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A new method for DTA measurement of enthalpy change during the pyrolysis of rubbers

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Abstract

A novel approach involving the use of DTA to measure quantitatively the enthalpy change during rubber atmospheric pyrolysis was developed and applied to tire rubbers: NR (natural rubber), SBR (styrene–butadiene rubber) and BR (butadiene rubber). Based on a new method of baseline determination, this approach detects precisely the overall enthalpy change during rubber pyrolysis, which consists of a linear heat capacity change, an exothermic peak and an endothermic peak. A mechanism study was carried out based on the simultaneous measurement of enthalpy and weight loss by TG/DTA. It revealed that the exothermic peak results from chemical reactions and that the endothermic peak is attributed to the evaporation of the pyrolysis products. The heats of reaction were determined to be -164, -560 and -906 kJ kg^{-1}, for NR, SBR and BR, respectively. The heat of vaporization varies between 170 and 200 kJ kg^{-1} which is very close to the values cited in the literature for hydrocarbons. The overall enthalpy change from 30°C to 510°C is endothermic and is 870, 550 and 325 kJ kg^{-1} for NR, SBR and BR, respectively. Using the theory of Borchardt and Daniels, the activation energies of the pyrolysis reactions were calculated to be 146, 133 and 158 kJ mol^{-1} for NR, SBR and BR, respectively.

Keywords: DTA; baseline; enthalpy; rubber; pyrolysis

1. Introduction

The enthalpy change which occurs during rubber pyrolysis consists of three parts: the heat capacity, the heat of reaction, and the heat of vaporization. Study of how the overall enthalpy as well as each of the three individual parts change with temperature

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provides an insight into the chemical and physical mechanisms involved during rubber pyrolysis. Most studies in the past dealt with either the specific heat capacities or the heat of reaction. To our knowledge, no investigation has been concerned with the heat of vaporization, or with the enthalpy change with respect to temperature (or time) over the entire pyrolysis temperature range.

Specific heat capacities of tire rubbers (NR, SBR and BR) have been determined for temperatures not involving pyrolysis reactions, usually between -50 to 150°C, using classical methods of calorimetrical measurement [1–3]. The heat of reaction has been investigated by thermal analysis techniques such as DTA (differential thermal analysis) and DSC (differential scanning calorimetry) [5–8]. Theoretically, DTA measures the overall enthalpy change as a function of temperature (or time) for the whole temperature range of measurements. In practice, however, the zero baseline of DTA measurement is difficult to determine, since it changes in shape and position with the experimental conditions. Without knowing the position of the baseline, it is impossible to determine the overall enthalpy change using DTA measurements. Up to now, DTA application was limited to the study of peaks on the DTA curves, for example to identify the endothermic or exothermic nature of chemical reactions, or to calculate the heat of reaction when the peak area is intensive. In this case, the baselines are constructed by connecting the initial and end points of the DTA peaks.

Sircar and Lamond [7] studied the heat of reaction during the decomposition of SBR (styrene–butadiene rubber) and BR (butadiene rubber) by DSC. An exothermic peak was reported in the temperature range of 300–450°C. Based on an assumed baseline, the exothermicity of BR was determined to be 945 kJ kg^{-1}, and the activation energy was estimated to be 134–146 kJ mol^{-1}. Brazier and Schwartz [5] calculated the heat releases during the pyrolysis of SBR and BR to be 660 and 880 kJ kg^{-1}, respectively. The heat of reaction during the NR (natural rubber) decomposition has been studied by DSC [6,9,10]. An exothermic peak at 372°C was reported. No result was reported concerning the exothermicity intensity.

In this work, a novel method of baseline determination is proposed for the enthalpy measurement using DTA. This method enables the determination of a baseline throughout the whole range of temperatures investigated. Based on the baseline, the overall enthalpy change during the pyrolysis of NR, SBR and BR was quantitatively determined, including the heat capacity, the heat of reaction and the heat of vaporization. Each of the three enthalpies was also determined individually after separation from the overall enthalpy change. The kinetic parameters of the rubber pyrolysis reactions were determined after calculation of the heat of reaction. This approach can help understand the chemical and physical mechanisms behind the enthalpy changes.

2. Experimental

The experimental apparatus used was a Seiko TG/DTA 220 which combines both TGA and DTA measurements. During the measurement, the heating rate was fixed at 10°C min^{-1} and the sweeping gas was high-purity N_2 at a flow rate of 100 ml min^{-1} under normal pressure conditions. Three types of tire rubbers were studied: NR (natural rubber), SBR (styrene–butadiene rubber) and BR (butadiene rubber). These vulcanized rubbers are the most commonly used elastomers in tire fabrication and were obtained from Goodyear Canada Inc. in Quebec City. The specimens were cut into small disks, with a diameter of 4 mm. The disk height varied between 0.5 and 3 mm, depending on the mass of sample required for a given test.

3. Result and discussion

Figure. 1 illustrates the enthalpy measurements during the SBR pyrolysis using DTA. Two DTA curves for the two SBR samples are shown with masses of 41.92 mg and 16.71 mg, respectively. The two curves both exhibit an exothermic peak at 378°C and an endothermic peak at 465°C, as already noted by Brazier and Schwartz [5] and Sircar and Lamond [7]. The previous studies involved a careful examination of the exothermic peak, including the peak area, as well as the possible chemical mechanisms involved. However, their DSC equipment would not allow experiments at high temperature. Therefore, the endothermic peak was not considered, nor was the enthalpy change in the overall temperature range of pyrolysis. In this work, an attempt has been made to determine the overall enthalpy change as a function of temperature over the complete pyrolysis conversion range, using a baseline throughout the whole temperature range of measurement. Then the three enthalpies, the heat capacity, the heat of reaction and the heat of vaporization, were seperated and determined.

3.1. Baseline determination

DTA is a useful instrument for performing enthalpy measurements. However, previous enthalpy studies using DTA failed to determine the overall enthalpy change

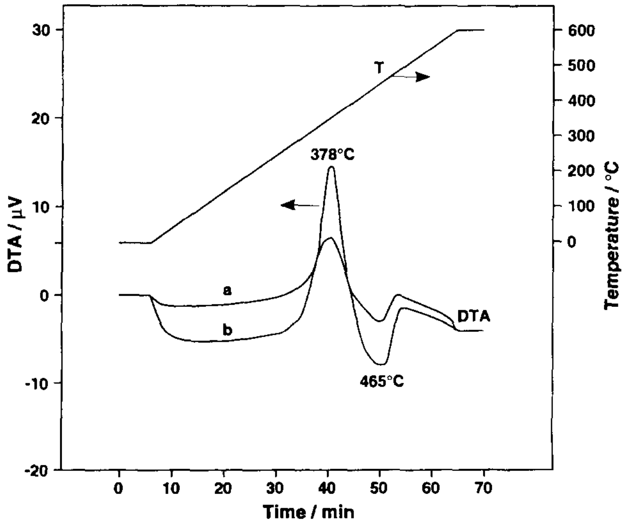

Fig. 1. DTA curves of SBR. Curve **a**, mass = 16.71 mg. Curve **b**, mass = 41.92 mg.

due to the difficulty of determining the baseline. Theoretically, the baseline of DTA measurements is the DTA trace measured with an empty pan (blank measurement), and is a straight line with respect to time. In practice, however, it is often a curve, due to the "instrument effect" of the DTA apparatus. The "instrument effect" produces an asymmetry of the heat transfer towards the reference and the sample pans, as well as an inconsistency of heat transfer between the blank measurement and the measurement with samples. As a result, considerable error can be introduced if the blank measurement is used as a baseline for enthalpy calculations.

Theories have been developed to determine the asymmetry and inconsistency of heat transfers during DTA measurements. However, most of the theories developed are either too complicated or over simplified, since the "instrument effect" varies with many factors, such as the sample properties and the experimental conditions [2]. Until now, DTA applications were basically limited to the study of the heat of reaction or heat of transition [11], i.e. the peaks on DTA curves. Correspondingly, DTA curves are mainly used for peak area calculations, which are often constructed by connecting the initial and end points of the peak investigated [12, 13].

In this work, a new method of baseline determination is proposed in order to determine the overall enthalpy change in the whole temperature range. This method uses the DTA curve for a small sample mass as the baseline for a larger mass sample, so that it eliminates the "instrument effect" during DTA measurement. In Fig. 1, for example, curve **a** (mass = 16.71 mg) is assumed to be the baseline of curve **b** (mass = 41.92 mg). The area between the two curves, therefore, provides the enthalpy change of a mass (25.21 mg) that equals the mass difference between sample **a** and sample **b** (as shown in Fig. 2). The theoretical aspects of this method will be published

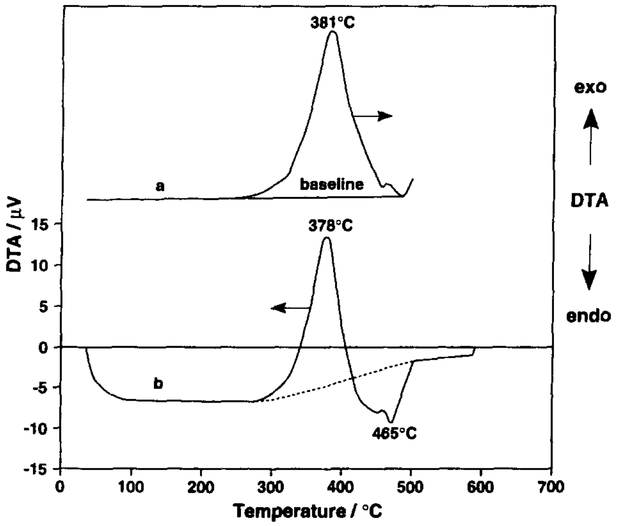

Fig. 2. Quantitative enthalpy change during the SBR pyrolysis measured by DTA. Curve **a**, measurement of Sircar and Lamond [9]. Curve **b**, measurement of this work.

elsewhere [14]. Experimentally, to ensure that the inconsistencies of heat transfer due to possible variations in the experimental conditions of the two measurements are kept to a minimum, a special three-step heating program was designed which consisted of isothermal periods before and after the heating process (see Fig. 1). Consequently, the DTA curves in Fig. 1 illustrate two zero-enthalpy change periods for the corresponding time periods. For the zero-enthalpy periods, the DTA curves depend only on the heat transfer conditions. In Fig. 1, the overlap of the zero periods of the two DTA curves can be used to check the reproducibility of the heat transfer conditions for the two DTA measurements. Occasionally, if there is a distance between the two curves, the baseline must be shifted down or up to overlap the isothermal periods of the two curves.

Figure 2 exhibits the overall enthalpy during SBR pyrolysis using a baseline determined by the proposed method (curve **b**). It has been compared with the previous enthalpy measurement made by Sircar and Lamond [9] (curve **a**). Curve **a** exhibits only one peak for the heats of reaction over the temperature range of 300–500°C. Curve **b** from this work shows a change in the overall enthalpy between 30 and 600°C, including a period of heat capacity change between 30 and 200°C, an exothermic peak at 378°C and an endothermic peak at 465°C.

The application of this method to the pyrolysis of NR and BR is shown in Figs. 3 and 4. Marked progress has been made in determining and understanding the overall enthalpy change of these two rubbers, since the previous enthalpy studies only investigated the single heat of reaction peak [5–7,9].

3.2. Proportional constant

In Figs. 2–4, the area under the DTA curves is proportional to the enthalpy change of rubber pyrolysis, which can be expressed by

$$\Delta H = -\alpha A \tag{1}$$

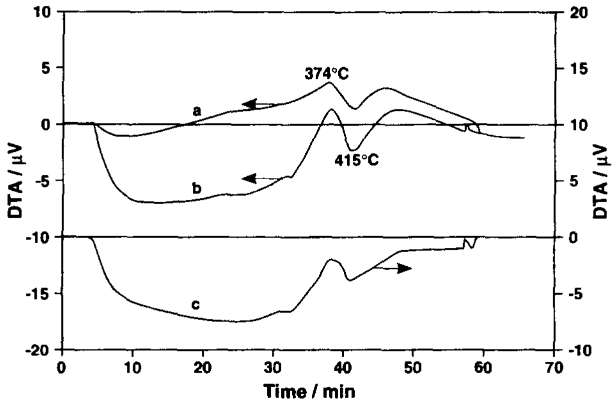

Fig. 3. Quantitative enthalpy measurement during the NR pyrolysis measured by DTA. Curve **a**, mass = 9.98 mg. Curve **b**, mass = 32.62 mg. Curve **c**, mass = 22.64 mg.

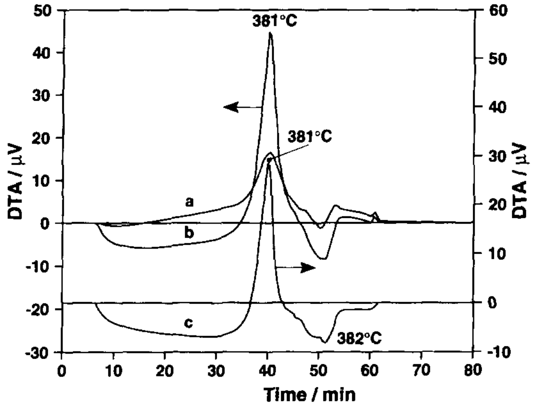

Fig. 4. Quantitative enthalpy measurement during the BR pyrolysis measured by DTA. Curve **a**, mass = 10.98 mg. Curve **b**, mass = 28.80 mg. Curve **c**, mass = 17.91 mg.

where α is the proportional constant, A is the DTA area and ΔH is the enthalpy change. The minus sign here is to convert the endotherms to positive and the exotherms to negative, since a DTA measurement conventionally plots exotherms upwards and endotherms downwards.

The proportional constant α can be determined experimentally or theoretically. Cunningham and Wilburn [2] have demonstrated theoretically a nonlinear relationship between ΔH and A, which depends on the thermal property of the samples, the conversion fraction due to chemical reactions and the heat transfer from the furnace to the sample. Ozawa et al. [15] developed a theoretical equation to determine the value of α as a function of several thermal properties. The experimental method involved a calibration of the DTA curve with materials of well-known enthalpy change [16]. In this work, since an overall enthalpy change has been obtained, from which the heat capacity shows good linearity between 80 and 250°C, the value of α can be calculated based on the specific heat capacity in this temperature range.

The specific heat capacities of NR, SBR and BR, which have been measured by others [1-3], are presented in Table 1. Although these equations were developed for unvulcanized rubbers, it is believed that vulcanized rubbers have very similar specific heats as unvulcanized rubbers (for example, $C_p = 1.89\,\mathrm{kJ\,kg^{-1}\,{}^\circ C^{-1}}$ for unvulcanized SBR and $C_p = 1.83\,\mathrm{kJ\,kg^{-1}\,{}^\circ C^{-1}}$ for vulcanized SBR at 25°C [17]). According to Eq. (1), the proportional factor α is determined as the ratio of the known specific heat capacity and the specific enthalpy change on the DTA curve at 100°C. This factor was found to be 0.777, 0.842 and $0.730\,\mathrm{kJ\,kg^{-1}\,{}^\circ C^{-1}}$ per μV for the specific enthalpy changes during the pyrolysis of NR, SBR and BR, respectively. The proportional factor changes for different rubbers probably due to slight differences in their thermal properties.

Table 1
Specific heat of NR, SBR and BR

Rubber	Specific heat/kJ kg^{-1}°C^{-1}	Ref.
NR	$1.917 + 3.44 \times 10^{-3}(T - 298)$	[1]
SBR	$1.895 + 3.18 \times 10^{-3}(T - 298)$	[4]
BR	$1.854 + 2.98 \times 10^{-3}(T - 298)$	[3]

3.3. *Physical and chemical phenomena involved in enthalpy change*

Figure. 5 shows the specific enthalpy during SBR pyrolysis, after normalization (using the 25.21 mg sample mass) and enthalpy calibration. Fig. 5 also indicates the rate of weight loss corresponding to the enthalpy change measured by the combined TG/DTA. The enthalpy change during rubber pyrolysis depends on both the physical and chemical changes involved. A simultaneous measurement of weight loss and enthalpy change provides an insight into the mechanism behind the enthalpy change. In Fig. 5, four periods of enthalpy change can be observed: (i) A linear endothermic period from 30 to 200°C. No weight change is observed for the corresponding temperature range on the DTG curve. Obviously, in this period the reaction heat is zero and only heat capacity exists; (ii) An intensive exothermic process starts at about 300°C and ends at about 450°C. The maximum rate of heat release is reached at 378°C. No intensive weight loss is observed on the DTG curve; (iii) An endothermic peak is observed between 450 and 510°C, with a peak temperature of 465°C. Correspondingly, from the DTG curve a very similar peak for the rate of weight loss is observed in the same temperature range. This phenomenon strongly suggests that the endothermic DTA peak is produced by the weight loss resulting from the evaporation of the pyrolysis products; (iv) When $T > 510$°C, a constant endothermic period is observed on

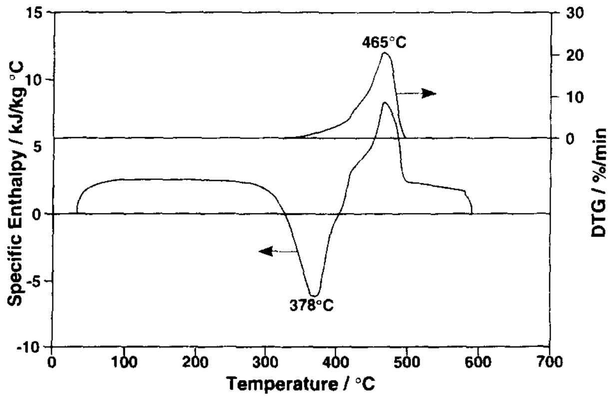

Fig. 5. Normalized enthalpy change and rate of weight loss during the pyrolysis of SBR.

the DTA curve. The DTG curve becomes constant showing the end of the weight loss. At this point, all the elastomers and other organic materials are decomposed and voltilized, except carbon black and minereal ingredients (ZnO, etc.). The heat consumption here is the heat capacity of the residues.

The overall enthalpy change in Fig. 5 is the summation of the heat capacity, the heat of reaction and the heat of vaporization. In order to determine each of them individually, the heat capacity value is determined separately. The separation is carried out on the assumption that the heat capacity is a linear function of temperature before (the heat capacity of rubber) and after (the heat capacity of carbon black and other residues) pyrolysis, and is proportional to the degree of conversion during pyrolysis (the dashed line in Fig. 2). Then the heat of vaporization is determined using a comparison of the enthalpy change and the weight loss behaviour.

3.4. Heat of vaporization

During the pyrolysis of SBR (Fig. 5), the weight loss peak on the DTG curve is very similar in shape to the endothermic peak on the DTA curve. Identical phenomena were found during the pyrolysis of NR and BR in Figs. 6 and 7. This suggests that the endothermicity during the pyrolysis of these rubbers is mainly produced by the vaporization of rubber pyrolysis products. The heat of vaporization is calculated by

$$\frac{\mathrm{d}H_v}{\mathrm{d}t} = h_g \frac{\mathrm{d}W}{\mathrm{d}t} \tag{2}$$

where $\mathrm{d}H_v/\mathrm{d}t$ is the heat of vaporization and $\mathrm{d}W/\mathrm{d}t$ is the rate of weight loss. The proportional constant, h_g, with units of kJ kg^{-1}, is the latent heat of vaporization of the pyrolysis products. The pyrolysis products have a very complex composition and, consequently, the data for the latent heat of rubber pyrolysis products could not be found in the literature. In this work, we assumed that the endothermic peak during

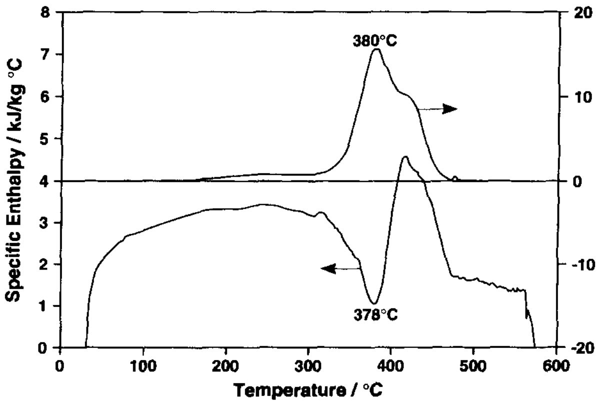

Fig. 6. Normalized enthalpy change and rate of weight loss during the pyrolysis of NR.

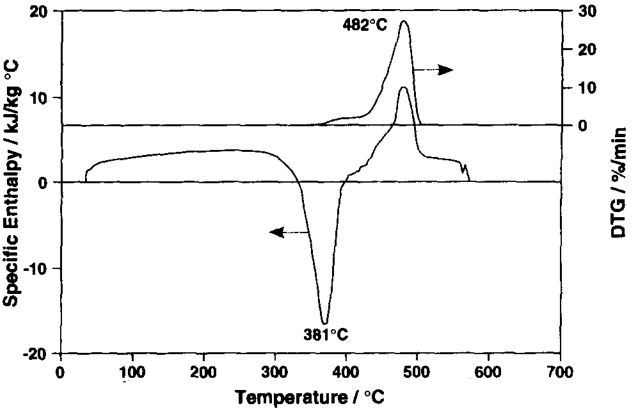

Fig. 7. Normalized enthalpy change and rate of weight loss during the pyrolysis of BR.

rubber pyrolysis is generated from the heat of vaporization, and the weight loss is mainly produced by the vaporization of the pyrolysis products (the condensable volatile products of SBR pyrolysis reach 90% by weight [18, 19]). The latent heat of pyrolysis products, h_g, can therefore be determined by curve fitting of the endothermic peak on the DTA curve and the rate of weight loss on the DTG curve.

The h_g of NR, SBR and BR are calculated to be 170, 180 and 200 kJ kg^{-1}, respectively. It is very interesting to notice that the three rubbers have similar values of h_g. This is because the h_g value presumably depends on the properties of the pyrolysis products. Previous pyrolysis studies showed that tire pyrolysis oil is basically composed of aromatic, olefinic and paraffinic hydrocarbons with molecular weights ranging from 300 to 500 Daltons [18, 20]. From a thermodynamic standpoint, the latent heat of aromatic, olefinic and paraffinic hydrocarbons lies between 200 and 230 kJ kg^{-1} [21], which is not far from the h_g values obtained in this work (see Table 2). This tends to support the above assumption that during the pyrolysis of tire rubbers the endothermic peak can be attributed to the evaporation of the pyrolysis products.

3.5. *Heat of reaction*

Table 2
Enthalpy change during the pyrolysis of NR, SBR and BR

Rubber	Heat of reaction h_r (kJ/kg)	Heat of vaporization h_g (kJ/kg)
NR	164	170
SBR	560	180
BR	906	200

The heat of reaction can be determined once the heat capacity and the heat of vaporization have been separated from the overall enthalpy change. Fig. 8 shows the heat of reaction during SBR pyrolysis. It is a heat release process between 200 and 500°C, which exhibits a maximum rate at 378°C. Figs. 9 and 10 exhibit the heat of reaction during the pyrolysis of NR and BR, by substracting the heat capacity and the heat of vaporization from the overall enthalpy change. The heat release during NR pyrolysis starts at 250°C and ends at 450°C, with a maximum value at 378°C. For BR, the heat release begins at 250°C and ends at 482°C, with a maximum value at 381°C.

The exothermicity during the pyrolysis of tire rubbers is calculated by integrating the area under the heat of reaction curves in Figs. 8–10. The heat releases of NR, SBR and

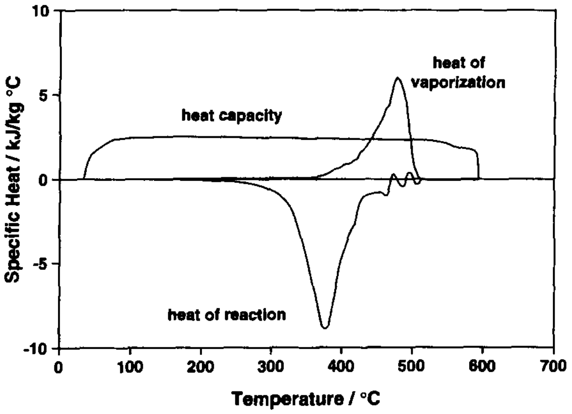

Fig. 8. The heat capacity, the heat of reaction and the heat of vaporization during the pyrolysis of SBR.

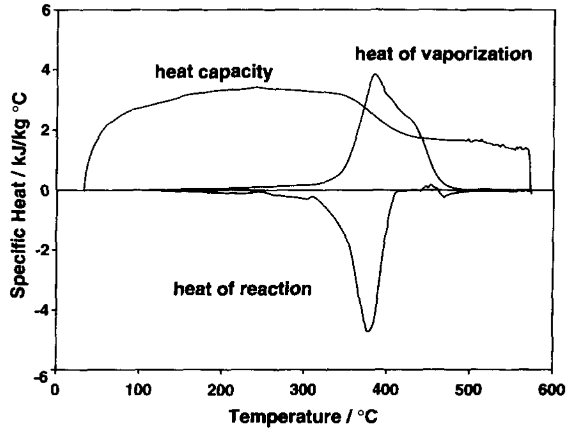

Fig. 9. The heat capacity, the heat of reaction and the heat of vaporization during the pyrolysis of NR.

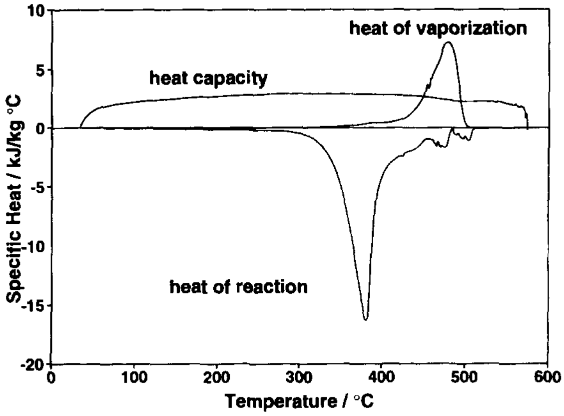

Fig. 10. The heat capacity, the heat of reaction and the heat of vaporization during the pyrolysis of BR.

BR are 164, 560 and 906 kJ kg^{-1}, respectively. These values are close to those from previous studies: Sircar and Lamond [7] reported a value of 945 kJ kg^{-1} for BR; Brazier an Schwartz [5] reported 660 and 880 kJ kg^{-1} for SBR and BR, respectively.

Once the overall enthalpy change over the whole temperature range is integrated, the total energy consumption during rubber pyrolysis is obtained. Over the temperature range between 30 and 510°C, the total heat changes during the pyrolysis of NR, SBR and BR are 870, 550 and 325 kJ kg^{-1}, respectively. These results are close to the results of Labrecque [22] who concluded that the total heat change during tire pyrolysis is 706 kJ kg^{-1}.

3.6. Kinetic parameters of pyrolysis reaction

Quite often kinetic studies of pyrolysis reactions consider the rate of weight loss to be the rate of reaction. This is not always true during the pyrolysis of different materials. When the evaporation of pyrolysis products occurs more rapidly than the pyrolysis reactions themselves, the rate of reaction controls the rate of weight loss. Under such conditions the kinetic process can be studied on the basis of the rate of weight loss. During the pyrolysis of tire rubbers, however, the weight loss process is much slower after the pyrolysis reactions. For the SBR pyrolysis (Fig. 8), the endothermic peak for evaporation occurs about 100°C after the exothermic peak of the chemical reactions. Thus the weight loss during rubber pyrolysis is independent of the chemical reactions and cannot help in understanding the chemical kinetics.

The chemical reactions during the pyrolysis of NR, SBR and BR occur in the temperature range 300–450°C and are exothermic. The mechanism of rubber pyrolysis reactions is still unclear. The mechanism may involve multiple chemical reactions, such as crosslinking and cyclization [23]. It is globally an exothermic process. In this work, the apparent kinetic parameters of rubber pyrolysis were calculated based on the heat release phenomenon.

According to the kinetic theory of Borchardt and Daniels [24], the heat of reaction is directly proportional to the number of moles reacted and the rate constant of decomposition

$$k = \frac{\mathrm{d}H_d}{\mathrm{d}t} \frac{1}{(\Delta H_d - \Delta H_d(t))} \tag{3}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k(1 - C) \tag{4}$$

where

$$\Delta H_d = \int_0^\infty \frac{\mathrm{d}H_d}{\mathrm{d}t}\mathrm{d}t \tag{5}$$

$$\Delta H_d(t) = \int_0^t \frac{dH_d}{\mathrm{d}t}\mathrm{d}t \tag{6}$$

where k is the apparent rate constant of rubber pyrolysis, H_d is the heat of reaction, C is the number of moles reacted. When k is calculated from Eq. (3), the kinetic parameters of rubber pyrolysis can be calculated based on the assumption of first-order reaction

$$\ln k = \ln Z - \frac{E}{R - T} \tag{7}$$

where E is the activation energy, Z is the pre-exponential factor, R is the ideal gas constant and T is temperature. The activation energies of NR, SBR and BR were calculated to be 146, 133 and 158 kJ mol^{-1}, respectively. Their values are within the range reported by Sircar and Lamond [7].

4. Conclusion

Previous enthalpy studies of rubber pyrolysis determined only a single exothermic peak on the DSC curve. In this work, a novel approach of enthalpy measurement using TG/DTA was developed, which allowed the overall enthalpy change over the whole temperature range of the measurements to be determined quantitatively. Also the heat capacity, the heat of reaction and the heat of vaporization are determined individually.

This novel approach involves a new method of baseline determination, the calculation of a proportional constant and the separation of the endothermic and exothermic peaks. The baseline is determined using a DTA curve of a small sample for the measurement of the same type of sample but of larger mass. The proportional constant is defined as the ratio of the heat capacity portion of the DTA curve to the specific heat of the sample. The separation of the overlap between the endothermic and exothermic peaks is carried out by assuming that the endothermic peak only corresponds to the heat of vaporization.

The overall enthalpy change of NR, SBR and BR has been studied using this approach. It was concluded that the overall enthalpy changes during the pyrolysis of tire rubbers are endothermic. From 30 to 510 °C, the energy consumption is 870, 550 and 325 kJ kg^{-1} for NR, SBR and BR, respectively. From 30 to 280°C, the enthalpy changes are linearly endothermic due to the increase in the heat capacity. Between 300 and 450 °C, the rubber pyrolysis reactions occur which results in an exothermic peak. The exothermicity was calculated to be -164, -560 and -906 kJ kg^{-1} for NR, SBR and BR, respectively. Between 450 and 510 °C, endothermic peaks results from the evaporation of the pyrolysis products. The heat of vaporization for NR, SBR and BR was estimated to be 170, 180 and 200 kJ kg^{-1}, respectively.

The traditional kinetic study of pyrolysis reactions considers the rate of the weight loss process to be the same as the rate of reaction, which is not the case during the pyrolysis of rubbers. This quantitative enthalpy study revealed that the weight loss process occured after the pyrolysis reactions. The weight loss of rubber pyrolysis only reflects the evaporation process of the pyrolysis products, which can be determined by the thermodynamic properties of the pyrolysis products. The exothermic peak before the weight loss was produced by the pyrolysis reactions. The mechanism probably involves multiple chemical reactions and is globally exothermic. In this work, the kinetic parameters of rubber pyrolysis were calculated according to the heat of reaction, using the theory of Borchardt and Daniels [24]. The calculated activation energies of the pyrolysis of NR, SBR and BR were 146, 133 and 158 kJ mol^{-1}, respectively. These values differ from the values obtained by Sircar and Lamond [7]; the variation can probably be attributed to the method of baseline determination.

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Nomenclature

A	area/m^2
C	number of moles reacted
E	activation energy/kJ mol^{-1}
h_g	latent heat of vaporization/kJ kg^{-1}
H	enthalpy/kJ
H_d	heat of reaction/kJ
H_v	heat of vaporization/kJ
k	apparent rate constant of rubber pyrolysis/s^{-1}
R	ideal gas constant/kJ $mol^{-1}K^{-1}$
T	temperature/°C

t	time/s
W	weight/kg
Z	pre-exponential factor

Greek letter

α	proportional factor

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