixture drastically change the shape of absorption bands.

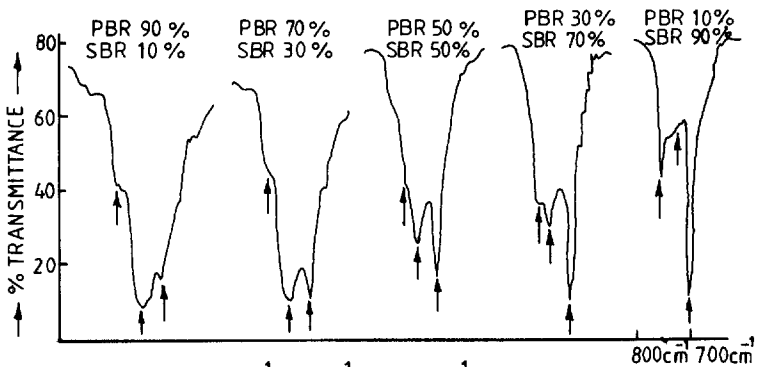

Fig.1 CHANGE IN 700Cm^{-1}, 740Cm^{-1} AND 760Cm^{-1} BENDS WITH COMPOSITION

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The assignment of different infra-red active bands is reported in the literature(3-4). In the present investigation the blends of three elastomers have been studied in the composition range 10%-70% and spectra have been analysed in the frequency region 1600 Cm^{-1} - 600 Cm^{-1}. Based on this analysis, best possible formulae for estimation of three rubbers in a blend have been developed. Once the absorbance of interested bands are known from IR spectra, present method gives directly the composition of different rubbers in a blend.

EXPERIMENTAL

The infra-red spectra of rubber samples were recorded on a Perkin-Elmer 567 spectrophotometer using CsI window. For these studies, rubber samples were first cut into small pieces and extracted overnight with acetone to remove the impurities. This sample was then dried, weighted and soaked in benze overnight and shaken finally at approximately 65°C to give a uniform solution. The film of rubber on CsI window was obtained by evoparating benzene from this solution. This film was finally used for infra-red studies.

RESULTS AND DISCUSSION

A careful analysis of infra-red bands of three elastomers and their different compositions was carried out to select bands for quantitative purpose. Only bands which were very sensitive for composition change and also maintain Lambert Beer law over a wide range of composition (5) were selected. This detailed study gave us the choice of infra-red active bands at 1316 Cm^{-1}, 1379 Cm^{-1} and 1493 Cm^{-1}. Using the absorbance of these bands, data for six calibration curves was obtained. This data was fitted by linear least square fit and the equation of different calibration curves shown in Table 1 were deduced. Here A1, A2 and A3 are absorbance of 1316 Cm^{-1}, 1379 Cm^{-1} and 1493 Cm^{-1} bands, Y is the absorbance ratio of bands and x is the composition (in wt%) ratio of two rubbers in a blend.

Table 1 : Equation of different calibration curves

Sr. No.	Equation of calibration curve	Y	x	In presence of
1.	Y = 0.407x - 0.039	A3/A2	SBR/NR	-
2.	Y = 3.075x - 0.063	A2/A3	NR/SBR	PBR
3.	Y = 0.286x + 0.126	A1/A2	PBR/NR	-
4.	Y = 1.459x + 0.337	A2/A1	NR/PBR	SBR
5.	Y = 0.912x - 0.033	A1/A3	PBR/SBR	-
6.	Y = 0.798x - 0.310	A3/A1	SBR/PBR	NR

Once equation of calibration curves were developed, analytical method similar to that reported by Karayenev et.al (6) has been used for composition estimation. A total of twelve results were obtained from six calibration curves. In order to extract the best method, twenty four test blends of known composition were prepared and the error square sum χ^2 i.e. sum of square of errors between calculated and observed composition were calculated. These χ^2 values for first five blends are shown in Table 2. Results show that the composition obtained from curve no.1 and curve no.4 give the best results

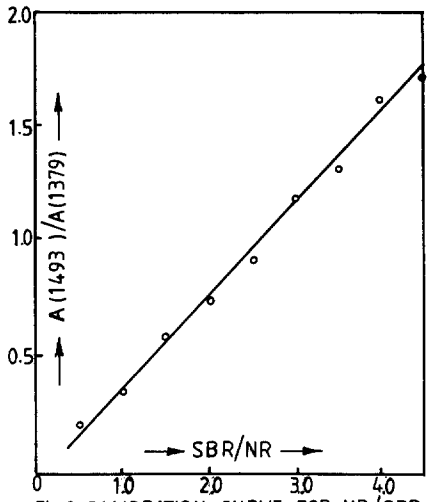

Fig.2 CALIBRATION CURVE FOR NR/SBR COMPOSITION

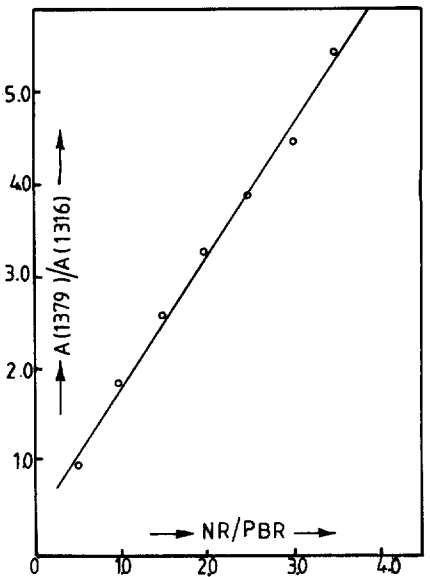

Fig.3 CALIBRATION CURVE FOR NR/PBR COMPOSITION IN THE PRESENCE OF SBR

Table 2 : Error square sum values from different sets of calibration curve

Curve Nos.	Set I	Set II	Set III	Set IV	Set V
1,3	35.6	178.2	96.8	85.8	79.5
1,4	0.1	39.5	6.7	6.9	6.8
1,5	394.3	306.8	166.7	102.1	67.3
1,6	1.7	53.2	6.7	31.4	122.0
2,3	35.4	121.8	43.9	36.4	35.6
2,4	0.2	21.4	4.3	25.4	31.1
2,5	398.8	307.9	166.9	111.9	83.8
2,6	1.6	53.1	0.2	27.1	110.2
3,5	143.5	325.0	178.3	101.3	69.6
3,6	73.3	73.6	27.3	89.7	189.4
4,5	187.4	472.8	331.3	170.5	82.9
4,6	2.9	131.4	6.8	27.2	117.2

over a wide range of composition. In fact, χ^2 values were checked for all the twenty-four test blends and it was concluded that curves no.1 and no.4 give the best result over the varying composition range of three elastomers. It is worth mentioning here that styrene percentage in SBR was 23.8 percent.

These best calibration curves obtained as a result of analysis are shown in Fig. 2 and Fig. 3.

Following formulae for the estimation of three elastomers in a blend were deduced from these calibration curves -

$$NR = \frac{100\ A^2_2 - 33.7 A_1 A_2}{D}$$

$$PBR = \frac{145.9\ A_1 A_2}{D}$$

and $$SBR = \frac{9.582\ A^2_2 - 82.801\ A_1 A_3 + 245.7 A_2 A_3 - 3.229\ A_1 A_2}{D}$$

where $$D = 1.09582\ A^2_2 + 1.08971\ A_1 A_2 + 2.457\ A_2 A_3 - 0.82801\ A_1 A_3$$

and A1,A2,A3 are absorbance of 1316 Cm^{-1}, 1379 Cm^{-1}, and 1493 Cm^{-1} bands. The agreement between known composition and calculated composition using these formulae is shown in Table 3 and examples of IR spectra used in estimation of some compositions are illustrated in Fig.4.

Table 3 : Determination of polymer compositions in blends

Sr. No.	Calculated compositions			Known compositions		
	NR	PBR	SBR	NR	PBR	SBR
1.	49.7	25.0	25.3	50.0	25.0	25.0
2.	19.1	14.8	66.1	20.0	10.0	70.0
3.	21.9	19.8	58.3	20.0	20.0	60.0
4.	21.7	28.0	50.2	20.0	30.0	50.0
5.	21.4	37.9	40.7	20.0	40.0	40.0
6.	24.6	44.5	30.9	20.0	50.0	30.0
7.	23.4	63.7	12.9	20.0	70.0	10.0
8.	9.7	23.9	66.4	10.0	20.0	70.0
9.	19.6	20.6	59.8	20.0	20.0	60.0
10.	31.5	20.0	48.5	30.0	20.0	50.0
11.	39.7	19.3	41.0	40.0	20.0	40.0
12.	49.6	20.0	30.4	50.0	20.0	30.0
13.	59.3	20.6	20.1	60.0	20.0	20.0
14.	70.3	18.5	11.2	70.0	20.0	10.0
15.	24.2	53.7	22.1	20.0	60.0	20.0
16.	53.2	25.3	21.5	50.0	30.0	20.0
17.	54.3	23.0	22.7	60.0	20.0	20.0
18.	61.3	19.3	19.4	60.0	20.0	20.0
19.	28.7	24.1	47.3	25.0	25.0	50.0
20.	35.0	29.9	35.1	33.3	33.3	33.3
21.	34.7	16.0	49.3	35.0	15.0	50.0
22.	40.7	19.1	40.2	40.0	20.0	40.0
23.	31.1	23.6	45.3	30.0	25.0	45.0
24.	8.7	24.3	67.0	10.0	20.0	70.0

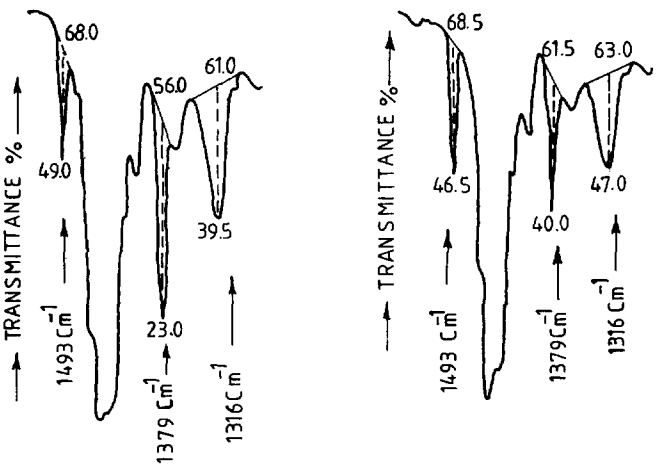

Fig. 4 IR SPECTRA OF BLENDS CORRESPONDING TO COMPOSITION OF Sr. No. 20 And 4 OF TABLE-3

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