Note

CHARACTERIZATION OF NATURAL RUBBER/POLYISOPRENE RUBBER BLENDS BY DIFFERENTIAL SCANNING CALORIMETRY

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Nearly every major rubber component in a tire is a blend of two or more rubbers [1]. Rubber blends are used to reduce production cost, facilitate fabrication and modify the final product performance. Thermoanalytical techniques such as DSC, TG and DTG have been used to identify rubbers in the blend [2-9]. Ghijsels and Mieras [10] used DSC to study the crystallization behavior of natural rubber (NR)/polyisoprene rubber (IR) blends. The results provided useful information about the effectiveness of blending. Sircar [11] determined the heat of thermal degradation of NR/IR blends with DSC.

In a previous communication [12], the differentiation between NR and IR from their DSC curves in oxygen atmosphere was described. A similar study was extended to NR/IR blends, hoping that the results might be useful in estimating the composition of the blends.

EXPERIMENTAL

The materials, experimental method and sample preparation are as described previously [12]. A Perkin-Elmer DSC-1B differential scanning calorimeter was used to obtain the DSC curves.

From the DSC curves in oxygen atmosphere, the oxidation exotherm peak temperature (T_p) and the heat of oxidation (ΔH_{ox}) of the sample were measured using a heating rate of 16 K min⁻¹. The activation energy of oxidation (E_a) was calculated using T_p values at different heating rates by means of Kissinger's method [13], as described previously [14,15]. For isothermal study, the sample was brought to 400 K and the time required for the appearance of the oxidation exotherm peak was taken as the induction period (t_i) .

RESULTS AND DISCUSSION

The DSC curves of NR, IR and various NR/IR blends scanned with a heating rate of 16 K min⁻¹ are shown in Figs. 1 and 2. The effect of blend composition on T_p , E_a , ΔH_{ox} and t_i are shown in Figs. 3 and 4 and are also given in Table 1.



Fig. 1. DSC curves of rubber samples. 1, IR (0.62 mg); 2, NR/IR(5/95) (0.63 mg); 3, NR/IR(10/90) (0.73 mg); 4, NR/IR(20/80) (0.61 mg); 5, NR/IR(33/67) (0.64 mg).

Fig. 2. DSC curves of rubber samples. 6, NR/IR(50/50) (0.69 mg); 7, NR/IR(67/33) (0.65 mg); 8, NR/IR(80/20) (0.65 mg); 9, NR (0.58 mg).

IR is characterized by a broad and shallow oxidation exotherm with a peak at 440 K while NR shows a sharp oxidation exotherm at 494 K. The blend shows a single oxidation exotherm positioned between 440 and 494 K, depending on the composition.



Fig. 3. Effect of blend composition on T_p and ΔH_{ox} .



Fig. 4. Effect of blend composition on E_a and t_i .

The addition of a small amount of NR to IR produced a significant effect on the shape and position of the oxidation exotherm, as shown in the DSC curve of the NR/IR(5/95) blend. On the other hand, the DSC curve of the NR/IR(80/20) blend was essentially the same as NR except that the exotherm appeared at a slightly lower temperature.

IR is also characterized by its lower $T_{\rm p}$, $E_{\rm a}$, $\Delta H_{\rm ox}$ and $t_{\rm i}$ as compared with NR, demonstrating the inferior oxidative stability of IR. By blending NR into IR, all four parameters were increased to higher values. The effect of blending on $T_{\rm p}$, $E_{\rm a}$ and $\Delta H_{\rm ox}$ is more pronounced at low NR to IR ratios. It appears that the shape of the oxidation exotherm as well as $T_{\rm p}$, $E_{\rm a}$ and $\Delta H_{\rm ox}$ of the blend can be used to estimate the composition of the blend if NR is the minor component. $t_{\rm i}$ appears to be a linear function of the amount of NR in the blend except at low NR levels; thus $t_{\rm i}$ is a better parameter for estimating the composition of the blend if NR is a major component. However, different calibration curves would be necessary for different sources of NR and IR in view of the report [11] that IR from different manufacturers has different heats of thermal degradation.

Blend	T_{p} (K)	E_{a} (kJ mole ⁻¹)	$\Delta H_{\rm ox}$ (kJ g ⁻¹)	t _i (min)
IR	440	67	1.54	10
NR/IR (5/95)	453	83	1.75	24
NR/IR (10/90)	461	88	2.04	54
NR/IR (20/80)	468	99	2.28	108
NR/IR (33/67)	477	102	2.45	195
NR/IR (50/50)	484	110	2.51	300
NR/IR (67/33)	488	112	2.60	375
NR/IR (80/20)	491	113	2.60	5 02
NR	494	118	2.68	600

TABLE 1 Effect of blend composition on T_p , E_a , $\triangle H_{ox}$ and t_i

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