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Note

THERMOANALYTICAL STUDIES OF RUBBER OXIDATION: CHARACTERIZATION OF NITRILE RUBBERS

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Thermoanalytical techniques such as DSC, DTA, TG and DTG are used to characterize rubbers [1–3]. The thermal degradation and oxidative degradation characteristics of rubbers, as shown by DSC, are useful in the identification of many rubbers.

Nitrile rubbers (NBR) are copolymers of butadiene and acrylonitrile. Commercial NBR samples usually contain 20–50% acrylonitrile. The resistance to hydrocarbons, abrasion and gas permeation of NBR improves with increasing acrylonitrile content of the rubber. Sircar and Lamond [4] used various thermoanalytical techniques to analyze NBR vulcanizates. They found that the heat of thermal degradation of NBR in a nitrogen atmosphere was virtually independent of the acrylonitrile content and various NBR samples could not be distinguished from one another by DSC alone. This communication reports that the different oxidation characteristics of NBR samples enable the use of DSC to estimate the acrylonitrile content of NBR.

EXPERIMENTAL

Three NBR samples containing 21, 33 and 41% of acrylonitrile were obtained from Scientific Polymer Products, Inc. Another NBR sample (Chemigum N-206, 45% acrylonitrile) was obtained from Goodyear. The NBR samples were purified by precipitation from 2-butanone solutions by methanol. The four samples are designated as NBR21, NBR33, NBR41 and NBR45 in the following discussion.

To prepare samples for DSC tests, purified NBR was dissolved in 2-butanone to make a 1% solution. Droplets of the solution were then placed in the DSC sample pan and allowed to dry in a vacuum oven at room temperature.

A Perkin-Elmer DSC-4 differential scanning calorimeter was used. The instrument was purged with oxygen at a flow rate of 50 ml min^{-1}. The heat

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of oxidation was based on the average of five runs using a heating rate of 20 K min^{-1}. The activation energy of oxidation (E_a) was calculated using the oxidation exotherm peak temperatures (T_p) at five heating rates (5, 10, 20, 40 and 60 K min^{-1}) by means of Kissinger's method [5], as described previously [6,7]. Isothermal studies were conducted at 410 K and the time required for the appearance of the first exotherm was taken as the induction time.

RESULTS AND DISCUSSION

The DSC curves of the four NBR samples in an oxygen atmosphere are shown in Fig. 1. Each sample shows three exotherms: a rather sharp exotherm followed by two broad exotherms. Each sample also shows a drastic drop in heat capacity around 720 K. The oxidation behavior of the NBR samples is in agreement with the general observation that diene rubber shows an oxidation exotherm around 473 K and a second bigger exotherm at a higher temperature followed by burning [3].

The first exotherm of the NBR sample is reproducible but not the second and the third exotherms. Sircar and Lamond [8] reported that the first oxidation exotherm of natural rubber was reproducible but not the subsequent exotherms. The good reproducibility of the first oxidation exotherm of natural rubber was also confirmed by Goh [6,7].

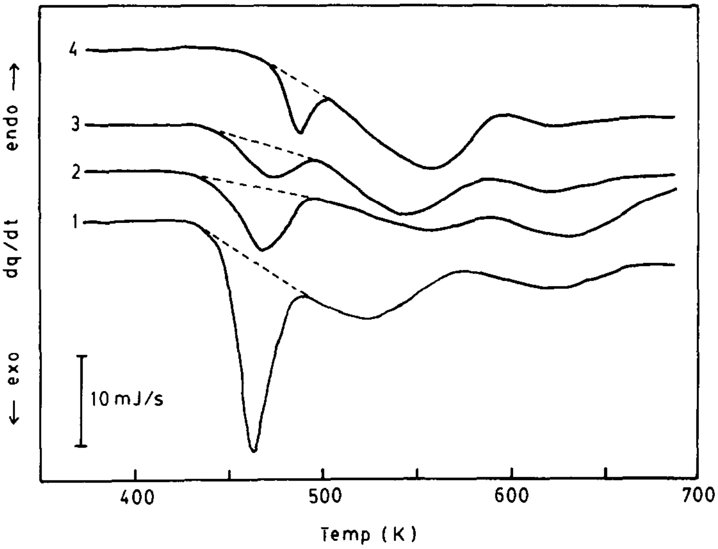

Fig. 1. DSC curves of NBR samples. (1) NBR21 (0.56 mg); (2) NBR33 (0.36 mg); (3) NBR41 (0.52 mg); (4) NBR45 (0.69 mg).

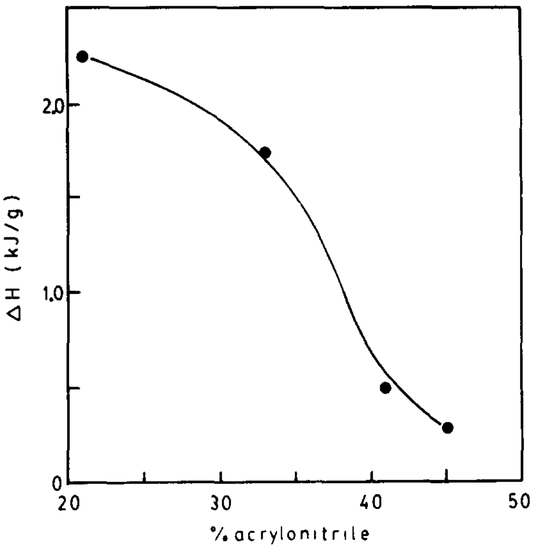

Fig. 2. Heat of oxidation of NBR

TABLE 1

Heat of oxidation (ΔH), activation energy of oxidation (E_a) and isothermal induction time (t_i) of NBR

	ΔH (kJ g^{-1})	E_a (kJ mol^{-1}) [a]	t_i (min)
NBR21	2.24 ± 0.03	82 ($r = -0.990$)	11
NBR33	1.74 ± 0.09	83 ($r = -0.996$)	15
NBR41	0.50 ± 0.02	98 ($r = -0.993$)	35
NBR45	0.29 ± 0.03	100 ($r = -0.997$)	82

[a] r is the correlation coefficient of the Kissinger plot.

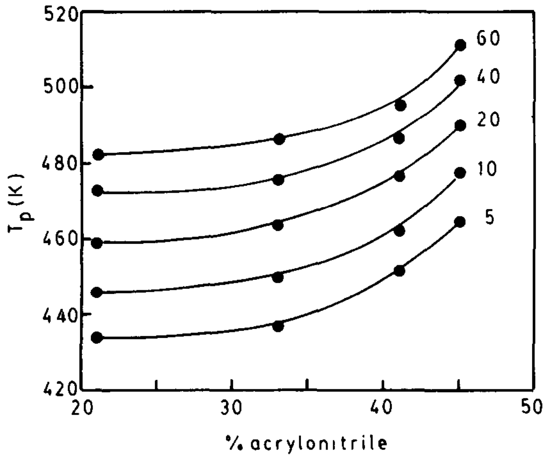

Fig. 3. Effect of heating rate on oxidation peak temperature (T_p) of NBR. Number denotes heating rate in K min^{-1}.

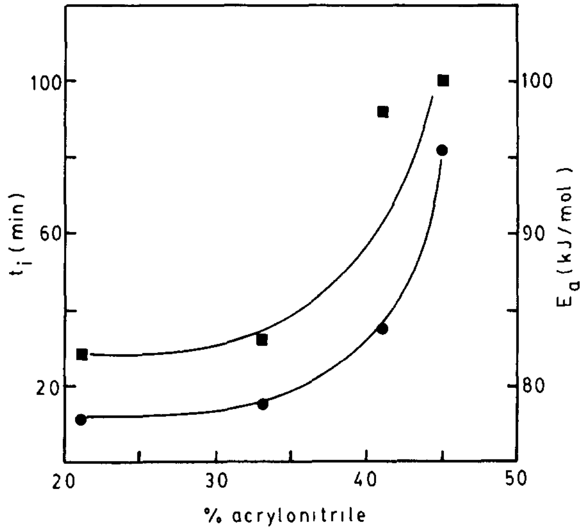

Fig. 4. Activation energy of oxidation (■) and isothermal induction time (●) of NBR.

It is apparent from Fig. 1 that the position and size of the first exotherm depends on the acrylonitrile content of NBR. As shown in Fig. 2 and Table 1, there is a significant decrease in the heat of oxidation when the acrylonitrile content increases from 21 to 41%. This is in contrast with the previous report that the heat of thermal degradation of NBR is independent of the acrylonitrile content [4].

As shown in Fig. 3, the oxidation peak temperature increases with increasing acrylonitrile content. The increase in T_p is most noticeable when the acrylonitrile content increases from 33 to 45%. The activation energy of oxidation and the isothermal induction time were also found to increase with increasing acrylonitrile content as shown in Fig. 4 and Table 1, indicating the better oxidative stability of NBR with a higher acrylonitrile content.

The above results show that the first oxidation exotherm of NBR is useful in estimating the composition of the rubber. An increase in the acrylonitrile content is accompanied by a decrease in the heat of oxidation and an increase in the activation energy, oxidation peak temperature and isothermal induction time.

REFERENCES

1 D.W. Brazier, Rubber Chem. Technol., 53 (1980) 437.
2 J.J. Maurer, in E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981, Chap. 6.

3 A.K. Sircar, J. Sci. Ind. Res., 41 (1982) 536.
4 A.K. Sircar and T.G. Lamond, Rubber Chem. Technol., 51 (1978) 647.
5 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
6 S.H. Goh, J. Elastomers Plast., 9 (1977) 186.
7 S.H. Goh and K.W. Phang, Thermochim. Acta, 25 (1978) 109.
8 A.K. Sircar and T.G. Lamond, Rubber Chem. Technol., 45 (1972) 329.