QUALITATIVE AND QUANTITATIVE DETERMINATION OF THE POLYMER CONTENT IN RUBBER FORMULATIONS

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Abstract

The objective of this paper is to show an easy and rapid way to determine qualitatively and quantitatively the type of polymer or polymer blend used in a rubber formulation. The most common polymers used manufacturing rubber products were tested and characterized by both their decomposition temperature and the curve profile. Thermogravimetric analysis, which is considered to be used mainly for quantitative purposes, turned out to be a rather useful analytical tool to obtain qualitative information of such elastomeric mixtures.

Introduction

Thermal analysis methods have gained increased importance in many different fields of analytical chemistry lately. These could be defined as experimental methods used to characterize a system (element, compound or mixture) by measuring certain changes on the chemical-physical properties at high temperatures.

Thermal stability of polymers and compound content in formulations have been one of the major applications of TG [1]. Concerning the vulcanizates analysis this thermal procedure has undertaken in order to provide a rapid, practical analysis of composition [2, 3]. As it is well known, there are several ASTM procedures [4–6] for obtaining highly detailed information about the composition of vulcanizates or other analytical methodologies [7], but, unfortunately, they can take too long to be of practical use on a routine basis. Therefore, in some cases their expense cannot be justified. In literature, it can also be found the combination of TG with other analytical techniques in order to get deeper into the polymer characterization [8], but once again, in-

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dustry requires methods with faster and easier implementations. That is the reason why TG has turned out to be a powerful tool in elastomer technology [9].

The innovating aspect of this work is not only the quantitative analysis, which has been extensively described previously in literature [1, 10], but also general qualitative information that can be deduced using TG experiences as the unique thermal method regarding the most common elastomers used. In that sense, some attempts have been made on characterizing polymer blends lately [11]. However, these works only dealt with few specific elastomer types without giving general trends to classify the formulation according to the polymer type contents.

In this paper, most of the elastomers used in the rubber industry have been characterized. The results obtained made possible the qualitative classification of the different types of polymer attending to both their decomposition temperature and/or their decomposition profile.

Experimental

A company that manufactures rubber hoses for automobiles supplied all the samples tested in this work.

A rubber formulation is a complex mixture of several chemicals, and, since the object of this paper is to characterize the polymer content, the rest of the ingredients of the formulation should not affect all the data obtained for the polymer. To prove that influence of other components of the mixture is not significant at all, a statistical calculation has been carried out. Variation coefficients of the decomposition temperature have been calculated as it is shown in Eq. (1):

$$VC = \frac{S}{\overline{X}} \tag{1}$$

where S – standard deviation, $\overline{X}$ – mean decomposition temperature.

The temperature of the sample must be known exactly to make sure the exothermic effects do not change the heating rate from its constant value [12]. That is the reason why small size samples must be used in thermogravimetric experiments. The amounts weighed for each experiment was approximately 15 mg. Since the sample size is rather small, it has to be taken carefully to assure it will be representative of the whole material analyzed.

The instrument was a Mettler TG30, equipped with a high performance balance [13] and an oven that can be programmed to achieve lineal increases of temperature.

The basic procedure for thermogravimetric determinations on rubber formulations consists of two steps. In the first one, the sample is heated in a nitrogen atmosphere to obtain information about the polymer and other volatile additives. The second step will give information about the fillers present in the mixture. This part of the analysis is carried out in an oxidant atmosphere. When only qualitatively information is required, the second step of the analysis can be avoided. But to have reliable quan-

titative data, both parts of the thermal analysis must be done. This will be further explained in the discussion of the results.

The experimental conditions are shown below (Table 1).

Table 1 Experimental conditions of TG

Atmosphere	Starting temperature/°C	Final temperature/°C	Heating rate/°C min^{-1}
Nitrogen	30	550	20
Air	300	1000	20

Results and discussion

All the experiment have been carried out with vulcanizate formulations, since it was proved that the vulcanization of the sample affects neither the decomposition temperature (T_d) nor the curve profile obtained (Figs 1 and 2). At the first moment, T_d was taken as the parameter for the identification of the polymer type. Working with cured rubber was preferred because raw materials tend to get damaged much easily when stored for long periods of time.
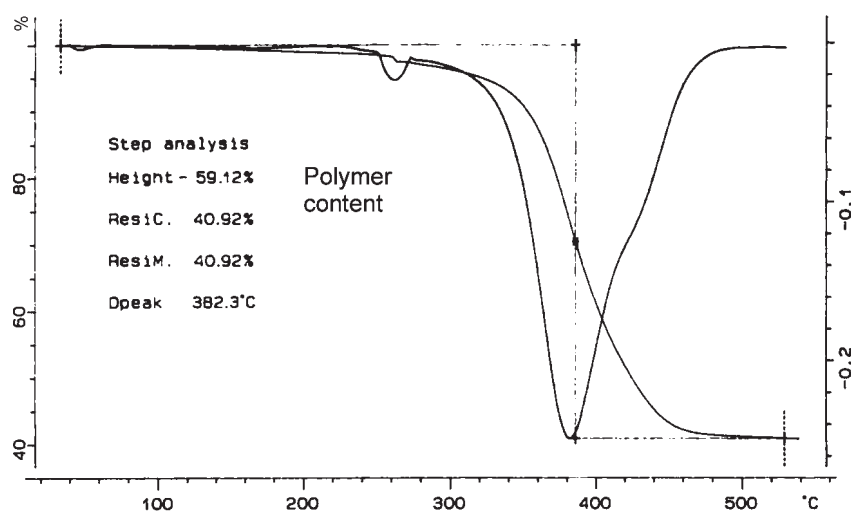

Fig. 1 TG of an uncured rubber sample (inert atmosphere)

As it has been stated before, it is necessary to know for sure that the decomposition of the polymer is not affected by the presence of the other ingredients in the mixture. Several analyses have been done on formulations containing the same polymer but different type of additives (Table 2). It can be noted that, though the presence of different additives have an influence on the decomposition temperature, it is not important enough to make not possible to distinguish between different polymers. This fact has been checked by
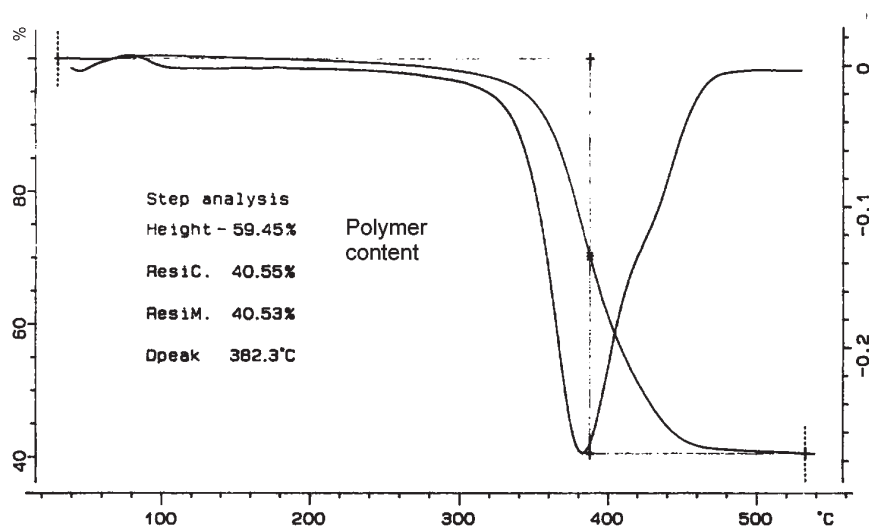
Fig. 2 TG of a cured rubber sample (inert atmosphere)

comparing the variation coefficient (VC) of both: formulations with the same polymer and formulations with different polymers. When working with mixtures containing the same polymer the VC calculated are less than 5%, while when different polymers are compared, the VC obtained are always above 10%.

Table 2 TG of formulations containing the same polymer

Formulation	Decomposition temperature/°C
Mixture 1 (natural rubber)	373
Mixture 2 (natural rubber)	382
Mixture 3 (chloroprene rubber)	305
Mixture 4 (chloroprene rubber)	323
Mixture 5 (chloroprene rubber)	303

Quantitative determination

As stated previously, the main application for TG has been the quantitative analysis. Analyzing vulcanizates by this thermal method the content of volatiles polymer and inorganic fillers can be determined. Through the experiments it was noticed that after the first step of analysis (i.e., heating in an inert atmosphere) the sample must be cooled down to 300°C before switching to the oxidant atmosphere. The complete decomposition of organic fillers would not be possible without this cooling down, leading to miscalculations on its content in the vulcanized (Figs 3 and 4).

Once the correct analysis conditions were established though, unexpected results were found when working with polymers containing chloro atoms. They are chloroprene (CR) and chlorosulfonylethylene (CSM), which are widely used in the
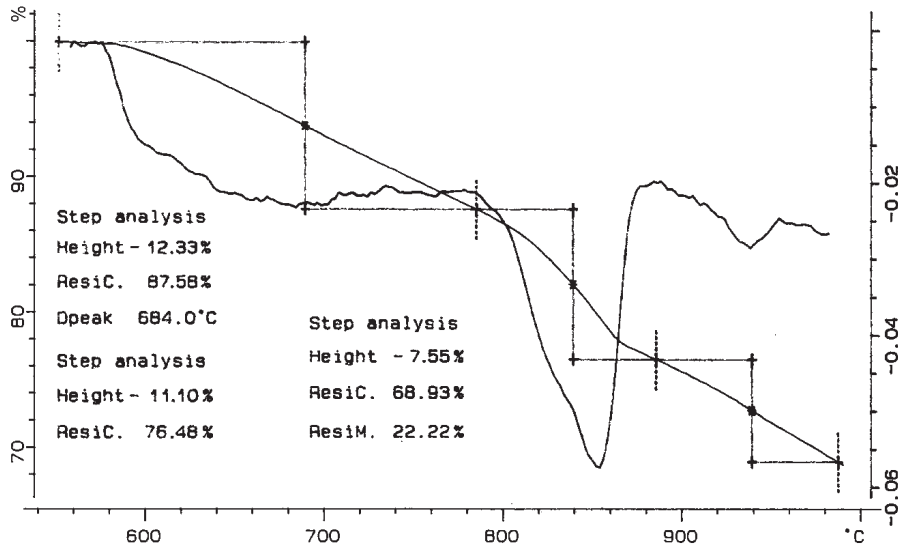
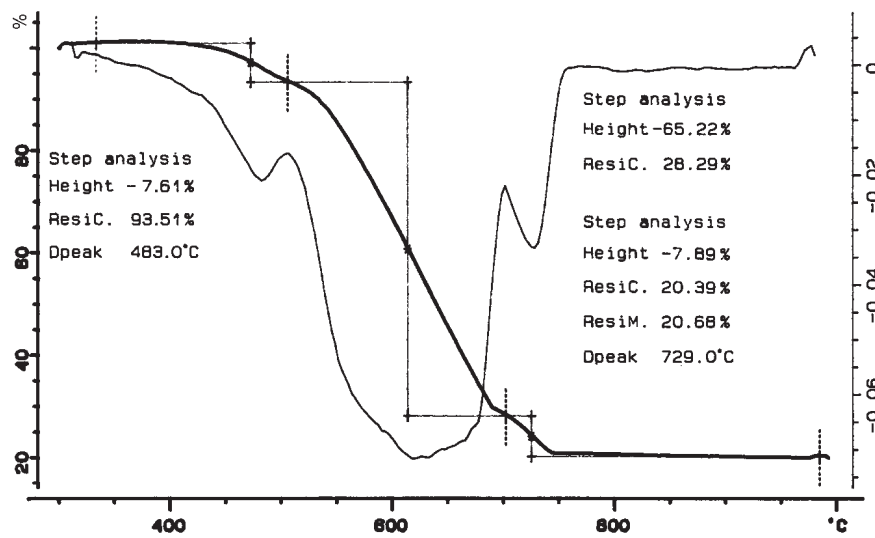**Fig. 3** Second step of the TG without cooling down

Fig. 4 Second step of the TG having cooled down

rubber industry. In the quantitative analysis of these kind of vulcanizates a lower amount of polymer and a higher amount of filler than expected have been calculated.

It has been shown in this paper, when there are chloro atoms attached to the polymer chains, the heating leads first to a giving off of chloride acid. The atoms of these acid molecules come from the polymer, so as HCl is giving off, the hydrogen content of the polymer decreases. Most of the carbon backbone left after HCl given
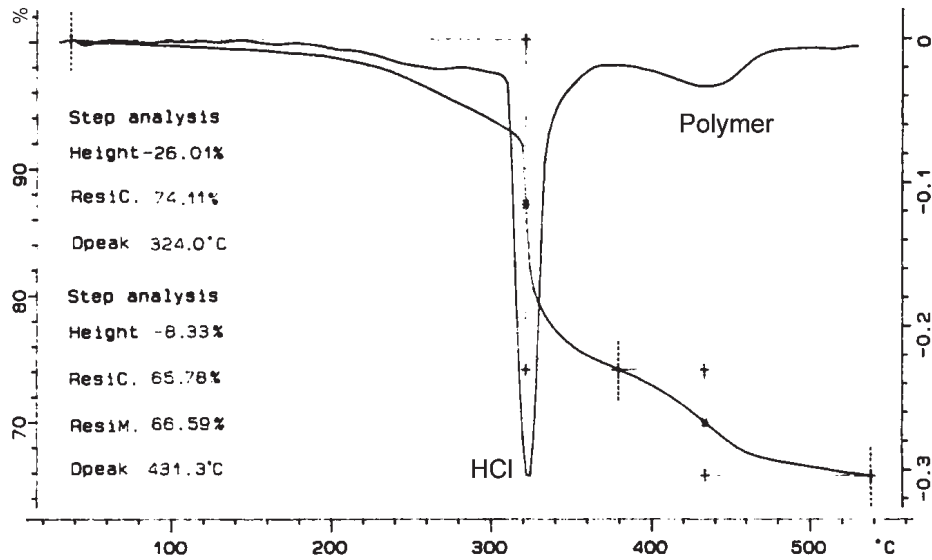
Fig. 5 TG of a chloroprene rubber sample

off consists of, practically, only carbon atoms, giving rise to a structure similar to that of the carbon black. These 'polymer chains', poor in hydrogen content will not decompose in a nitrogen atmosphere, they will behave as the carbon black filler decomposing during the second step of the analysis (i.e., the one carried out in an oxidant atmosphere). That is the reason why when analyzing the filler content of the formulation, an unexpected decomposition peak appears. This corresponds to the decomposition of the rest of the polymer poor in hydrogen (graphitized polymer) because of the giving off of HCl (Fig. 5).
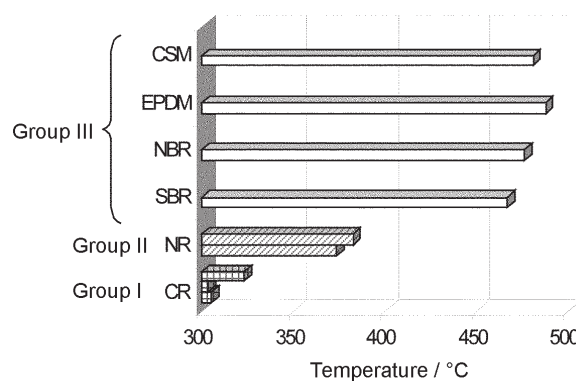

Fig. 6 Qualitative classification attending to the decomposition temperature

Qualitative determination

The first results obtained show, TG does not seems as powerful as it was expected to be. The decomposition temperatures split the elastomers into three main groups: chloroprene rubber (CR) [14], with decomposition temperatures at around 300°C; natural rubber (NR) [14] which decomposes approximately at 380°C; and a third group containing the rest of the vulcanizates studied (Fig. 6).

The temperature difference between NR and CR is big enough to make possible their identification applying only to the decomposition temperature. Furthermore, the decomposition curve of the chloroprene rubbers have a characteristic profile due to
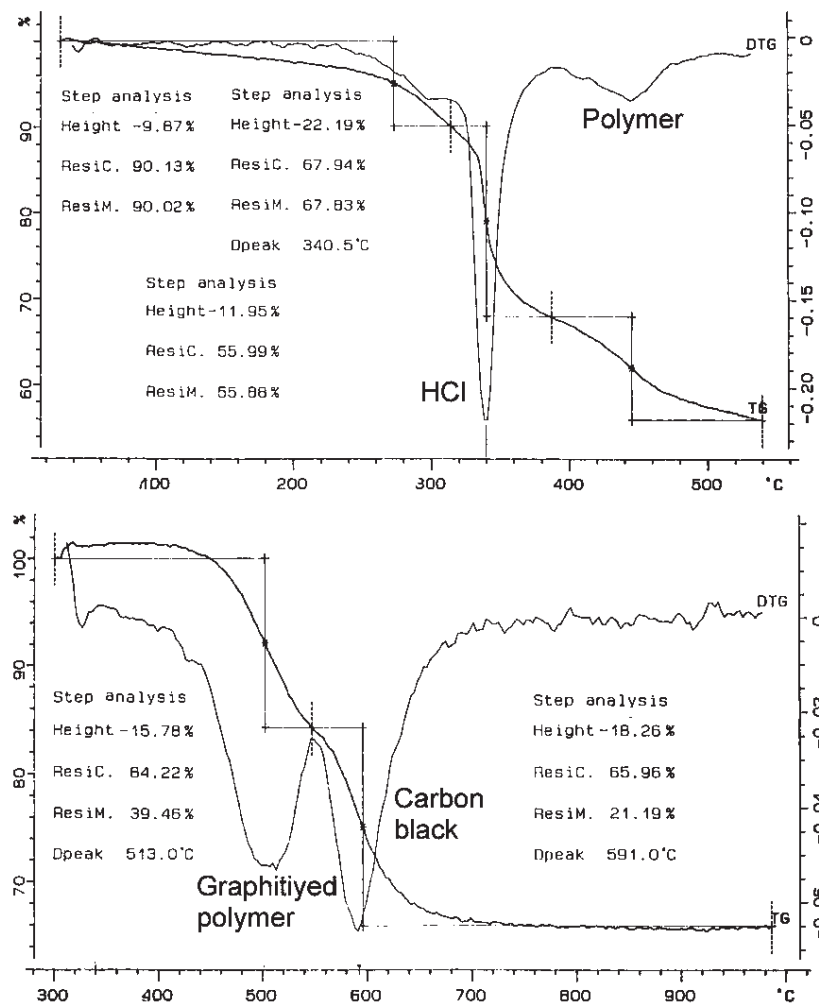

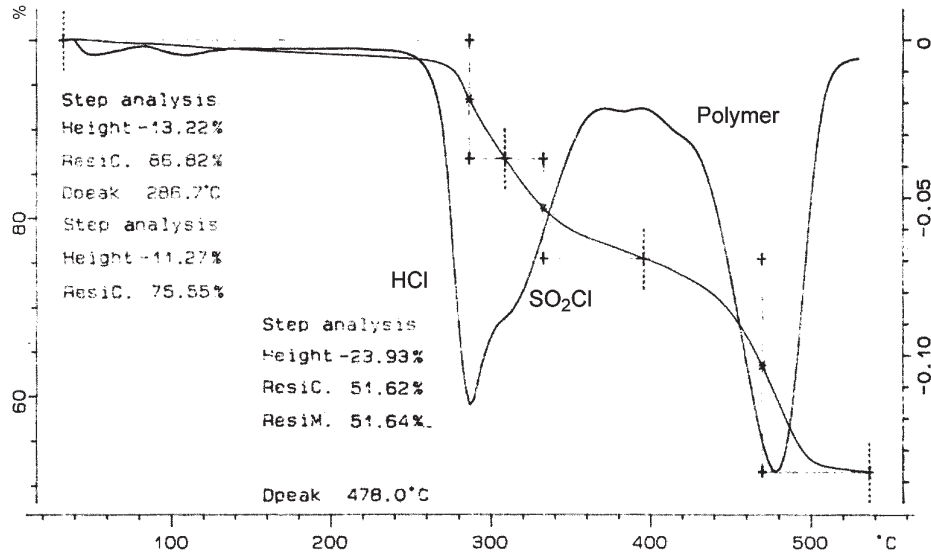**Fig. 7** TG and DTG of chloroprene rubber

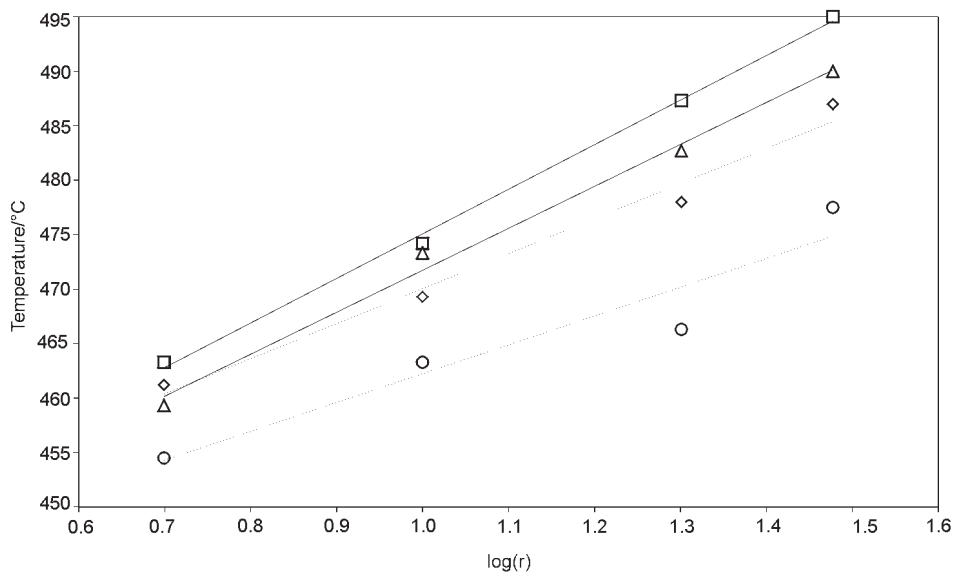**Fig. 8** TG and DTG of chlorosulfonyl poly(ethylene) rubber

Fig. 9 T_d vs. log(r) for the mixtures corresponding to the third group. □ – EPDM(1), Δ – EPDM(2), ◇ – CSM, o – NBR

the giving off of HCl while heating. The loss of HCl can be detected in the derived curve as a sharp peak (Fig. 7).

Concerning the third group (NBR, EPDM, SBR and CSM) only the chlorosulfonyl poly(ethylene) can be distinguished from the others observing its decomposition profile (Fig. 8). As stated above for CR, having CSM rubbers chlorine atoms attached to its carbon backbone structure, a giving off of HCl occurs. Besides, for this specific kind of polymer it can be observed as well, a decomposition peak due to the sulfonyl chloride formation, which is thermally favored.

Within another group of experiments, the evolution of the decomposition temperature (T_d) while the heating rate (r) varies was studied in order to check if further information on the polymer can be obtained. The results obtained showed an increase of T_d with an asymptotic tendency as the heating rate goes faster. In Fig. 9 it can be noticed that within the third group, except for the mixtures containing EPDM, all the rest have approximately the same slope value. The fact that EPDM rubber mixtures give rise to a significant different slope value has been statistically proved using a double hypothesis test.

The fact that T_d *vs.* log(r) gives rise to a straight line, the Ozawa method has been applied in order to find out if such a difference in the slope value is due to differences in the activation energy (E_a). This methodology has only been tested previously with differential scanning calorimetry (DSC) data, and it consists of checking if Eq. (2) rectifies.

$$\ln(r) = a - \frac{E_a}{R} \frac{1}{T_d} \qquad (2)$$

where r – heating rate, a – constant value, E_a – activation energy, R – gas constant, T_d – decomposition temperature.

The regression for all the mixtures has been calculated and a first estimation of the activation energy of the decomposition has been obtained (Table 3).

Table 3 E_a for several elastomers calculated by the Ozawa method

Elastomer	Activation energy/J mol^{-1}
EPDM(1)	−1601
EPDM(2)	−1549
CR	−1991
NBR	−1922
NR	−1207
CSM	−1880

Conclusions

In this paper, TG analysis has been shown as an easy and rapid way to determine the polymer type in a rubber formulation. This technique allows the identification of NR,

CR, CSM, EPDM and, NBR and SBR. The analysis of the last two rubbers will require to be complemented by other analytical techniques for its specific identification such as FTIR [16] or pyrolisis-gaschromatography. The detection of acrilonitrile or styrene in the pyrograms will determine if the type of polymer is NBR or SBR respectively [15]. Concerning the EPDM rubbers, it has been shown that the different behavior of its decomposition *vs.* temperature rate is the parameter that identifies the type of elastomer within the mixture.

Quantification of the polymer content has been described for the most commonly used elastomers. TG turned out to be the fastest analytical technique to obtain a rather complete information about rubber formulations.

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