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Using DTA to quantitatively determine enthalpy change over a wide temperature range by the “mass-difference baseline method”

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Abstract

In thermal analysis, the apparatus commonly used to quantitatively measure enthalpy change is the DSC while the DTA equipment is used for qualitative measurements. In this work a new method, called the “mass-difference baseline method”, is proposed to attempt to use DTA for quantitative measurement. The presented method employs the DTA curve derived from a small mass sample as the baseline for a large mass sample using the same material. Such an approach diminishes the asymmetric heat transfer problem attributed to the “apparatus effect” and “sample influence”, thus greatly improving the linearity between the DTA curve and enthalpy change. The theoretical basis of this method is presented and discussed in this paper. The method has been tested for the determination of the enthalpy change of graphite and elastomers over a large temperature range from 30°C to 600°C. Compared with DSC, one important advantage of this method is that it allows enthalpy measurement to be carried out in an open system allowing a sample mass loss during the measurement. For example, during the measurement of elastomers, intensive decomposition and 70% of the sample mass loss occur. The DTA quantitative measurement successfully determines the heat capacity changes as well as the heat of reaction and heat of evaporation, which all occur during the enthalpy changes of the material subjected to decomposition. However, the accuracy of this method is still not high enough for high accurate enthalpy measurement. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DTA; Enthalpy; Heat; Capacity; Baseline

1. Introduction

The DTA method has a long use history to determine the transition temperature and the enthalpy changes caused by physical changes or chemical reactions. The most important advantages of a DTA apparatus are its easiness in use and its availability over a wide range of experimental conditions, for example, high temperature, high pressure and vacuum. As for enthalpy measurement, DSC allows quantitative measurement and DTA is mainly used for qualitative measurement of the exo- or endothermic nature of physical changes or chemical reactions. One advantage of DTA is that it enables the measurement of the enthalpy change in an open system, thus allowing simultaneous recording of changes in the sample mass, while DSC requires a constant sample mass during the enthalpy change measurement.

The difference between DSC and DTA is that DSC directly measures the energy change of a sample while DTA measures the temperature difference between the

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reference and the sample pan, $\Delta T=T_s-T_r$, which is then converted to enthalpy change, ΔH, through conversion factors. A major difficulty in DTA measurement is that the conversion factors are rarely constant and are difficult to determine. The reason is that the DTA signal is influenced not only by the enthalpy changes of the sample but also by the asymmetric heat transfer from the environment to the sample and the reference materials. This asymmetric heat transfer phenomenon can be influenced by many factors [1]. The relationship between these factors and the heat transfer is complex and difficult to express with mathematical equations. Conventionally, when DTA is used for enthalpy measurement, a simplification is made which assumes a proportional relationship between ΔT and ΔH and ignores the influences of the asymmetric heat transfer from the environment to the sample and the reference materials [2]. Such an assumption is practical when a significant transition heat is measured over a narrow range of temperatures. However, if the DTA measurement is carried out over a wide temperature range, considerable error can be introduced using this simplification, as enthalpy changes may involve significant variation in both specific heat and the transition heat. That is because in this case, the asymmetric heat transfer influences may have the same magnitude as the enthalpy changes.

In this work, a new method called the "mass-difference baseline method" is proposed which attempts to use DTA for quantitative enthalpy measurement over a wide temperature range. This method considers the asymmetric heat transfer influence on the enthalpy measurement, and tries to diminish this influence by means of subtracting a baseline that is constructed in a new way. It thus greatly improves the linearity between the DTA signal and the enthalpy change. The theoretical correlation between the DTA signal, the enthalpy change and the heat transfer influences are presented and discussed. To test the method, the enthalpy changes of graphite and elastomers were measured over a wide temperature range (30–600°C). The measured heat capacity of graphite was compared with the literature values. The enthalpy change of elastomers involves heat capacity changes, heats of reaction and heats of evaporation, which are experienced during the elastomer pyrolysis and the evaporation of the pyrolysis products. In previous studies, the heat capacity change and the reaction heat of elastomer pyrolysis have been studied separately by different techniques such as DSC and traditional calorimetric apparatus [3–7]. Each of the these studies was carried over a limited temperature range. In this work, the presented method allows an enthalpy change of elastomer to be determined over a large temperature range with one measurement. The result will provide an integral overlook of enthalpy changes of elastomers, including the heat capacity changes, the heats of reaction and the heats of evaporation, varying continuously from 30°C to 600°C.

2. Theory

The DTA apparatus used in this work is the TG/DTA model 220 manufactured by Seiko. As shown in Fig. 1, the instrument uses two horizontal balance beams, on the tip of which the sample holder and reference holder are fixed. The thermocouples for detecting the sample and the reference temperatures are welded to the sample and the reference holders. Both the sample and the reference sides are heated by the same heating source, which is the furnace wall. The principal heat transfer mechanisms to the sample and the reference are the radiation from the furnace and the heat convection from the carrier gases. As shown in Fig. 1, the DTA signal represents the change in the temperature difference between the sample and the reference. It is determined by both the enthalpy change of the sample and the heat transfer difference from the heating source. Mathematically, the relation-

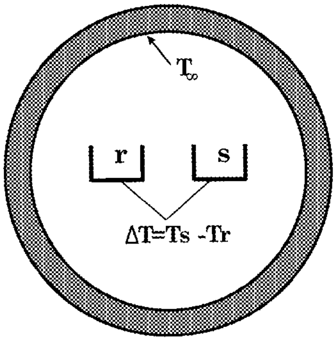

Fig. 1. The DTA apparatus of Seiko with horizontal balance beams.

ship between the DTA signal and the enthalpy change can be expressed by a well known energy balance equation from Vold [2].

On the sample side:

$$m_p C_{P,p} \frac{dT_s}{dt} + m_s C_{P,s} \frac{dT_s}{dt} + m_s \frac{dQ}{dt} = \alpha_s A_s (T_\infty - T_s) \quad (1)$$

and on the reference side:

$$m_p C_{P,p} \frac{dT_r}{dt} = \alpha_r A_r (T_\infty - T_r), \quad (2)$$

where m_p and $C_{P,p}$ are the mass and the specific heat capacity of the sample pan on both the reference and sample side; m_s and $C_{P,s}$ represent the mass and the specific heat capacity of the sample; Q is the transition heat produced by phase change or chemical reactions; α_s and α_r are the overall heat transfer coefficients from the furnace to the sample and the reference side, respectively, including both heat radiation and heat convection; T_∞ is the furnace temperature.

Subtracting Eq. (2) from Eq. (1), and knowing that $dH/dt = C_{P,s}(dT_s/dt) + dQ/dt$ and $\Delta T = T_s - T_r$, one obtains:

$$\Delta T = \frac{m_s}{\alpha_s A} \frac{dH}{dt} + \frac{m_p C_{P,p}}{\alpha_s A} \frac{d(\Delta T)}{dt} + \frac{(\alpha_s - \alpha_r)}{\alpha_s} (T_\infty - T_r). \quad (3)$$

The second term on the right-hand side can be ignored as it is much smaller than the other terms. Consequently, one obtains,

$$\Delta T = \frac{m_s}{\alpha_s A} \frac{dH}{dt} + \frac{(\alpha_s - \alpha_r)}{\alpha_s} (T_\infty - T_r). \quad (4)$$

Eq. (4) shows that the temperature difference, ΔT, is determined by the enthalpy change ΔH and the heat transfer difference between the sample and the reference, $(\alpha_s - \alpha_r)(T_\infty - T_r)$. In Vold's theory [2], this heat transfer difference was ignored, with the assumption that $(\alpha_s - \alpha_r)$ equals zero. In practice, however, this assumption is rarely true when the measurement is carried out over a wide range of temperatures.

Fig. 2 shows three DTA curves measured under two different conditions: curve **a** is obtained in the presence of empty reference and sample pans. Under such conditions, ΔH in Eq. (4) is zero, thus the DTA signal represents only the heat transfer difference $(\alpha_s - \alpha_r)(T_\infty - T_r)/\alpha_s$; curve **b** and curve **c** are obtained with the sample loaded on the sample side (the samples loaded are sapphire and graphite for curve **b** and curve **c**, respectively). Their DTA signals incorporate both the heat transfer influence $(\alpha_s - \alpha_r)(T_\infty - T_r)/\alpha_s$, and the enthalpy change ΔH of the samples. A comparison between curve **a** with curves **b** and **c** illustrates the significance of the heat transfer phenomena during the DTA measurement. As shown in Fig. 2, curve **a** varies over a range 0–15 μV. Curves **b** and **c** vary between −6 and 3 μV. This shows that the heat transfer influence during DTA measurements has the same significance as the enthalpy change of samples. Thus during enthalpy calculations, a large error can be introduced if the heat transfer contribution in Eq. (4) is ignored.

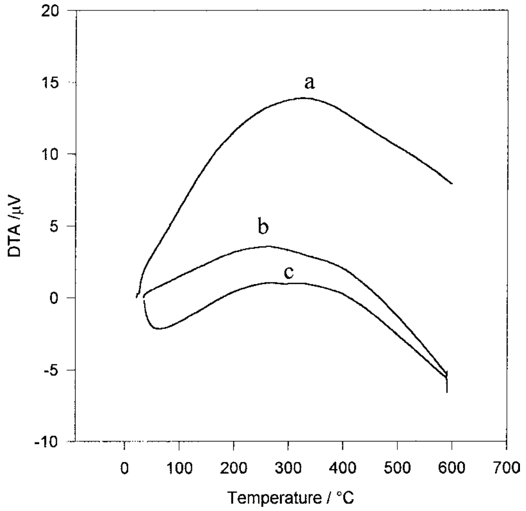

Fig. 2. The significance of the heat transfer influence on the enthalpy measurements. Curve **a**: DTA measurement in the presence of empty reference and sample pans. Curve **b**: DTA measurement with sapphire sample loaded on the sample pan. Curve **c**: DTA measurement with graphite sample loaded on the sample pan.

In Fig. 2, curve **a** is always positive, implying a larger heat transfer on the sample side than the reference side. The heat transfer difference can also be negative, if the heat transfer is larger on the reference side. As shown in Fig. 2, curve **a** is varying nonlinearly with temperature, showing a complex relationship between the heat transfer and the environment conditions. Wendlandt [8] published a detailed discussion of the heat transfer influence on a DTA curve. He concluded that the heat transfer influence during DTA measurements results from an asymmetric heat transfer towards the reference and the sample pans. There are mainly two reasons for this asymmetry: (i) the sample holders in the DTA furnace are located asymmetrically, which is called the "instrument effect"; and (ii) different thermal properties of the sample and the reference, for example the emissivity and the thermal conductivity, which is called the "sample influence". As many construction and operation factors are involved in the "instrument effect" and the "sample influence", the asymmetric heat transfer phenomena in a DTA measurement is difficult to calculate or to eliminate using mathematical assumptions.

In this work, a new way of eliminating the heat transfer term is proposed which is based on a new method of baseline construction.

2.1. The "mass-difference baseline method"

Traditionally, the DTA baseline is measured when both the sample pan and reference pan are empty (see curve **a** in Fig. 2). In this case, the energy balance of the reference and the sample pans can be expressed as follows:

$$\Delta T = \frac{(\alpha_s - \alpha_r)}{\alpha_s}(T_\infty - T_r). \tag{5}$$

Subtracting the baseline Eq. (5) from sample measurement Eq. (4), one gets:

$$\Delta T_1 - \Delta T_2 = \frac{m_{s,1}}{\alpha_{s,1}A}\frac{dH}{dt} + \left(\frac{(\alpha_{s,1} - \alpha_{r,1})}{\alpha_{s,1}} - \frac{(\alpha_{s,2} - \alpha_{r,2})}{\alpha_{s,2}}\right)(T_\infty - T_r). \tag{6}$$

Eq. (6) implies that if the term of heat transfer difference ($\alpha_{s,1}-\alpha_{r,1}$) for the sample measurement is equal to the one related to the baseline measurement, ($\alpha_{s,2}-\alpha_{r,2}$), then the area between the sample measurement and the baseline is proportional to the enthalpy change of the sample.

Fig. 3 shows the results of DTA measurements of sapphire and graphite after subtracting the conventional baseline. Curve **a** was produced by the DTA curve of sapphire (curve **b** in Fig. 2) after subtracting the baseline (curve **a** in Fig. 2). Curve **b** results from the DTA curve of graphite (curve **c** in Fig. 2) after subtraction of the baseline. In Fig. 3, curves **c** and **d** are the specific heat of sapphire and graphite from literature [10,11]. Obviously, both curve **a** and curve **b** are totally different with curves **c** and **d**. This reveals that the heat transfer influences during DTA measurements is hard to eliminate by simply subtracting a baseline constructed in a conventional way. The reason is that such a baseline has different heat transfer coefficients, ($\alpha_s-\alpha_r$), when compared with DTA curves with the samples loaded.

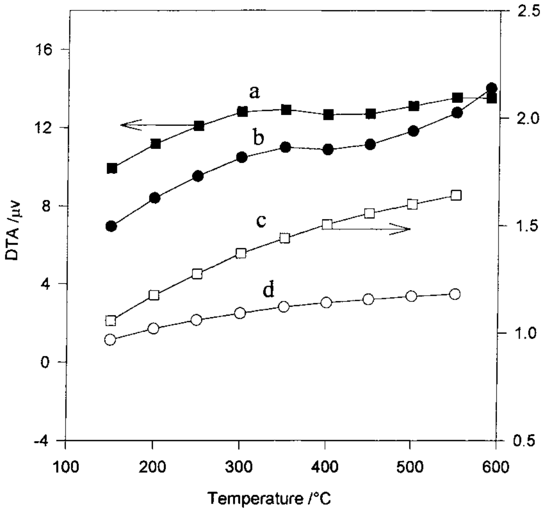

Fig. 3. Enthalpy measurements using conventional baselines. Curve **a**: enthalpy change of sapphire. Curve **b**: enthalpy change of graphite. Curve **c**: the specific heat of sapphire from literature. Curve **d**: the specific heat of graphite from literature.

However, curves **a**, **b** and **c** in Fig. 2 should have the same value of α_r, since the same empty reference pan was used for all the measurements. The problem is on the sample side, where the sample is loaded during the sample measurements but is empty during the baseline measurement. Consequently, a different heat transfer coefficient α_s is obtained in these two tests due to the following possible reasons: (i) the test involving a sample has a different emissivity than the test involving an empty sample pan; and (ii) the test involving a sample has a different effective thermal conductivity than the test involving an empty sample pan, since the former depends on the thermal conductivity of both the sample and the sample pan.

In this work, a new method called the "mass-difference baseline method" is proposed in order to eliminate the heat transfer influence during DTA measurements. The method uses the DTA curve of a small mass sample as the baseline for the DTA measurement of a large mass sample, thus ensuring the same heat transfer coefficient, α_s, for the baseline and the sample runs. With this approach, a simple subtraction of the baseline from the DTA measurement curve eliminates the heat transfer influences ($\alpha_s - \alpha_r$) in Eq. (5).

Fig. 4 illustrates the heat capacity measurement of sapphire obtained using this new method. Curve **a** (m=17.43 mg) is used as the baseline for curve **b** (m=37.20 mg). Obviously, both curves have the same trend during the temperature evolution and exhibit the same value of heat transfer coefficient α_s. The only difference between them is the intensity of the ΔT change, due to a difference in their sample mass. A subtraction of these two curves produces the enthalpy change of a mass equal to the mass difference (m=19.77 mg) for the two measurements (see curve **c**).

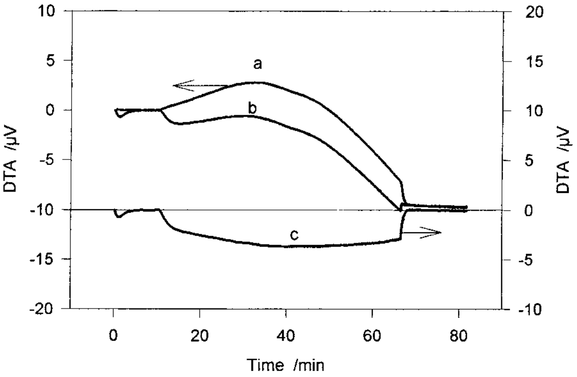

Fig. 4. Heat capacity measurement using the "mass-difference baseline method". Curve **a**: DTA curve of sapphire with m=17.43 mg. Curve **b**: DTA curve of sapphire with m=37.20 mg. Curve **c**: area between curve **a** and curve **b**.

2.2. Enthalpy calculation

By subtracting the baseline constructed using this method, the heat transfer contribution $((\alpha_{s,1} - \alpha_{r,1})/\alpha_{s,1} - (\alpha_{s,2} - \alpha_{r,2})/\alpha_{s,2})(T_\infty - T_r)$ in Eq. (6) is eliminated. One obtains

$$\Delta T_1 - \Delta T_2 = \frac{(m_{s,1} - m_{s,2})}{\alpha_s A} \frac{dH}{dt} \tag{7}$$

with $K_1 = \alpha_s A$ and $\mathrm{DTA} = K_2 \Delta T$, this leads to

$$\frac{dH}{dt} = K_1 K_2 \frac{(\mathrm{DTA}_1 - \mathrm{DTA}_2)}{(m_{s,1} - m_{s,2})} \tag{8}$$

or

$$\frac{dH}{dt} = K_1 K_2 \frac{(\mathrm{DTA}_1 - \mathrm{DTA}_2)}{(m_{s,1} - m_{s,2})}, \tag{9}$$

where m is the sample mass and $(\mathrm{DTA}_1 - \mathrm{DTA}_2)$ is the area between two DTA curves. There are two conversion factors, K_1 and K_2. Factor K_1 is determined by the heat transfer from the furnace to the sample, which depends on the sample property and operating conditions. Since the heat transfer in a DTA furnace is complex, the relationship between K_1 and the operating conditions is difficult to express mathematically. However, when the sample properties and operating conditions are fixed for each test, K_1 can be assumed to be a constant over the whole temperature range of measurements [9]. K_2 is an apparatus related parameter and is a function of temperature. The relationship between K_2 and the temperature is identical for all the DTA tests.

From Eq. (9), the following correlation can be obtained:

$$\frac{K_2}{K_2'} = \frac{K_1'}{K_1} \frac{\mathrm{DTA}}{\mathrm{DTA}'} \frac{(dH/dt)'}{(dH/dt)}, \tag{10}$$

where K' are conversion factors at a certain temperature. As K_1 is independent with temperature for any specific test and with $K_1 = K_1'$ one obtains

$$\frac{K_2}{K_2'} = \frac{\mathrm{DTA}}{\mathrm{DTA}'} \frac{(dH/dt)'}{(dH/dt)}. \tag{11}$$

Here K_2/K_2' is a function of temperature. The correlation $K_2/K_2' = f(t)$ can be determined for a standard material. Once $K_2/K_2' = f(t)$ is determined, it is identical for all the DTA tests of other materials. Knowing that $K_2/K_2' = f(t)$, the following equation can be obtained to calculate the enthalpy change from a DTA curve:

$$\frac{dH}{dt} = \frac{K_2}{K_2'} \frac{(dH/dt)'}{\mathrm{DTA}'} \mathrm{DTA}, \tag{12}$$

where DTA′/(d*H*/d*t*)′ is the ratio of the DTA signal and the enthalpy change of the measured material at a certain temperature.

3. Results and discussion

3.1. Experimental

The experimental apparatus used was a Seiko TG/DTA model 220. It simultaneously measures the enthalpy change and weight loss of the sample. The heating rate used for the measurement is 10°C/min and the sweeping gas was high purity N_2 at a flowrate of 100 ml/min under normal pressure. The standard material used for the calibration was powdered α-sapphire from Seiko. The graphite sample was marked AC-4722T from Anachemia. Three types of elastomers were tested in this work: SBR (styrene-butadiene rubber), NR (natural rubber) and BR (butadiene rubber). The elastomer samples were obtained from Goodyear Canada in Que., Canada.

3.2. Conversion factor K_2/K_2'

In this work, the standard material α-sapphire was used to calculate the conversion factor K_2/K_2'. Table 1 presents the measured DTA value, the specific heat from literature [10] and the calculated conversion factor K_2/K_2' using Eq. (11). As shown in Fig. 4, the DTA curve of sapphire has a thermal nonstable period before T=150°C. Thus in Table 1, the first point of the K_2/K_2' calculation is at T=150°C. The DTA′ and the C_P' are the values taken at T=150°C.

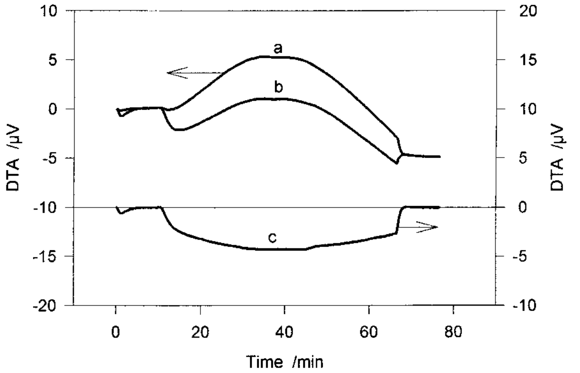

Fig. 5. Heat capacity measurement of graphite. Curve **a**: DTA curve of graphite with m=7.47 mg. Curve **b**: DTA curve of graphite with m=28.03 mg. Curve **c**: area between curve **a** and curve **b**.

3.3. Specific heat measurement

To verify the new method, the specific heat capacity of graphite was measured and the results were compared with literature values. Fig. 5 exhibits the DTA measurement of graphite. Curve **a** and curve **b** are two DTA curves with masses of 7.47 and 28.03 mg, respectively. Curve **c** is the area between the two curves, which is proportional to the specific heat of graphite. With the conversion factor K_2/K_2' in Table 1, the specific heat of the graphite sample is calculated using Eq. (12). Table 2 shows the calculated specific heat and the comparison with literature values. During the calculation, it was found that there is a deviation of ±15%, if only one DTA test is used for the calculation. In Table 2, an average DTA data of four DTA measurements is used and the relative deviation of measurement decreases to ±5%. The literature values of

Table 1
Conversion factor $K_2/K_2' = f(T)$

T (°C)	C_P [11] (kJ/kg °C)	C_P/C_P'[a]	DTA (μV)	DTA/DTA′[b]	K_2/K_2'
150	2.04	1	2.04	1	1
200	2.14	1.05	2.18	1.07	1.01
250	2.22	1.09	2.29	1.13	1.03
300	2.30	1.13	2.28	1.12	0.99
350	2.36	1.16	2.30	1.13	0.98
400	2.41	1.18	2.17	1.06	0.90
450	2.43	1.19	2.08	1.02	0.85
500	2.47	1.21	1.92	0.94	0.78
550	2.49	1.22	1.72	0.84	0.69

[a] C_P' is the specific heat of sapphire at T=150°C.
[b] DTA′ is the measured DTA value at T=150°C.

Table 2
Specific heat of graphite

T (°C)	DTA (mean) (μV)	C_P (cal) (kJ/kg °C)	C_P (lit[a]) (kJ/kg °C)	Deviation (%)
150	1.90	1.07	1.07	0.00
200	2.10	1.17	1.17	0.18
250	2.18	1.20	1.26	4.74
300	2.29	1.31	1.34	2.35
350	2.40	1.39	1.41	1.16
400	2.39	1.49	1.47	−1.64
450	2.20	1.45	1.52	4.67
500	2.07	1.50	1.57	4.30
550	1.91	1.56	1.62	3.48

[a] [11,12].

the specific heat of graphite are only slightly different from the value reported by Lucks [11,12]. In Table 2, an average value from the two tests carried out by Lucks is used.

In Figs. 4 and 5, one can observe an isothermal period for each DTA curve before and after the heating process. The enthalpy change in the isothermal period is neutral. The shape of the DTA curve in this period depends only on the heat transfer conditions. Thus the overlap of the isothermal 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 downward or upward to overlap the isothermal periods of the two curves.

During the measurement, a deviation of <±15% was found for the enthalpy results obtained from different tests with the same sample mass. This is probably caused by the differences in sample shape and sample loading position. It implies that the proposed method reduces but still not completely eliminates the heat transfer influence. Getting an average value from repeated measurements can improve accuracy, but this will be costly and tedious.

The ASTM standard (ASTM E1269) requires covering the crucibles with lids on both the reference and sample sides during a specific heat measurement. The purpose is to decrease the difference in radiation heat transfer, between the two sides since the two lids have the same emissivity. This method is practical for specific heat measurement when there is no heat of transition involved. However, when DTA is used to measure an enthalpy change attributed to chemical reactions or phase changes that is often accompanied by a mass loss, using the ASTM method may produce error of measurement. There are mainly two reasons for this: firstly, putting a cover on the sample pan may disturb the rate of weight loss, and thus influence the result of the enthalpy measurement; secondly, the reaction products accumulate and then modify the atmosphere around the sample pan. This may cause a difference in heat transfer between the two sides because the thermal properties of the pyrolysis products are different from those of the pure purge gas.

Obviously, the proposed method avoids the above problems since it uses opened sample pans and allows the reaction products leaving the sample as soon as they are produced.

As a conclusion, the proposed method is not suitable for specific heat measurements compared with DSC. The advantage of this method is to quantitatively measure the continuous enthalpy change over a wide temperature range when both mass loss and enthalpy changes are involved.

3.4. *Enthalpy change of elastomers over a wide temperature range*

The enthalpy changes of elastomers are very important thermal property data for the pyrolysis study of used tires which in turn represent environmental problems [13]. Under normal conditions, elastomers are pyrolyzed over the temperature range 30–550°C. In previous studies, the specific heat has been measured using classical methods of calorimetric measurement in the temperature range −50°C to 150°C [3–5]. The heat of reaction (250–500°C) has been studied by DSC

[6,7]. However, to our knowledge, no investigation has been carried out on a continuous enthalpy change measurement of elastomers over the entire temperature range of pyrolysis, during which heat capacity changes and heat of reaction and heat of evaporation are involved. During pyrolysis, 65–70% of the mass of the elastomers is lost. In such a case, DTA has an advantage over DSC as it enables the enthalpy change to be measured in an open system while the sample mass is simultaneously changing. The combined TGA and DTA allow simultaneous enthalpy and mass change measurements, which helps understand the mechanism of enthalpy changes. Besides, the organic products evolved during the pyrolysis modify the atmosphere around the sample pan, which may influence the heat transfer process because thermal properties of the pyrolysis products are different from those of the pure purge gas. The proposed method has the advantage of decreasing such an influence as the same phenomena occur with the baseline test.

Fig. 6 exhibits the enthalpy change during SBR pyrolysis using a baseline determined by the proposed method. The measurement was carried out over the temperature range 30–600°C and under 1 atm. with a nitrogen flow of 100 ml/min. It shows an exothermic peak at 378°C, as already noted previously by Brazier and Schwartz [6] and Sircar and Lamond [7], and an endothermic peak at 465°C. Sircar and Lamond [7] have measured the transition heat involved in the exothermic peak, using DSC. However, the DSC equipment used by the authors did not allow experiments at high temperature, and did not consider the endothermic peak, nor the enthalpy change over the overall temperature range of pyrolysis. As shown in Fig. 6, the new method of enthalpy measurement allows a quantitative measurement of the enthalpy change to be performed over a wide range of temperatures. Fig. 6 shows a continuous enthalpy change with an overlap of several energy change mechanisms. It includes a linear heat capacity change (30–200°C), an exothermic peak due to the heat of reaction (378°C), an endothermic peak for the latent heat of evaporation (465°C), and a linear heat capacity change of the residue (500–600°C).

Figs. 7 and 8 show the enthalpy measurements during the pyrolysis of NR and BR. Similarly, to

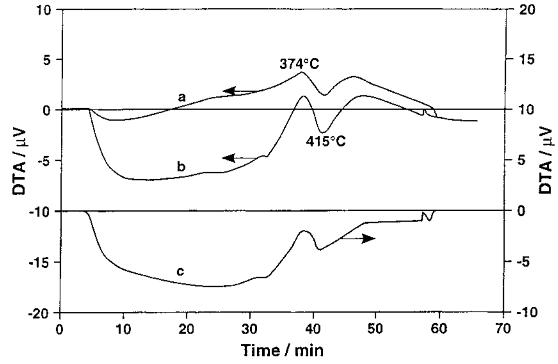

Fig. 7. Enthalpy measurement of NR. Curve **a**: DTA curve of NR with m=9.98 mg. Curve **b**: DTA curve of NR with m=32.62 mg. Curve **c**: area between curve **a** and curve **b**.

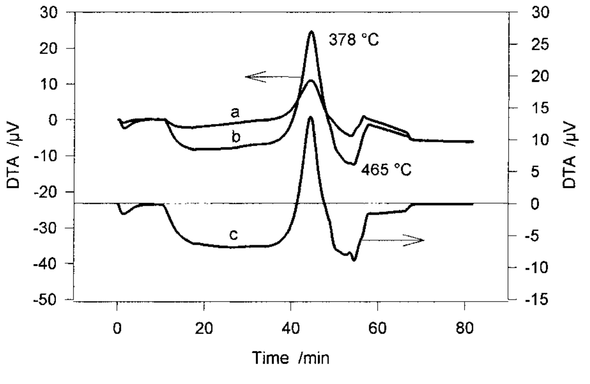

Fig. 6. Enthalpy measurement of SBR. Curve **a**: DTA curve of SBR with m=16.71 mg. Curve **b**: DTA curve of SBR with m=41.92 mg. Curve **c**: area between curve **a** and curve **b**.

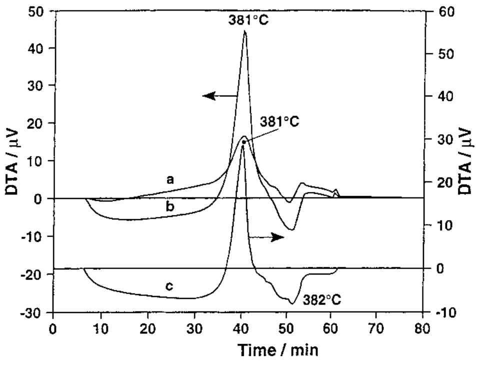

Fig. 8. Enthalpy measurement of BR. Curve **a**: DTA curve of BR with m=10.89 mg. Curve **b**: DTA curve of BR with m=28.80 mg. Curve **c**: area between curve **a** and curve **b**.

Table 3
Specific heat of SBR, NR and BR

T (°C)	DTA (μV)			C_P (kJ/kg °C)		
	SBR	NR	BR	SBR	NR	BR
150	2.51	3.11	3.35	2.35	2.30	2.23
200	2.52	3.33	3.62	2.33	2.42	2.38
250	2.52	3.40	3.73	2.29	2.43	2.41
300	2.52	3.30	3.76	2.38	2.45	2.52
350	2.51	3.11	3.74	2.40	2.33	2.54
400	2.50	2.14	3.66	2.60	1.76	2.71
450	2.45	1.70	3.44	2.70	1.48	2.69
500	2.40	1.61	2.88	2.88	1.54	2.46
550	2.10	1.43	2.53	2.85	1.53	2.44

the enthalpy change of SBR pyrolysis, these figures show four periods of enthalpy changes, including a linear heat capacity change before rubber pyrolysis, an exothermic period during the pyrolysis reactions, an endothermic period after the chemical reactions and a period of linear heat capacity change after transition heat. With the help of the TG measurement of the sample mass change, the corresponding physical and chemical mechanisms behind these enthalpy changes were studied by Yang et al. [14]. The study revealed that the exothermic peak on the DTA curves of rubber pyrolysis can be attributed to the pyrolysis reactions and the endothermic peaks result from the evaporation of the pyrolysis products.

In the literature, it is known that under low temperature conditions where no pyrolysis occurs, the specific heat capacities of elastomers increase linearly with temperature [3–5]. After pyrolysis, the residue is mainly composed of carbon black which represents approximately 30% of the initial mass. The specific heat capacity of carbon black is similar to that of graphite. During the pyrolysis reactions, it is assumed that the specific heat of SBR changes linearly with the mass change, from the specific heat of rubber to that of carbon black. The heat of evaporation is assumed to be proportional to the rate of mass change. Based on these assumptions, the specific heat capacity, the heat of reaction and the heat of evaporation can be separated and calculated individually. The details of the calculations can be found in the authors' previous publication [14].

Given that the specific heat capacities of SBR [3], NR [4] and BR [5] at 150°C are 2.35, 2.30 and 2.23 kJ/kg °C, respectively, the specific heat capacities of these three elastomers over the whole temperature range of measurements have been calculated and are listed in Table 3. Quite different specific heats are obtained for the three rubbers, which might be questionable. For example, when T>500°C, the residue from the three rubbers are all basically composed of pyrolytic carbon black. They should have very similar of specific heat values. In Table 3, the residue from NR has a specific heat closed to that of graphite. The specific heats of SBR and BR, however, are much higher than that of graphite. This shows that DTA has a lower accuracy than DSC in quantitative enthalpy measurement.

Having determined the specific heats, the heats of evaporation were calculated and the following results were obtained: 180, 170 and 200 kJ/kg for SBR, NR and BR, respectively. The heats of reaction were determined to be 560, 164 and 906 kJ/kg, respectively. These results are in close agreement with those of Brazier and Schwartz [6] who have reported heats of reaction of 660 and 880 kJ/kg for SBR and BR, respectively.

4. Conclusions

A theoretical study of the heat transfer and the energy balance in a DTA instrument indicated that a proportional relationship between the enthalpy change and a DTA curve can be obtained if the baseline has the same heat transfer coefficient as the sample measurement. A new method of DTA measurement, called the "mass-difference baseline method" is thus proposed which uses the DTA curve of a small mass sample as baseline for another, larger mass sample. As a consequence, this method allows the quantitative measurement of the enthalpy changes over a wide range of temperatures using DTA.

This method has been successfully tested to determine the enthalpy changes of graphite and elastomers over the temperature range 30–600°C. A comparison of the measured heat capacity of graphite with the literature value shows a deviation of ±15%. Applying this method to measure the enthalpy change during the pyrolysis of NR, SBR and BR rubbers provided a detailed knowledge of the heat capacity, the heat of reaction and the heat of evaporation as a function of temperature over a wide temperature range. Such results have not been obtained using other thermal analysis methods to our knowledge.

In comparison with the DSC method, the proposed method using DTA for enthalpy measurement has the following advantages: (i) it is available for a wide range of experimental conditions, for example, high temperature, high pressure and vacuum; (ii) it can be used to measure the enthalpy change in an open system allowing simultaneous mass change, while DSC requires a constant sample mass during the measurements. As a consequence, it is easier to understand the chemical and physical mechanisms behind the enthalpy changes when DTA is combined with TGA. The disadvantages are twofold: (i) this method is less accurate than DSC for quantitative enthalpy measurements; (ii) it requires a preliminary knowledge of the specific heat of the sample at one temperature point, in order to calculate the enthalpy change over the entire range of temperatures.

5. Nomenclature

A	heat transfer area (m^2)
a	thermal diffusivity (m^2/s)
C_p	specific heat capacity (kJ/kg K)
H	enthalpy (kJ)
K	conversion factor
m	sample mass (kg)
Q	transition heat (kJ)
T	temperature (K)
T_∞	furnace temperature (K)
T_0	initial temperature of the sample (K)
t	time (s)

Greek letters

α	overall heat transfer coefficient (W/m^2 K)
β	heating rate (K/s)

Subscripts

p	sample pan
s	sample
r	reference

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