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Thermochimica Acta 444 (2006) 65–70

thermochimica acta

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Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR

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Received 19 October 2005; received in revised form 21 February 2006; accepted 23 February 2006

Abstract

The employment of used tyres as a new source of raw materials for different applications can be a partial solution to the great environmental problems generated by these products concerning their disposal at waste depots. In this study, high-resolution thermogravimetric analysis (Hi-Res TGA) is used to quantify the elastomer composition of SBR/NR in tyre formulations. This technique provides the ability to generate TGA derivative profiles (DTGA), which can be used to distinguish different formulations from appropriate calibration curves. Infrared spectroscopy (FTIR) is also employed for composition quantification of used tyres and the results are compared to those obtained by Hi-Res TGA. Both analysis methods give satisfactory results when applied to elastomer mixtures of known composition and to tyre rubbers of unknown composition. The study confirms the accuracy of high-resolution TGA–DTGA technique for rapid quantitative determination of elastomer blends in used tyres.

Keywords: Used tyres; Elastomers; Hi-Res TGA; FTIR

1. Introduction

Tyre recycling or reprocessing are one of the preferable processes, according to the so-called waste management hierarchy, under environmental aspects. The re-use of tyres in alternative applications is one example of this, as the basis polymer can be reused in new formulations with the consequent cost saving in raw material, and preserving both natural resources and environment. In addition to the reincorporation of the elastomer in new formulations, a controlled pyrolysis of vulcanized elastomers allows the recover of oil and carbon black, which in turn can be reused.

A piece of rubber for tyres is basically a mixture of two or more polymers, carbon black, inorganic compounds (calcium carbonate, silica, etc.) and a relatively high number of organic substances as plasticizers, lubricants, antioxidants, vulcanization agents and so on, that are considered to be dissolved in the polymer matrix. The formulation breakdown and the identification and quantification of each of its components are a laborious task, which has been done by different, time consuming techniques. A standard tyre formulation for trucks as well as cars is that which incorporates as basis polymer a physical blend of natural rubber (NR) with a styrene/butadiene containing elastomer (SBR) in adequate proportions for a specific application.

The physical and mechanical properties of blends of SBR, NBR and NR are sensitive to small variations in the amounts of individual polymers used. Therefore, it is necessary to develop a variety of analytical tools to monitor blend compositions. Thermogravimetric analysis [1–9] and pyrolysis-GC/MS [10,11] have been employed extensively to study the feasibility of characterizing NR/SBR and BR/NR blends. TGA is one of the most employed techniques in these cases due to its rapidity and to a lesser necessity of sample manipulation compared with other methods in conventional analysis. Specifically, differential thermal gravimetric analysis (DTGA) has a considerable value for estimating the basic composition of vulcanizates [3–8]. Elastomer DTGA curves are used as “fingerprints” in the identification of many single elastomers and blends, finding that the peak height of the derivatives TGA (DTGA), is dependent on the amount of each elastomer in the sample. Therefore,

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doi:10.1016/j.tca.2006.02.027

quantitative determination has been attempted from DTGA peak heights. Nevertheless, this approach only works well when the DTGA curves of each elastomer are separated, being necessary to prevent any overlapping of different peaks.

High-resolution TGA [3,12,13] has been employed in this study as it gives greater resolution when compared to conventional TGA. In Hi-Res TGA the heating rate of the sample material is dynamically and continuously modified in response to changes in the rate of decomposition of the material so as to maximize weight change resolution. This approach allows very high heating rates to be used in regions where no weight changes occur, whereas heating rate is decreased when a weight change is detected. This method gives narrower and more intense derivative weight loss peaks with the result of a greater resolution from competing and overlapping weight losses, and even with a substantial reduction of the experimental time.

Up to date however, it has been impossible to determine by this technique the relative content of styrene and butadiene in SBR rubber. This drawback is due to the impossibility of differentiating the weight loss steps of both polymers during degradation process under experimental conditions. One solution to this problem is the use of Fourier transform infrared spectroscopy (FTIR) [14], as this technique allows performing relative quantification of both components, once absorption bands for each of them have been selected. However, in the case of heavily filled rubbers, as is our case, it is necessary to characterize the blends from the spectra obtained from blend pyrolysis products and no from the polymers themselves.

For many years the pyrolysis method suggested by Harms [15] was the only means available for the infrared examination of many insoluble resins and rubbers. The more recently discovered ATR method has greatly facilitated the examination of a number of these intractable materials. Nevertheless, there are many heavily filled insoluble samples from which it is not possible to obtain satisfactory spectra by this technique. In addition, their quantitative analysis is of doubtful value, except in some special applications, as the band intensities in relation to those in a transmission spectrum, increase with decreasing wavenumber, and are subject to variation due to inadequate contact with the prism surface. It is for these samples that the pyrolysis method is particularly appropriate. The difficulties associated with the identification of intractable, cross-linked rubbers and similar insoluble, filled materials can be sometimes overcome by spectroscopic examination of the collected liquid pyrolysis products. If the thermal degradation can be performed in a reproducible manner, the IR spectra of the products will be characteristic of the investigated polymer [16,17].

In this work samples of tyres, made of SBR/NR elastomers, of known composition, were studied both by high-resolution thermogravimetric analysis (Hi-Res TGA) and Infrared spectroscopy (FTIR). The quantitative composition of the elastomers in each sample was determined from calibration curves obtained from DTGA peak heights and Infrared absorption peaks, respectively. Styrene composition in SBR was quantified using Infrared spectroscopy.

The aim of this work is the elaboration of a precise determination of the relative content of both rubbers (NR and SBR) in unknown formulations from both new tyres as those coming from recycled material.

2. Experimental

2.1. Sample preparation

Thirteen sulphur-cured rubber samples of known composition were supplied by Finkanema, S.L. The elastomer components of the tyres studied were natural rubber (NR 901007) and styrene-butadiene rubber (SBR 1808, 23.5% S). The proportions of each elastomer varied between 0 and 100% in weight. Organic additives extraction from the samples was carried out using acetone as extracting solvent for 3 h in a Soxhlet device, and the resulting samples were kept for 12 h at room temperature in order to eliminate any residual solvent. Finally, all the tyre rubbers were cryogenically crushed and sieved to a size of about 1 mm.

2.2. Thermogravimetric analysis

Thermal analysis was carried out in a high-resolution Thermobalance (TA instrument, TGA-Q500). The heating rate was 40 °C/min and the resolution used “4”. This means that the apparatus operates similarly to the traditional constant heating rate ramp segment when no weight change is occurring, 40 °C/min in this study, while the heating rate is varied dynamically when a weight change occurs. When a loss of weight is detected in Hi-Res TGA technique, the heating rate slows in response to the increasing rate of mass loss and the system tries to keep it at the lowest value (0.01 °C/min) until the end of the weight loss.

Approximately 10 mg of sample was heated from room temperature up to 600 °C with a continuous N_2 flow at 75 ml/min; then the sample was cooled down to 400 °C, the purge atmosphere was changed to air, and the sample was heated again until a constant weight was achieved at 800 °C. Sample weight and its rate of weight loss was continuously measured as a function of temperature. The total analysis time was approximately 75 min.

2.3. Pyrolysis-FTIR

A small quantity of purified polymer was introduced in a small tube and put in contact with the flame of a Bunsen burner, according to [18]. Volatile products, which condense at room temperature, were collected on a metallic spatula inserted in the tube at the moment of vapour evolution. The condensed liquid, collected along the time the entire polymer mass was reduced to inorganic residue, was carefully deposited on KBr windows in such a way to obtain acceptable homogeneity. The experiment was carried out at least three times per sample in order to obtain reproducible results. This point was checked by means of the corresponding infrared spectra.

Infrared spectra were collected in a Fourier transform spectrometer Nicolet, Magna 560 in transmission mode, at a resolution of 2 cm^{-1} and a minimum of 16 scans were signal averaged.

The quantitative analysis from all infrared spectra was carried out with the help of “Turbo Quant” software based on the method of partial least squares (PLS). This program uses an algorithm that examines specific composition dependent absorption regions for each component. In all cases the program considered the film thickness as a constant value because all spectral regions selected to carry out the calibration calculation were previously normalized to the CH_2 and CH_3 stretching vibration region (2960–2820 cm^{-1}).

3. Results and discussion

3.1. Thermogravimetric analysis

TGA–DTGA results, using high-resolution TGA approach, obtained from one tyre sample with 40/60 NR/SBR elastomer composition, are displayed in Fig. 1. This approach permits, in a shorter experimental time and with a higher resolution of the weight loss events than with a traditional thermogravimetric method, the separation of tyre main components: oil, polymer, carbon black and inert filler. The first weight loss under N_2 flow, between 200 and 300 °C, corresponds to 9% of the total weight of the tyre sample and is attributed to the volatilization of processing oil or any other low boiling-point components. The next mass loss of 37% observed in N_2 flow, which has a maximum rate at 350 °C, is due to the decomposition of natural rubber (NR), whereas the weight loss of 25% with a DTGA peak at 424 °C corresponds to styrene-butadiene rubber (SBR). These temperatures have been assigned according to the obtained results from pure component thermogravimetric analysis. Finally, when air atmosphere is activated, oxygen reacts with carbon black and leads to the fourth weight loss at 563 °C. The non-volatile residue (~6%) corresponds mainly to inorganic fillers.

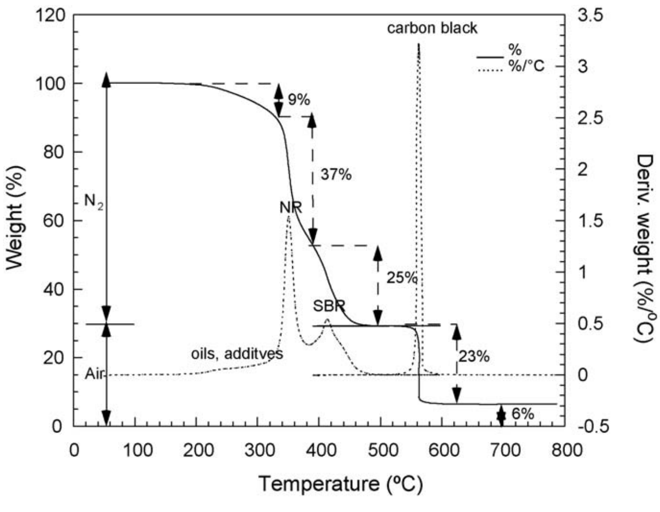

Fig. 1. Hi-Res TGA–DTGA curves of NR/SBR (40/60) vulcanizates.

Fig. 2 shows weight loss TGA and DTGA curves for some tyre samples with different NR/SBR elastomer composition. TGA curves (Fig. 2a) show that there are clearly two areas of weight loss between 300 and 500 °C, producing two peaks on DTGA curves (Fig. 2b). The first peak at ~350 °C is due to the decomposition of NR, while the second peak, at a higher temperature, ~420 °C, is characteristic of SBR. As a result, it is possible to distinguish NR, which decomposes mainly at lower temperatures, from SBR although NR has a little weight loss around SBR decomposition temperature.

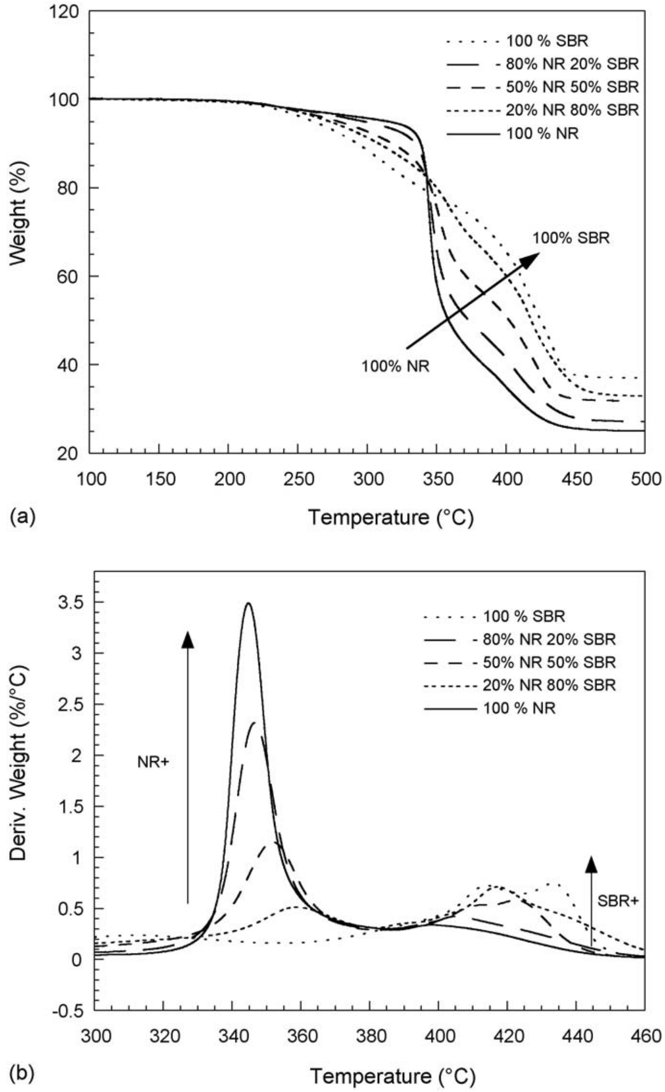

Fig. 2. (a) TGA weight loss and (b) DTGA curves for NR/SBR blends of different elastomer compositions. All curves are obtained using Hi-Res 4 at a heating rate of 40 °C/min.

Furthermore, it has been observed (Fig. 2b) that the DTGA peak of NR shifts to a higher temperature when SBR content increases in the blends, indicating increased thermal stability [9].

It is well known that the derivative weight loss curves are generally more sensitive to subtle differences in weight loss than the parent curve, and hence they can be used to identify and quantify the ratio of elastomers in blends. One way to quantify this ratio from DTGA curves is through the correlation of peak heights to the content of each component [3,4,6,7] and the representation of the ratio of DTGA peak heights versus the percentage of one of the elastomers. The calibration curve for NR/SBR blends obtained from the ratio of peak heights of NR (H_{NR}) and SBR (H_{SBR}) respectively is shown in Fig. 3. The relationship between

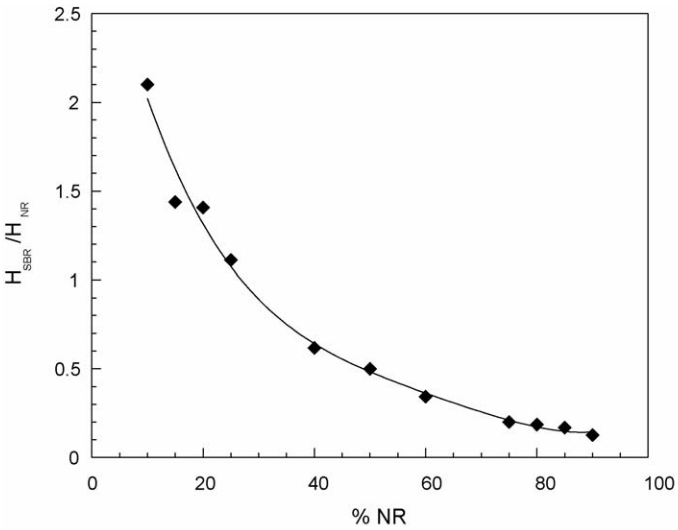

Fig. 3. Plot of the ratio of the peak heights (H_{SBR}/H_{NR}) vs. %NR to determine the elastomer composition in the tyres studied.

weight percent of NR and peak height ratio (H_{SBR}/H_{NR}) is not linear [7] and it has been fitted to a polynomial equation type as shown in Eq. (1)

$$\%\mathrm{NR} = 115 - 231\frac{H_{\mathrm{SBR}}}{H_{\mathrm{NR}}} + 255\left(\frac{H_{\mathrm{SBR}}}{H_{\mathrm{NR}}}\right)^2 - 138\left(\frac{H_{\mathrm{SBR}}}{H_{\mathrm{NR}}}\right)^3 + 28\left(\frac{H_{\mathrm{SBR}}}{H_{\mathrm{NR}}}\right)^4 \quad R^2 = 0.99 \tag{1}$$

Another way to quantify elastomer composition is from a calibration curve obtained by correlating a temperature that corresponds to a fixed % weight loss of the original sample weight with one of the elastomer content in the blend [10,19]. For example, in this work %NR in the sample is related with the temperature that corresponds to a 70% weight loss of the sample ($T_{70\%}$) and, as shown in Fig. 4, the correlation yielded a straight line with $R^2 = 0.98$.

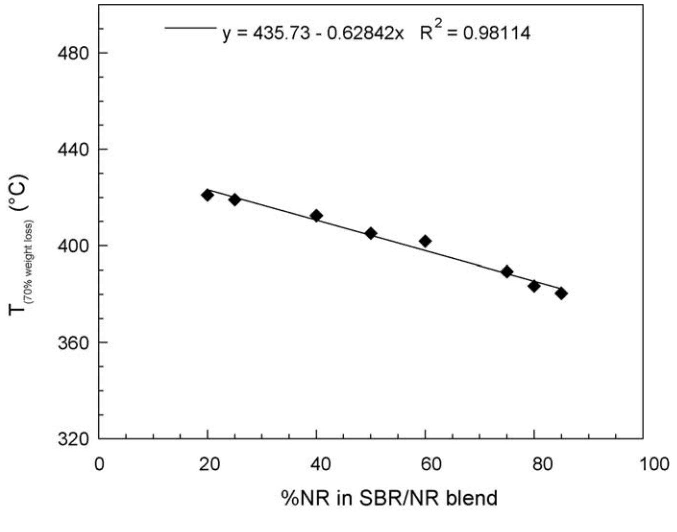

Fig. 4. Plot of 70% weight loss temperature ($T_{70\%}$) vs. %NR used to determine the percent of NR in NR/SBR tyre blends.

Table 1
Comparison between real NR/SBR blend ratios and predicted ones by Hi-Res TGA

Real NR/SBR	Predicted NR/SBR (H_{SBR}/H_{NR} method)	Predicted NR/SBR ($T_{70\%}$ method)
85/15	83/17	88/12
80/20	80/20	83/17
75/25	78/22	74/26
60/40	61/39	54/46
50/50	48/52	49/51
40/60	41/59	37/63
25/75	25/75	26/74
20/80	18/82	23/77
Sample composition of “unknown formulations”		
70/30	70/30	73/27
70/30	68/32	66/34

Comparing real NR/SBR blend ratios of tyre samples to those predicted by both calibration curves tests the accuracy of the high-resolution thermogravimetric method. The results shown in Table 1 suggest that no significant differences are observed between both calibration curves, although the results obtained by DTGA height method are closer to the real ones. In any case, the precision obtained using Hi-Res thermogravimetric is considerable.

3.2. Pyrolysis-FTIR analysis

Three independent pyrolysis experiments for each sample were carried out, according to ASTM D377, 00 procedure, and infrared spectra of room temperature condensed pyrolysis products were obtained. Each infrared spectrum is an averaged spectrum of the three spectra.

Fig. 5 shows the infrared spectrum of the pyrolysis products of a NR/SBR (40/60) blend. According to bibliography [14,18–22] there are several bands that must be used in order to identify the components of pyrolyzates. Thus, the diagnostic bands for SBR and NR pyrolysis products are those shown in Fig. 6. The spectral region shown in this figure corresponds to the out of plane bending vibrations of aromatic =C–H and C=C groups of Polystyrene at 750 and 700 cm^{-1}, respectively, and the out of plane bending vibrations (o.o.p) of =C–H of vinyl

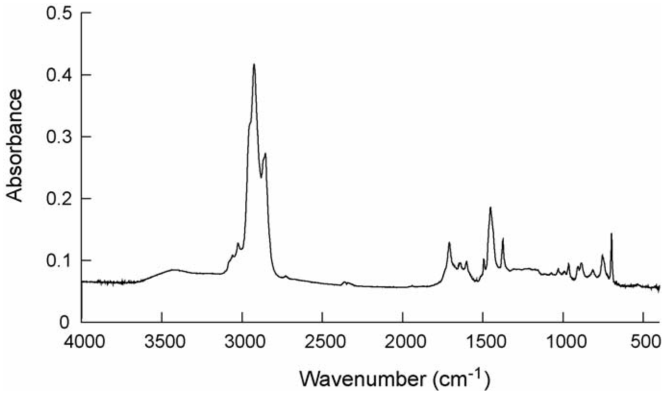

Fig. 5. Infrared spectrum of a NR/SBR (40/60) blend.

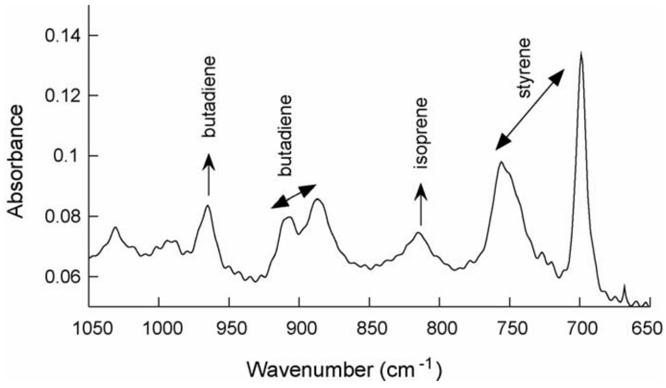

Fig. 6. Infrared spectrum in the region between 1050 and 700 cm^{-1} for a NR/SBR (40/60) blend.

groups (990 and 910 cm^{-1}) and trans –CH=CH– at 960 cm^{-1} of butadiene. The band centered at 815 cm^{-1} can be assigned to the same type of vibrations of NR. The election of this spectral region is due to the fact that the degradation products of each blend component display clearly separated bands assignable at each component.

NR degradation at temperatures between 300 and 500 °C gives place to the formation of variable length oligomers as a consequence of polymeric chain random scissions. At higher temperatures the evolution of isoprene, dipentene and different unsaturated volatile products takes place [23]. On the other hand, PS degrades in such a way that monomer is considered the main degradation product together with about 30% of low molecular weight oligomers [24]. These two types of products are included in the quantification process by FTIR as both of them display bands attributable to the o.o.p deformation vibrations of the aromatic ring.

Thermal degradation of polybutadiene at temperatures close to 400 °C gives rise to the production of monomer and low molecular weight oligomer structures [23]. Therefore, in SBR degradation in the temperature range studied, a mixture of polybutadiene and polystyrene oligomers as well as styrene and butadiene monomers will be collected.

In order to obtain FTIR calibration curves, the following steps must be fulfilled:

Table 2
Comparison between real S/B/NR blend ratios and predicted ones by FTIR

S/B/NR (%) (real composition)	S/B/NR (%) (predicted composition)
20/60/20	18/57/24
10/30/60	8/31/61
5/20/75	5/24/71
10/40/50	12/35/53
2.5/7.5/90	2.7/8.8/89
4/11/85	3/11/85
5/15/80	5/13/83
0/0/100	0.8/7/92
24/76/0	22/52/27
Sample composition of “unknown formulations”	
5/25/70	5/25/70
0/30/70	1/32/67

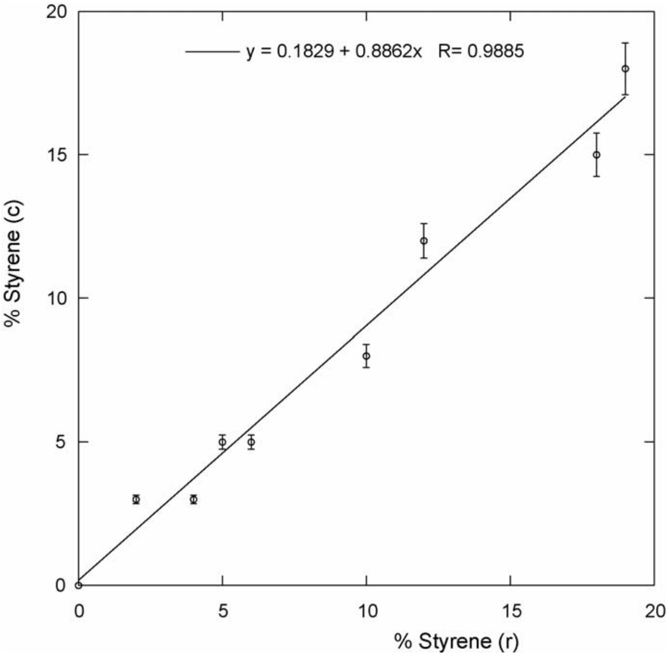

Fig. 7. FTIR calibration curve for the determination of % styrene.

- Selection of absorption regions as integration limits. In this case we have selected the following regions for the three components: styrene: region between 715 and 683 cm^{-1}. NR: region between 850 and 785 cm^{-1}. Butadiene: region between 1010 and 855 cm^{-1}.
- Elimination of the film thickness factor by the normalization of the component band areas with respect to the area of an invariable region. In this work, the bands corresponding to CH_2 and CH_3 stretching vibration have been selected.

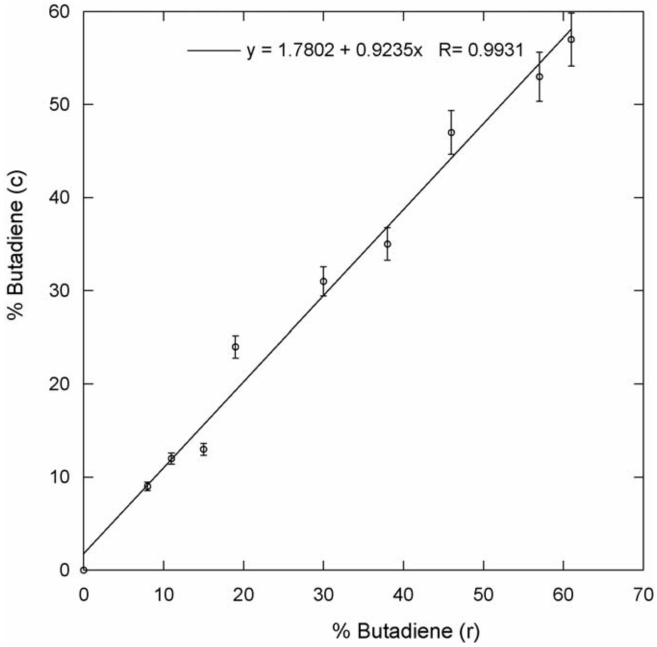

Fig. 8. FTIR calibration curve for the determination of % butadiene.

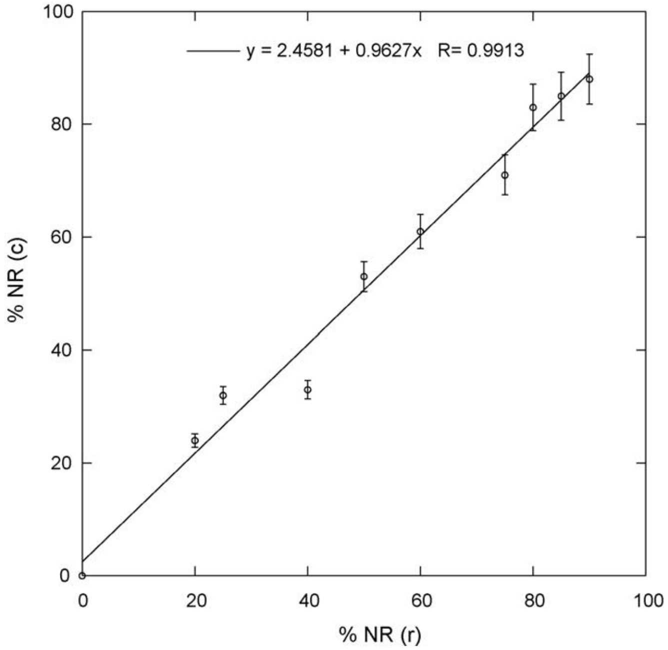

Fig. 9. FTIR calibration curve for the determination of % natural rubber.

The computer software “Turbo Quant” calculates component composition from the relative area of the spectra of all known composition samples, using the PLS method to perform this calculation. In this work nine blend samples of different composition were used for this purpose. Two other samples were used as “unknown composition” samples to determine the feasibility of the method. Table 2 summarizes the obtained results. The representation of the calculated values for each component by the program versus the real ones leads to the calibration curve for each component shown in Figs. 7–9.

The results obtained for the two unknown composition samples from both TGA and FTIR techniques, shown in Tables 1 and 2, are in good agreement, indicative of the validity of the two employed methods. Furthermore, by means of FTIR it is possible to determine the relative composition of styrene/butadiene of SBR.

4. Conclusions

From the obtained results it can be concluded that, once the pyrolysis experimental process is controlled, FTIR results are very similar to those obtained by High Res-TGA, what implies that both techniques are adequate to perform compositional analysis of vulcanizates. It must be pointed out, however, that High Res-TGA presents the advantages of being a straightforward and faster method when compared with pyrolysis/FTIR. However, TGA’s drawback is its inability to determine the relative compositions of styrene and butadiene in SBR samples.

Acknowledgment

The authors want to acknowledge the Basque Government for the financial support, under the frame of Intek program (2002).

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