

## Note

**DIFFERENTIATION OF NATURAL AND SYNTHETIC  
POLYISOPRENES BY DIFFERENTIAL SCANNING CALORIMETRY**

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Recently, thermoanalytical techniques have been used to distinguish between natural rubber (NR) and synthetic *cis*-1,4-polyisoprene (IR). It was observed that vulcanizates of NR and IR had different DSC and DTG curves in an atmosphere of nitrogen [1–3]. In addition, the heat of thermal degradation of IR vulcanizate was larger than that of the NR vulcanizate [1,2]. These differences were attributed to the higher level of cyclization caused by the polymerization catalyst residues in IR [1,2]. These techniques were also used to distinguish NR and IR in blends of butadiene rubber and styrene–butadiene rubber [4]. Similarly, the vulcanizates of natural and synthetic *trans*-1,4-polyisoprenes could be distinguished from one another by their DSC and DTG curves [1]. However, unvulcanized NR and IR had the same DTG curve in an atmosphere of nitrogen [1,2]. The heat of thermal degradation of unvulcanized NR and IR could not be determined by DSC because of the evolution of volatiles during thermal degradation [2]. Therefore unvulcanized NR and IR cannot be distinguished by these techniques. This communication reports that as a result of the different oxidative stability of various unvulcanized polyisoprenes they can be distinguished by their DSC curves in an atmosphere of oxygen.

## EXPERIMENTAL

The following rubbers were used: natural rubber (pale crepe grade), synthetic *cis*-1,4-polyisoprene (Natsyn 2200, Goodyear), natural *trans*-1,4-polyisoprene (gutta percha) and synthetic *trans*-1,4-polyisoprene (*Trans*-PIP 100, Polysar).

A Perkin-Elmer DSC-1B differential scanning calorimeter was used. The instrument was calibrated according to the manufacturer's operating manual. The instrument was purged with oxygen at a flow rate of 20 ml min<sup>-1</sup>. A heating rate of 16 K min<sup>-1</sup> was used.

To prepare samples for DSC tests, the rubber was dissolved in benzene to make a 2% solution. A droplet of the solution was placed in the sample pan and allowed to dry. Each sample weighed between 0.6 and 0.7 mg. Because of the high dirt content of the gutta percha sample, the solution was filtered before use.

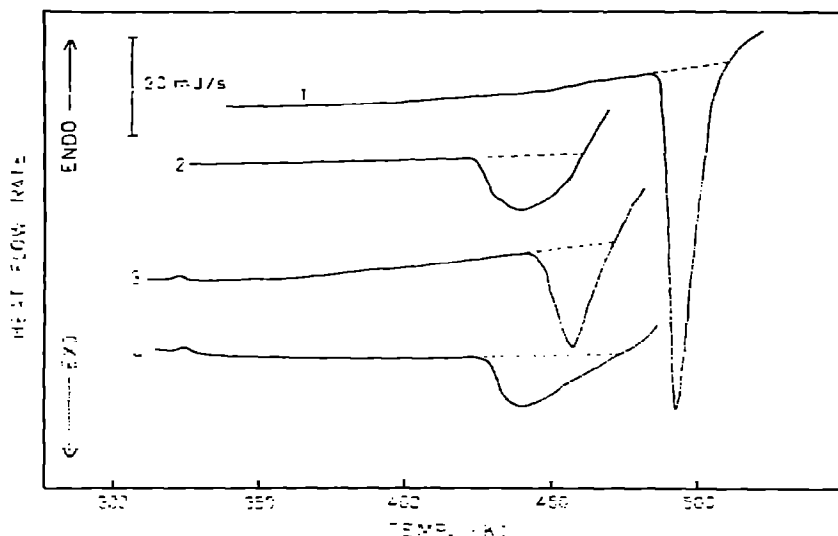


Fig. 1. DSC curves of various polyisoprenes. Curve 1, Natural rubber (sample weight: 0.74 mg); curve 2, Natsyn 2200 (sample weight: 0.62 mg); curve 3 gutta percha (sample weight: 0.68 mg); curve 4, *Trans*-PIP 100 (sample weight: 0.68 mg).

The area of the oxidation exotherm was determined using the cut and weighed method. Since the DSC curve does not return to the original baseline after the appearance of the exotherm, the area measured was based on the extrapolation of the low temperature baseline as shown in Fig. 1. The reported heat of oxidation was based on the average of eight runs with an average deviation of about 3–4%.

## RESULTS AND DISCUSSION

The DSC curves of various raw polyisoprenes are shown in Fig. 1. Natural rubber shows a sharp and narrow oxidation exotherm at 493 K, while its synthetic counterpart shows a broader exotherm at 440 K. The position of the oxidation exotherm of NR is in good agreement with that previously reported by Sircar and Lamond [5]. The better oxidative stability of NR is due to the natural antioxidants in the raw NR. Removal of the natural antioxidants in NR by acetone extraction gave rise to a broader oxidation exotherm at lower temperatures [6]. The inferior oxidative stability of IR is due to the presence of the polymerization catalyst residues. The catalytic effects of metallic ions on the oxidation of rubbers are well known [7–11].

The heats of oxidation of NR and IR are  $2680 \text{ J g}^{-1}$  and  $1535 \text{ J g}^{-1}$ , respectively. This is in contrast to the larger heat of thermal degradation of IR than NR [1,2]. The heat of oxidation of NR obtained in this work is larger than the value of  $728 \text{ J g}^{-1}$  for purified NR recently reported by Ponce-Velez and Campos-Lopez [12]. The difference is mainly due to the

different sample size and sample preparation used in these studies. Because of the low thermal conductivity of rubbers, good contact between rubber sample and sample pan is essential in order to obtain reproducible DSC results [13]. Therefore large sample size and improper contact between rubber and sample pan will lead to a disproportionately smaller exotherm. In the present work, small sample size and the use of the solution casting method to prepare the DSC sample ensure good contact between rubber and sample pan, which in turn produce a sharper and larger oxidation exotherm.

The DSC curves of the *trans*-1,4-polyisoprenes are characterized by their melting endotherms around 323 K. Similar to the *cis*-1,4-polyisoprenes, the natural *trans*-1,4-polyisoprene has a better oxidative stability than its synthetic counterpart. Gutta percha shows an oxidation exotherm at 457 K, while *Trans*-PIP 100 shows a broader exotherm at 440 K. The heats of oxidation of gutta percha and *Trans*-PIP 100 are  $1585 \text{ J g}^{-1}$  and  $1510 \text{ J g}^{-1}$ , respectively.

In conclusion, the different oxidative stabilities of various polyisoprenes provide a convenient means of differentiating them by DSC.

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