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IDENTIFICATION OF ELASTOMER BLENDS BY THERMAL ANALYSIS

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ABSTRACT

Identification of a number of commercial polyblends as well as vulcanized elastomer blends has been studied by differential scanning calorimetry (DSC) in nitrogen and oxygen between 0°C and 500°C. The raw blends included are PVC–NBR and ABS resin. The vulcanized elastomer blends studied are EPDM–BR, –SBR, or –NR; chlorobutyl–BR, –SBR, or –NR; CR–NR, –BR, or –SBR; and NR–BR, –SBR. DSC patterns for degradation are retained in the blend and polymeric constituents can be identified from their thermographs in most cases.

INTRODUCTION

Identification of raw and vulcanized elastomers by differential scanning calorimetry (DSC) has been reported recently[1]. It was shown that thermographs obtained for degradation of elastomers in nitrogen (thermal degradation) and oxygen (thermo-oxidative degradation) can serve as "fingerprints" for identification of the polymeric constituents. In view of the recent interest in vulcanizates prepared from blends of elastomers, we extended this method to industrially important elastomer blends.

EXPERIMENTAL

A DuPont 900 console fitted with a DSC module was used. Details of the experimental methods have been described earlier[1]. Thermographs were recorded between 0 and 500°C in a stream of nitrogen or oxygen at 0.2 liter per minute. A heating rate of 10°C $\min^{-1}$ was employed.

The following raw polymers were studied: blend of PVC and NBR: Paracril OZO, a 50/50 coprecipitated latex blend of NBR and PVC, Uniroyal Chemical Co.; acrylonitrile–butadiene–styrene copolymer: Abson–ABS resin, B. F. Goodrich Chemical Co.

The elastomers used were of technical grade and have been previously described[1]. The basic recipe for vulcanized elastomers is rubber, 100; black, 60; PBNA*, 1; stearic acid, 1.5; Circosol 4240**, 7.5; zinc oxide, 5; sulfur, 1.8; Santocure***, 1.5.

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*Phenyl-β-naphthylamine.

**Naphthenic oil, Sun Oil Co.

***N-cyclohexyl-2-benzothiazole sulfenamide.

Blends have a 50/50 ratio of the elastomers mentioned. Some adjustment of the above recipe was made in the case of special elastomers in order to have a comparable degree of cure.

RESULTS AND DISCUSSION

Raw polymers

Nitrogen thermographs are given in Fig. 1 for Paracril OZO, a commercially available PVC–NBR blend, and for a laboratory mixed 50/50 blend of PVC and NBR. Apart from slight differences in peak temperatures, the thermographs have identical features and could almost be synthesized by combining those of the component polymers[1]. This shows that the individual characteristics of the component polymers are retained in the thermographs of the blend.

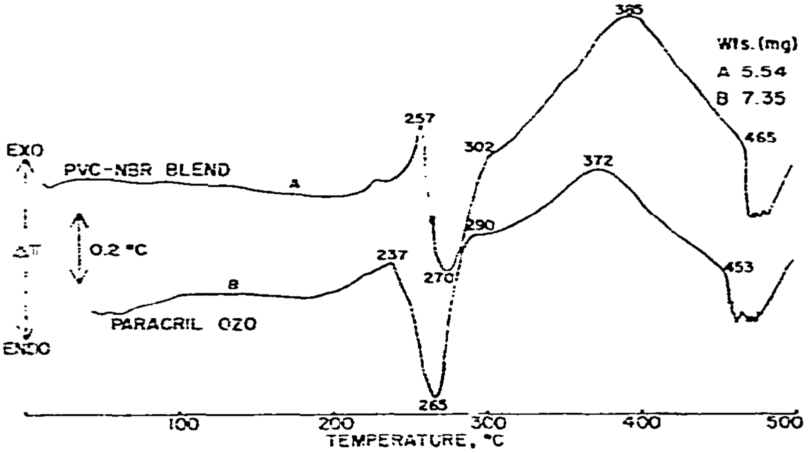

Fig. 1. Thermographs of PVC–NBR blends in nitrogen.

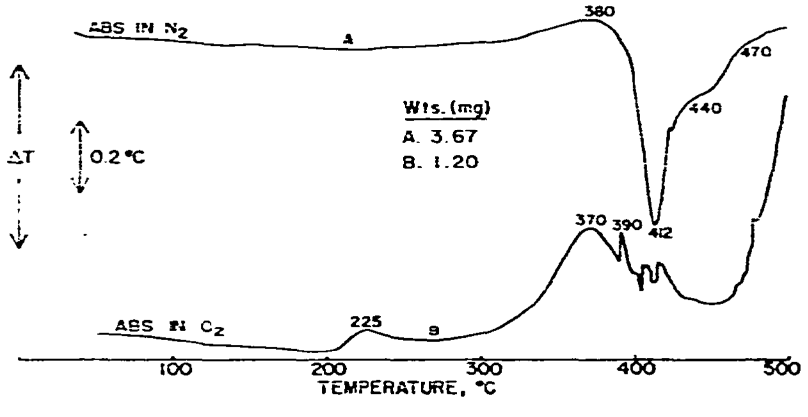

Fig. 2. Thermographs of ABS resin.

Nitrogen and oxygen thermographs of an ABS resin are shown in Fig. 2. The prominent feature in the thermograph for ABS degradation in nitrogen is a sharp endotherm at 412°C, arising from styrene depolymerization[1]. The butadiene cyclization exotherm peak is quite shallow and occurs at 380°C; the breaks at 440 and 470°C show the endotherm for butadiene decomposition[1] around 450°C superimposed on the styrene transition. These results are in agreement with the DTA thermographs recently published by Yamagami et al.[2]. The oxygen thermograph for ABS shows features characteristic of SBR and NBR (exotherms around 225°C and 370°C).

Vulcanized elastomer blends

A number of technically important vulcanized elastomer blends were selected for study. All blends contained a 60 phr loading of N-347 black. The compounding ingredients used did not significantly affect the shape of the thermographs, which is in agreement with previous observations[3].

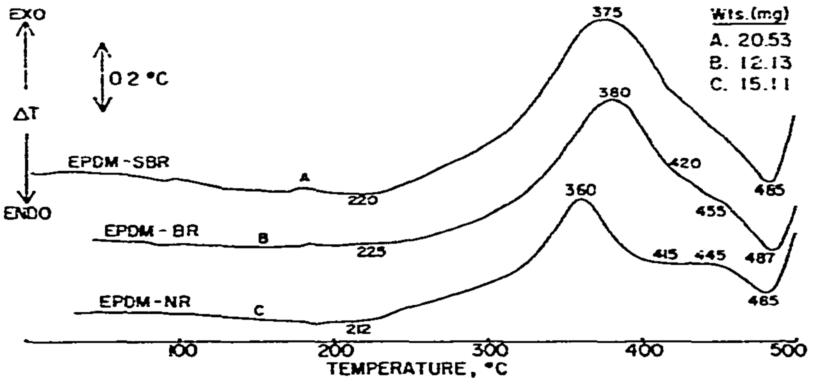

Fig. 3. Thermographs for vulcanized blends of EPDM with BR, SBR, and NR in nitrogen.

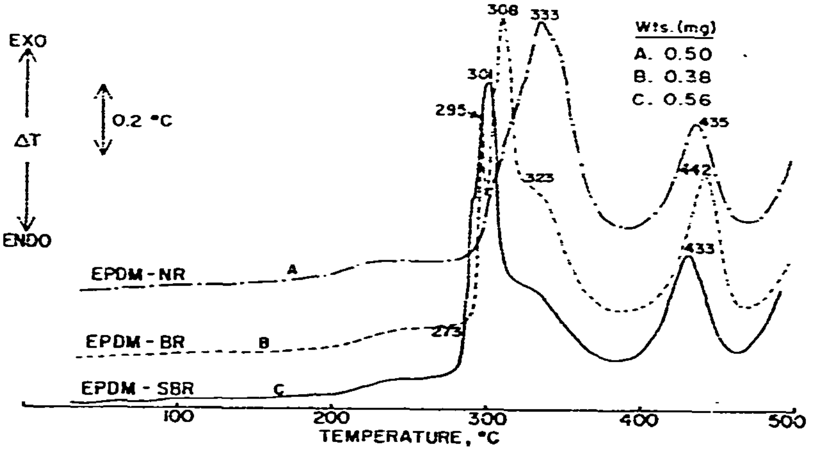

Fig. 4. Thermographs for vulcanized blends of EPDM with BR, SBR, and NR in oxygen.

Figures 3 and 4 show thermographs for blends of EPDM with BR, SBR, or NR in nitrogen and oxygen, respectively. The nitrogen thermographs exhibit features expected of the individual polymers: the exotherms for BR and SBR occur around 380 °C (but are not as sharp due to dilution by EPDM); the NR peak occurs at 360 °C and encloses a smaller area; and the endothermic decomposition peak at 485 °C (characteristic of EPDM[1]) is seen in all cases. In the region between these exo- and endotherms, there are discontinuities corresponding to differences in the catastrophic breakdown of the component polymers. Such differences distinguish the blend with NR from those with BR or SBR.

Because of the superposition of exothermic oxidation reaction on the already complex thermal degradation patterns of the blends, the thermographs in oxygen are much more complex and defy immediate interpretation. However, the NR–EPDM blend can be easily distinguished from the other two from the shape and position of the exotherm at 333 °C (Fig. 4).

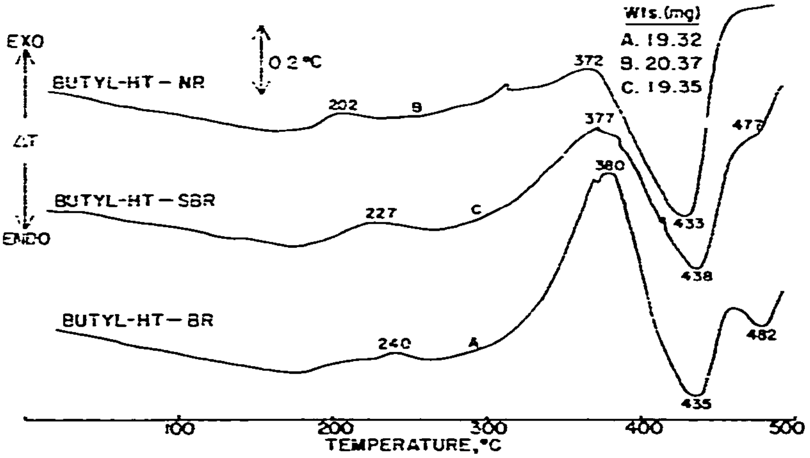

Fig. 5. Thermographs for vulcanized blends of chlorobutyl with BR, SBR, and NR in nitrogen.

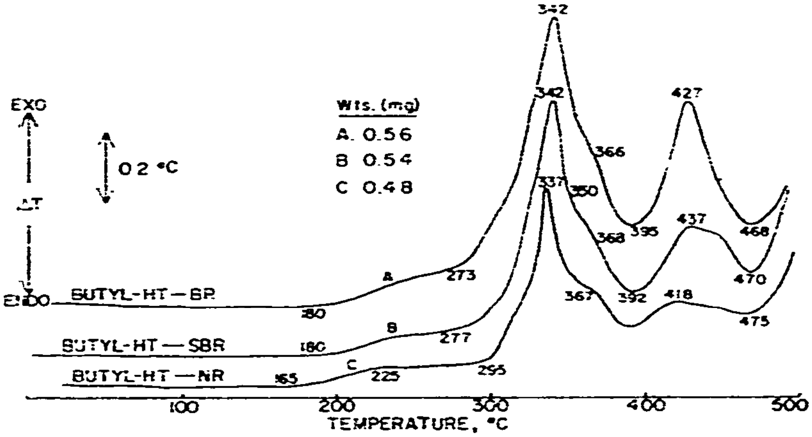

Fig. 6. Thermographs for vulcanized blends of chlorobutyl with BR, SBR, and NR in oxygen.

Figures 5 and 6 represent similar thermographs for the blends of chlorobutyl rubber with either BR, SBR, or NR. Chlorobutyl has been used instead of butyl to ensure comparative cures for both components. This would not change the thermographs significantly since butyl and chlorobutyl have very similar degradation patterns[1]. Again, the characteristic features of the individual elastomers are visible in nitrogen thermographs of the blends. The thermographs show exotherms for NR, BR and SBR around 202, 225 and 240 °C, respectively, exotherms for BR and SBR around 375 °C and the endothermic decomposition for chlorobutyl at about 435 °C. The exotherm for NR is rather small and peaks around 370 °C. In addition, the blend with BR shows a separate endotherm (peak 482 °C), corresponding to degradation and volatilization of BR. In the case of blends with SBR, this shows up only as a slight inflection and, of course, no effect is observed in blends with NR. Thermographs in oxygen show a sharp peak at 427 °C for blends with BR and less distinct peaks for the blend with SBR or NR in addition to the common exothermic peak around 340 °C (characteristic of chlorobutyl).

Vulcanized SBR–BR and NBR–BR blends have been discussed in separate communications[3,4]. Figure 7 shows the thermographs obtained on heating the blend of NR with either BR or SBR in both nitrogen and oxygen. Both exothermic and endothermic reactions are observed when NR is degraded in nitrogen[1]; however, the peaks for NR are quite small and, thus, the thermographs of the blends are very similar to those of the BR or SBR component except that a slanted base line and somewhat irregular curves are often observed (see NR–SBR). The presence of NR is also indicated by a lower initiation temperature for the exotherm (160–180 °C as against 230–250 °C for BR or SBR alone) and often a slight inflection at the early stage indicating a two-stage reaction.

The oxygen thermographs for both blends have a peak around 380 °C, characteristic of BR or SBR and a peak around 245 °C or lower, characteristic of BR, SBR, NR, or IR.

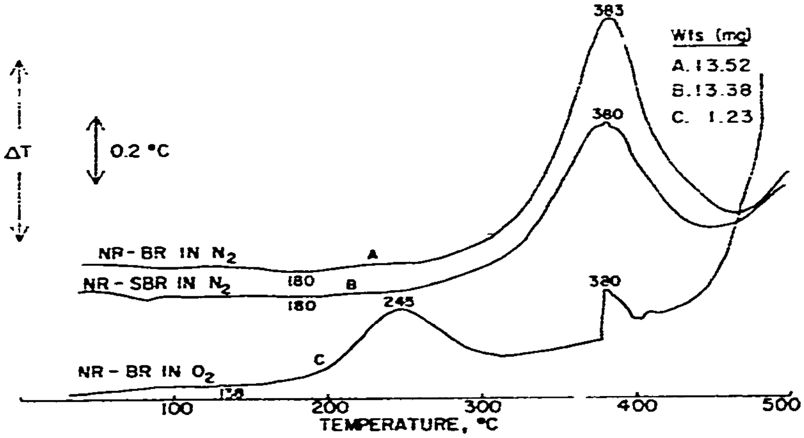

Fig. 7. Thermographs for vulcanized blends of NR with BR and SBR.

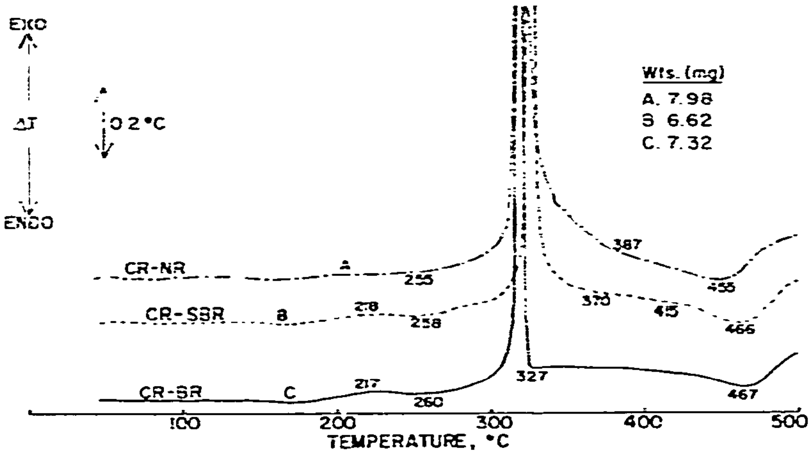

Fig. 8. Thermographs for vulcanized blends of CR with NR, BR, and SBR.

Nitrogen thermographs are given in Fig. 8 for blends of CR with BR, SBR, or NR. The prominent feature of these thermographs is the very sharp CR exotherm at 320°C, which is attributed to the sulfidation of CR[1]. Blends with either BR or SBR have, in addition, a relatively flat exotherm at around 220°C. The CR exotherm in CR–BR blends drops very sharply and ends at 327°C, while the same for the CR–SBR blend drops somewhat slower and ends at 370°C. The slope of the high temperature end of the CR exotherm in CR–NR blends is considerably less steep than of the other two blends. All the blends show high-temperature (around 460°C) endotherms for decomposition of BR, SBR, and NR. In contrast to the other two, the NR endotherm occurs at a slightly lower temperature and the line joining the CR exotherm to the endotherm forms a smooth curve. The oxygen thermographs show a prominent CR exotherm around 310–320°C, and only minor differences for the other components. (The oxygen thermographs have not been included.)

CONCLUSION

Results of this investigation show that DSC patterns for degradation of the component elastomers are retained in the blend. From the nature and location of the DSC peaks in nitrogen and oxygen, an idea about the nature of the component elastomers may be obtained in the cases studied. Such studies may be of considerable help in the preliminary identification of many industrially important elastomer blends.

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4 A. K. Sircar and T. G. Lamond, "Estimation of butadiene in vulcanized NBR and blends by thermographic analysis", to be published.