Determination of the Phase Transitions Enthalpy and the Polymers Degree of Crystallinity by Differential Scanning Calorimetry. Effects of the Calibration and Experimental Conditions

K. Gyurova, I. Petrova, A. Popov, V. Velev, H. Hristov, T. Angelov

Abstract* — By using of thermal analyzer STA 449 F3 Jupiter (NETZSCH – Germany), the effects of the calibration and experimental conditions on the enthalpy values of the polymorphous transitions and melting of KNO_3 were studied. The melting enthalpy and the degree of crystallinity of poly(ethylene oxide)(PEO) used as a solutions model for DSC analyses have been investigated. Similar data were obtained for a number of commercial crystallizing polymers (PP 6631, Hostaflon 1502, etc.). The thermo physical characteristics obtained by several types of DSC calibration by enthalpy curves are discussed. Were varied different experimental conditions and namely: heating rate – 5, 10 and 20 deg/min; crucibles – corundum or platinum; gaseous medium – air (static) or nitrogen (flowing at rate of 20 ml/min). Certain dependencies of the direction and degree of change of the studied characteristics from the calibration and experimental conditions were found, as well as for the temperature interval of the transformation.

Keywords: DSC, experimental conditions, phase transition enthalpy, calibration.

I. INTRODUCTION

Differential scanning calorimetry (DSC) is a method widely used for the investigation of polymeric materials [1-5]. The existing in the literature data pertaining to the determined by DSC thermal physicochemical transformations of substances are not always accompanied by data on all conditions of calibration and analysis. Therefore it is important to know to what extent the data obtained by characterization of new objects and comparative tests are comparable to the data obtained under different conditions of analysis and calibration as well as to each other or literary data. Typical for the thermal methods is the presence of multiple experimental factors that influence the obtained results [6-9].

Revised Manuscript Received on 30 March 2015.

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The principles and regulations for the DSC are given in UPAC Technical Report [10], etc. Thermal analysis practices show that it is not always possible to reproduce absolutely identical conditions of analysis and calibration, as well as to calibrate by enthalpy at any change of the analysis conditions. In some cases, it leads to significant errors while in others – the obtained data are not comparable. There are a number of studies devoted to finding the possible sources of errors and unreliability [11-15] in DSC analyses.

For the assessment of the comparability of the enthalpy of processes occurring under different conditions of calibration and analysis require multiple experiments. However, it should be noted that these studies are labor-intensive and multivariate which makes it quite difficult to carry out a sufficient number of experiments. The purpose of the present work is to contribute to clarify the influence of some experimental conditions on the values of enthalpy determined by DSC analysis in terms of comparability of the experimentally obtained values of the specific heats of phase transitions and polymers degree of crystallinity.

The selection of model compounds was carefully appointed with the aim of the experimental work related to physical transformations of organic polymers which usually occurs at temperatures below 300 -350°C.

II. EXPERIMENTAL

A. *Materials*

The main model compounds used in the study were standard KNO_3 and nascent PEO and, for comparison, several of the well known commercial polymer brands.

KNO_3–p.a., Fluka. The temperatures, ΔH of polymorphous transition and melting were calculated and established using data from DSC analyses carried out under different conditions (Table 1 and Fig.1).

PEO - produced by “Neochim”, Dimitrovgrad, Bulgaria with Mm=1.8x 10^6, obtained viscometrically. Its crystallinity degree (α =79.5%, reference data) was calculated using the melting heat of 100 % crystalline polymer (222 J/g) and ΔH for melting of the polymer studied was calculated and established using data from DSC analyses performed under different conditions (Table 2 and Fig.2).

The polymer used – poly (propylene) - PP 6631 (Fig.3), super high density poly(ethylene) – SHDPE and HDPE are produced by "Lukoil-Neftochim-Burgas, and PEPTFE-Hostaflon 1502, produced in Germany.

B. Methods

Using the thermal analyzer STA 449 F3 Jupiter TG/DSC/DTA (NETZSCH – Германия) with the thermocouple type S, the effect of calibration and experimental conditions on the values of the enthalpies of the polymorphous transition and melting of KNO_3 and the enthalpy of melting and degree of crystallinity α, % of poly(ethylene oxide), used as model compounds in DSC analyses. For comparison, similar data were obtained for a number of commercial brands of crystallizing polymers (PP 6631, SHDPE, HDPE, Hostaflon 1502, etc.).

C. Methodology

The effects of the following experimental factors were studied:

The ways of calibration by enthalpy of DSC curves:

- by melting of 6 standard metals – In, Sn, Bi, Zn, Al, Au – in corundum crucibles;

- by sapphire with ø = 5.2 mm, d = 1 mm – in corundum crucibles;

- by sapphire with ø = 6.0 mm, d = 1 mm – in platinum crucibles;

The calibrations are made by heating rate 20 deg/min in corundum crucibles and air (static) medium.

Two kinds of crucibles for the analyses:

- corundum, equipped with a lid with small opening in it;

- platinum equipped with a lid with small opening in it.

Three heating rates: 5, 10 and 20 deg/min. Two kinds of gaseous medium: air (static) and nitrogen (20 ml/min).

The average per cent deviations, ±d, % of the experimental values obtained (from 3 analysis runs) compared to the data generally accepted in the literature [6,7,10,11,16] training material of NETZSCH] on the temperatures and enthalpies of the thermal transformations and etc. were determined.

III. RESULTS AND DISCUSSION

It can be seen from the DSC curves presented and the phase transition heats determined from them under different calibrations (Figs.1 and 2, tables 1 and 2) that the data obtained after calibration with metals were comparable to these obtained after calibration with sapphire performed in corundum crucibles. Much higher differences in enthalpy values were observed by changing the crucibles used for calibration or analysis. Besides, at this stage of the studies, there are indications that the temperature interval of the transformation observed is not insignificant so far as possible notion divergence from the reference values is concerned. Further deeper studies are expected to elucidate whether this concept has enough grounds.

For calibration in corundum and analysis in corundum crucibles at low temperature transformations, (up to 200°C), the maximal divergence observed was d = ±2 % while at temperatures higher than 300°C it could exceed d = -15 % with the direction being towards values lower than the reference ones.

For the calibration in corundum and analysis in platinum crucibles, however, the dependence of the deviation of the transformation temperature absolute value was the opposite – it was higher at lower temperatures, an average of d = +15 % and lower at higher temperatures, an average of d = +5 % but, in both cases, its direction was towards higher values than these generally accepted in the literature.

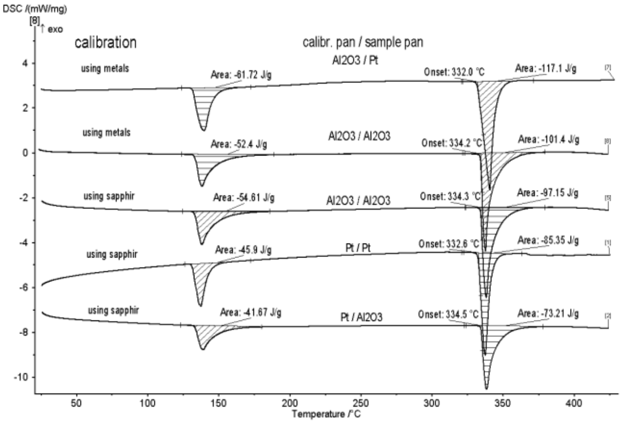

Fig. 1. DSC plots of KNO_3, obtained by 20 deg/min and different conditions of calibration and analysis.

For calibration in platinum and analysis in corundum crucibles, an average values of d = 7 % was observed in the low temperature region while in the high temperature region it was up to d = -20%. For the calibration in platinum crucibles and analysis in corundum ones, the divergences were higher in direction of decrease, especially at higher temperatures with an average of d = - 25 %. In these cases, the results were slightly better at heating degree of 10 than these at 5 and 20 deg/min.

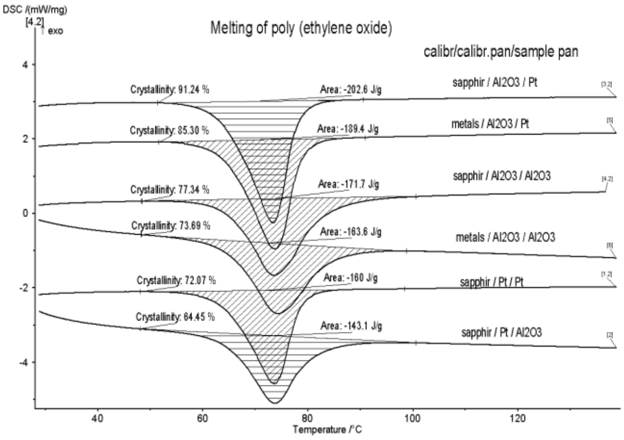

Fig. 2. Original DSC plots of PEO, obtained by 10 deg/min and different conditions of calibration and analysis.

Received data for some polymers:

PP-6631, $T_m = 165^0$ C; α = 41% (cal. in corundum – anal. in Pt); α = 35% (cal. and anal. in Pt.); (35-45% ref.data).

SHDPE, $T_m = 142^0$ C; α = 70% (cal. in corundum – anal.in Pt); α = 56% (cal. and anal. in Pt); (65-70% ref.data).

HDPE, $T_m = 140^0$ C; α = 65% (cal. in corundum – anal. in Pt); (60-65% ref. data).

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"Hostaflon" 1502, $T_m = 340^0$ C; α = 88.33% (cal. in corundum – anal. in Pt), (80-90%, ref.data).

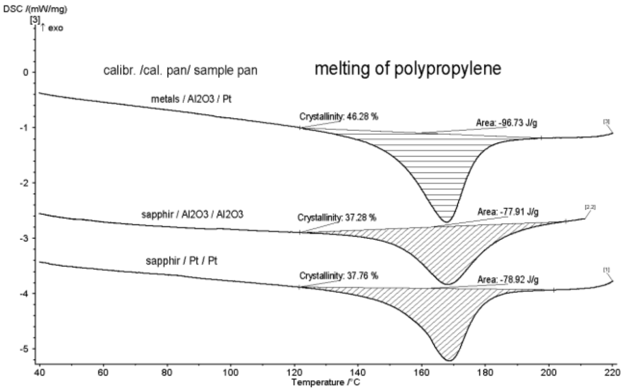

Fig. 3. Original DSC plots of PP-6631, obtained by 20 deg/min and different conditions.

The results obtained can be explained with the higher heat conductivity of platinum compared to corundum, which in some cases, plays a positive role and could compensate for the deviation while in others it could result in loss of heat.

These effects might superpose inducing further heat loss in the environment due to deformation of the platinum crucibles and/or poor lid tightening. In this respect, the corundum crucibles appear to be more steadfast, although more inert, and the results may be considered to be more reliable. The change of heating rate might also contribute to limiting the heat loss. The DSC curves of KNO_3 presented are another illustration of the effects of the material of analysis crucibles on the shape of the thermal effects. If both the calibration and analyses are carried out in platinum crucibles, thermal effects of the highest symmetry and best defined beginning and end are observed.

Table 1. Thermal characteristics of KNO_3, obtained by different conditions of calibration and analysis

Heating rate	Calibration	Calibration pans	Sample pans	N_2, ml/min P1 - PG	Onset$_{tr}$ °C	ΔH$_{tr}$, J/g (±d, %)	Onset$_m$° C	ΔH$_m$	
								J/g	(±d, %)
	Refer. data				128.0	-53.8 0	337.0	-117.6	(0)
	ΔH	Al2O3	Pt	-	131.5	-61.1 (+13)	332.0	-116.9	(-0.6)
		Al2O3	Al2O3	-	133.4	-53.0 (-0.1)	334.2	-100.3	(-14)
20 deg/min	c_p - sapphire	Pt	Pt	-	131.9	-49.6 (-7.8)	332.7	-88.3	(-24)
	Ø6 mm	Pt	Al2O3	20 - 20	133.2	-45.6 (-15)	334.5	-74.2	(-36)
	c_p - sapphire	Al2O3	Pt	-	131.4	-64.8 (+20)	333.8	-124	(+0.5)
	Ø5.2 mm	Al2O3	Al2O3	-	132.6	-53.2 (-0.9)	334.0	-91.2	(-22)
		Al2O3	Al2O3	20 - 20	133.0	-54.7(+1.6)	334.3	-97.2	(-17)
	ΔH	Al2O3	Pt	20 - 20	131.2	-63.9 (+18)	333.7	-129.5	(+10)
		Al2O3	Al2O3	20 - 20	132.4	-51.4 (-4.5)	333.7	-103.2	(-12)
10 deg/min	c_p - sapphire	Pt	Pt	20 - 20	132.0	-51.1 (-5)	333.5	-96.7	(-17)
	Ø6 mm	Pt	Al2O3	20 - 20	132.4	-51.4 (-4.5)	333.7	-103.2	(-12)
	c_p - sapphire	Al2O3	Pt	20 - 20	132.6	-66.4 (+23)	333.4	-127.7	(+8)
	Ø5.2 mm	Al2O3	Al2O3	20 - 20	132.1	-52.5 (-2)	333.5	- 96.2	(-18)
	ΔH	Al2O3	Pt	20 - 20	131.6	-61.5 (+14)	333.5	-122.5	(+4)
		Al2O3	Al2O3	20 - 20	131.3	-49.4 (-8)	333.5	-95.1	(-19)
5 deg/min	c_p - sapphire	Pt	Pt	20 - 20	131.5	-49.1 (-8.5)	333.7	-90.8	(-22)
	Ø6 mm	Pt	Al2O3	20 - 20	130.9	-39.7 (-26)	333.5	-78.9	(-32)
	c_p - sapphire	Al2O3	Pt	20 - 20	130.9	-60.8 (+13)	334	-119.8	(+2)
	Ø5.2 mm	Al2O3	Al2O3	20 - 20	131.2	-52.3 (-2.5)	333.6	-95.8	(-18)

Table 2. Thermal characteristics of KNO_3, obtained by different conditions of calibration and analysis.

Heating rate	Calibration	Calibration pans	Sample pans	N_2, ml/min P1 - PG	Onset$_{tr}$ °C	ΔH$_{tr}$, J/g (±d, %)	Onset$_m$ °C	ΔH$_m$	
								J/g	(±d, %)
	Refer. data				128.0	-53.8 0	337.0	-117.6	(0)
	ΔH	Al2O3	Pt	-	131.5	-61.1 (+13)	332.0	-116.9	(-0.6)
		Al2O3	Al2O3	-	133.4	-53.0 (-0.1)	334.2	-100.3	(-14)
20 deg/min	c_p - sapphire	Pt	Pt	-	131.9	-49.6 (-7.8)	332.7	-88.3	(-24)
	Ø6 mm	Pt	Al2O3	20 - 20	133.2	-45.6 (-15)	334.5	-74.2	(-36)
	c_p - sapphire	Al2O3	Pt	-	131.4	-64.8 (+20)	333.8	-124	(+0.5)
	Ø5.2 mm	Al2O3	Al2O3	-	132.6	-53.2 (-0.9)	334.0	-91.2	(-22)
		Al2O3	Al2O3	20 - 20	133.0	-54.7(+1.6)	334.3	-97.2	(-17)
	ΔH	Al2O3	Pt	20 - 20	131.2	-63.9 (+18)	333.7	-129.5	(+10)
		Al2O3	Al2O3	20 - 20	132.4	-51.4 (-4.5)	333.7	-103.2	(-12)
10 deg/min	c_p - sapphire	Pt	Pt	20 - 20	132.0	-51.1 (-5)	333.5	-96.7	(-17)
	Ø6 mm	Pt	Al2O3	20 - 20	132.4	-51.4 (-4.5)	333.7	-103.2	(-12)
	c_p - sapphire	Al2O3	Pt	20 - 20	132.6	-66.4 (+23)	333.4	-127.7	(+8)
	Ø5.2 mm	Al2O3	Al2O3	20 - 20	132.1	-52.5 (-2)	333.5	- 96.2	(-18)
	ΔH	Al2O3	Pt	20 - 20	131.6	-61.5 (+14)	333.5	-122.5	(+4)
		Al2O3	Al2O3	20 - 20	131.3	-49.4 (-8)	333.5	-95.1	(-19)
5 deg/min	c_p - sapphire	Pt	Pt	20 - 20	131.5	-49.1 (-8.5)	333.7	-90.8	(-22)
	Ø6 mm	Pt	Al2O3	20 - 20	130.9	-39.7 (-26)	333.5	-78.9	(-32)
	c_p - sapphire	Al2O3	Pt	20 - 20	130.9	-60.8 (+13)	334	-119.8	(+2)
	Ø5.2 mm	Al2O3	Al2O3	20 - 20	131.2	-52.3 (-2.5)	333.6	-95.8	(-18)

In calibration is carried out in corundum crucible and analysis in platinum one, the symmetry is not so prominent but the beginning and the end are not affected.

Under calibration in platinum crucible and analysis in corundum one, the peak beginning is not affected while the end is prolonged like in the case when both the analysis and calibration are performed in corundum crucible. Thus, the present study shows once again that the beginning of certain physical effect can be used by researchers in comparative analysis. This, of course, is true for polymers too although it is not so obviously.

VI. CONCLUSION

The initial results obtained from a methodical study on the optimization of the experimental conditions and methods of DSC curves calibration using the enthalpy are presented aiming to determine the specific heats of phase transitions and the degree of crystallinity of polymers. Standard KNO_3 and PEO were used as the main model compounds.

The results obtained so far were considered enough to formulate the following conclusions:

1. The highest effect on the values of enthalpy exerted the type of crucibles used for the analysis.

1.1. By calibration with sapphire in corundum crucible, the results obtained were close to these obtained by calibration with pure metals in corundum crucible.

1.2. The calibrations and analyses in corundum crucibles should preferably be carried out at temperatures below 200°C

while at higher temperatures the calibrations should be carried out in corundum crucibles but the analyses – in platinum ones.

1.3. The highest possibility of errors (more than 20%) over the whole temperature interval showed the calibration in platinum crucibles and analysis in corundum ones but at high temperatures – the analysis in platinum crucibles, too. It is important to take into account the possible deformations and insufficient tightening of the platinum crucibles lid which leads to loss of heat.

1.4. If the aim is to obtain symmetric and well-shaped thermal effects, the analysis is better be carried out in platinum crucibles while the calibration could be performed in corundum ones. For analyses in corundum crucibles, the end of the thermal effects is significantly prolonged while their beginning is not affected.

2. Due to the multi-variance of the thermal analyses, the methodical studies are quite laborious and time consuming but they appear to be valuable with respect to thermal analysis practices. They should be carried on aiming to find possibilities to reduce data divergence.

ACKNOWLEDGMENT

Part of the present work has been supported by Grants-2015 from Fund for Scientific Research of Konstantin Preslavsky University, Shumen.

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