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IDENTIFICATION OF NR AND IR IN BLENDS OF BR AND SBR BY THERMAL ANALYSIS

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ABSTRACT

NR or IR can be distinguished in blends of BR or SBR by their DSC exotherm area and DTG peak height ratio. Exotherm areas are additive for blends of NR and less than additive for those of IR. As a result, only those blends where NR or IR are the major components can be characterized.

INTRODUCTION

A method for the identification of natural rubber (NR) and synthetic polyisoprene (IR) in vulcanizates has recently been published[1]. The method is based upon the higher DSC exotherm area and double DTG peaks for IR. This was attributed to a higher level of cyclization in the synthetic product, which probably arises as a result of catalysis by residual inorganic material present therein. This cyclized material decomposes at a higher temperature, giving rise to the second DTG peak. The purpose of the present work is to extend the method to blends of NR or IR with BR or SBR. BR and SBR also undergo exothermic cyclization, the area of which is proportional to the amount of butadiene in the compound[2]. It was surmised that the exotherm area of these blends will be higher with IR than NR. Since blends rather than the single elastomers are being increasingly used in industrial products, their identification is of considerable practical interest.

EXPERIMENTAL

The experimental technique is exactly the same as described previously. A Du Pont 900 console fitted with a DSC module was used to obtain the DSC curves[1]. As before, the exotherm area in cm^2 per mg polymer was used without conversion to heat of reaction. For unknown samples, the total polymer was determined from the TG curve, the temperature for onset of decomposition (320–340 °C) being determined from the DTG curve.

The thermogravimetric (TG) and derivative thermogravimetric (DTG) apparatus have been described previously[3].

The elastomer samples, as well as vulcanizing ingredients, were of technical grade and used as received. The following grades were used: IR (Natsyn 2200), NR (AMA-7), BR (Ameripol CB-441), and SBR 1712. The basic recipe had polymer: 100, carbon black (N375): 50, zinc oxide: 5, stearic acid: 3, sulfur: 2.5, and MBTS: 0.6. A cure time of 30 min at 145 °C was used for all the vulcanizates.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of the vulcanized compounds studied. It may be observed that the peak temperature for IR is considerably lower than the other three elastomers and that the exotherm area per mg polymer follows the order of OE-BR (6.60 cm^2), OE-SBR (3.85 cm^2), IR (3.35 cm^2), and NR (0.85 cm^2). Exotherm areas compare very well with published values[1-4]. Based on 40 tests with IR (Natsyn 2200), the 95% confidence limits were ± 7% for individual tests and ± 3% for com-

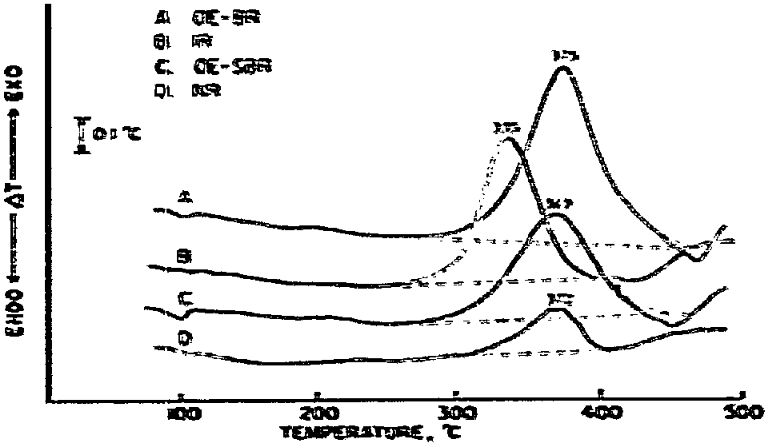

Fig. 1. DSC curves of NR, OE-SBR, IR, and OE-BR vulcanizates (A, 6.27 mg; B, 7.21 mg; C, 5.05 mg; D, 7.41 mg).

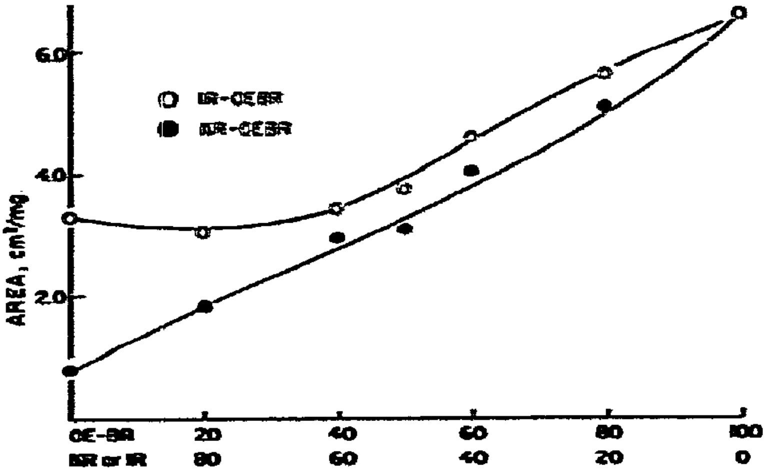

Fig. 2. Effect of NR or IR on the exotherm area of OE-BR vulcanizates.

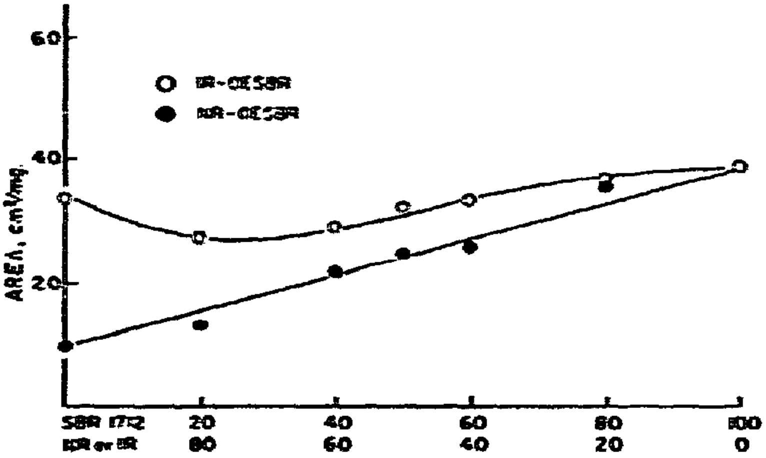

Fig. 3. Effect of NR or IR on the exotherm area of OE-SBR vulcanizates.

TABLE I

EXOTHERM AREAS FOR NR/OE-SBR AND IR/OE-SBR BLENDS

Polymers	Ratio	Exotherm actual	Area, cm² calculated additive
NR		0.55	
NR/OE-SBR	20:80	3.52	3.25
NR/OE-SBR	40:60	2.61	2.65
NR/OE-SBR	50:50	2.48	2.35
NR/OE-SBR	60:40	2.18	2.05
NR/OE-SBR	80:20	1.30	1.45
OE-SBR		3.85	
IR		3.35	
IR/OE-SBR	20:80	3.65	3.75
IR/OE-SBR	40:60	3.35	3.65
IR/OE-SBR	50:50	3.22	3.60
IR/OE-SBR	60:40	2.91	3.55
IR/OE-SBR	80:20	2.74	3.45

puted average of five tests. The effects of different compounding ingredients has been reported before[1]. Within the range of technical recipes (sulfur, 1.75–2.75; carbon black, 30–75), variation of the different ingredients has minimal effect.

Figure 2 shows the effect of dilution of OE-BR with either NR or IR. Corresponding curves for OE-SBR are presented in Fig. 3. It may be observed that whereas the exotherm area of blends of NR with either BR or SBR follows a more or less linear curve with composition, those for IR do not. IR does not act completely as a diluent as the exotherm areas are slightly higher than for BR or SBR alone, but much lower than the additive value. This may be due to the fact that IR has a relatively big endotherm around 410–420 °C (Fig. 1) which negates the gain to the BR or SBR

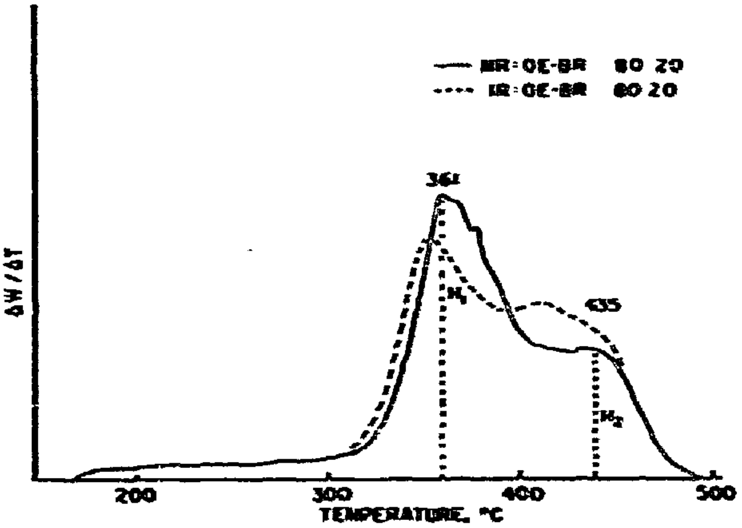

Fig. 4. DTG curves of NR/OE-BR and IR/OE-BR blends (——— 9.55 mg; ----- 9.95 mg).

exotherm. The lower peak temperature for IR may also have an adverse effect on the exotherm area. On the other hand, NR endotherm is very small and its peak temperature is about the same as BR or SBR, so the exotherm areas are about equal to the additive value. This is illustrated in Table I for NR/OE-SBR and IR/OE-SBR, where both calculated additive and actual experimental values are presented. The approximate additive value for NR/OE-BR or NR/OE-SBR systems indicates nonintervention of cyclization or cross-linking reactions, probably by formation of cross-bonds of two polymers.

As a result of the different behavior of IR and NR, the large difference in exotherm areas of these polymers is minimized in the blends studied, although NR blends still have much lower exotherm areas. It is apparent from Figs. 2 and 3 and Table I that NR and IR can be positively distinguished in these blends by their exotherm areas when IR or NR composition is 40% or above. Also, the peak temperature for IR blends in this range is normally below 360 °C as compared to 370 °C or higher for NR blends. However, peak temperature can serve only as an indication, as it varies with composition.

DTG curves also provide some help in distinguishing NR and IR where these polymers are the major components in the blend. This is exemplified in Fig. 4 for the 80 parts NR or IR, 20 parts OE-BR blends. The peak height ratio H_1/H_2 is 2.18 for NR-BR as compared to 1.40 for IR-BR compound. For compositions lower than 60% IR or NR, the peak height ratios are very similar. At these compositions, the characteristic second peak for IR (420–430 °C) merges with the BR or SBR peaks and so is indistinguishable.

TG curves do not show any characteristic difference, but are necessary for unknown samples in order to calculate the amount of polymer so that the area/mg polymer can be evaluated.

Characterization of BR or SBR in these blends poses no problem, due to large differences in exotherm area, glass transition temperature, and DTG peak temperatures[3]. When this is known, the thermographs will not only identify NR or IR but also will provide an approximate idea of the ratio of the polymers from the exotherm area, with the limitations mentioned above.

CONCLUSION

IR and NR can be distinguished in a blend of either BR or SBR if the polyisoprenes constitute more than 40% of the total polymer.

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