Thermochimica Acta, 190 (1991) 155–161
Elsevier Science Publishers B.V., Amsterdam

The identification of blowing agents in cellular PVC compounds by DSC
Part 1. The detection and identification of sodium bicarbonate

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(Received 27 February 1991)

Abstract

The determination of sodium bicarbonate concentrations in PVC cellular compounds by DSC has revealed a linear relationship between concentration and the decomposition enthalpy of the compound Both the detection limit and the sensitivity of the method are reported Furthermore, it is shown that the detection limit is significantly less than the concentration of the compound known to be present in typical cellular polymer formulations Therefore, the DSC method described herein could be used for the analysis and quality control of sodium bicarbonate in PVC cellular compounds.

INTRODUCTION

Cellular PVC usually has a foam-like core surrounded by a solid layer or skin. This cellular structure is often achieved by the incorporation of chemical blowing agents into the parent compound. On heating, usually during processing, these blowing agents decompose generating a gas within the molten PVC which on expansion and cooling produces a foam-like structure.

The identity and amount of blowing agent determines the physical nature of the cellular structure and thereby the properties of the final product. A method for the qualitative and quantitative determination of blowing agents in cellular PVC powder compound before processing is therefore necessary, especially for quality control purposes.

For the analysis of low levels (approx. 1–2%) of blowing agent in cellular PVC compounds, DSC offers the advantages of (a) no sample pretreatment, and (b) specificity. These should reduce the likelihood of interference in the determination by other additives present in the compound.

The work described here is concerned with the development of a method using DSC for the detection and quantitative analysis of sodium bicarbonate, a common blowing agent in cellular PVC powder compounds.

0040-6031/91/$03 50

EXPERIMENTAL

DSC

A Mettler TA 3000 system, consisting of a DSC 20 high-sensitivity furnace, was used. The furnace atmosphere was flowing nitrogen (46–52 cm^3 min^{-1}) and the heating rate was 5 °C min^{-1}. Sample masses (11.3 mg) were contained in boat-shaped aluminium pans (supplied by Mettler) with crimped lids which had two holes pierced through them. The reference consisted of an empty pan with a crimped lid also with two holes. The temperature range for each analysis was from 50 to 200°C.

Sample materials

The sodium bicarbonate (Hydrocerol) was supplied by Boehringer Ingelheim Chemicals [1]. A range of cellular PVC compounds consisting of different concentrations of sodium bicarbonate (0%, 0.5%, 1.0%, 1.3%, 1.5% and 2.0% Hydrocerol) were made, based on a typical formulation as given in Table 1. Each of the above compounds was prepared by weighing into a large pan, and then mixing in a small Henschel high-speed mixer of 3 kg capacity.

In addition, a production sample of cellular PVC powder compound was supplied by Hydro Polymers Ltd.

RESULTS AND DISCUSSION

Each individual compound containing sodium bicarbonate was analysed five times by DSC to obtain a mean value for the "blowing enthalpy", ΔH_B (given in Table 2).

Similar measurements were performed on the compound without sodium bicarbonate to confirm the absence of any competing thermal event near to that produced by the blowing agent.

TABLE 1

Typical composition of cellular compound containing sodium bicarbonate

Material	Composition (%)
Resin	87.5
Process aid	5.2
Filler	1.8
Lubricant	1 1
Stabiliser	1 3
Pigment	1 8
Blowing agent	1 3

TABLE 2

Variation of enthalpy with sodium bicarbonate concentration in PVC cellular compound

Conc (%)	Enthalpy (J g^{-1})				T_p (°C)		
	x_i	$\bar{x}$	s_x	%RSD	x_i	$\bar{x}$	s_x
0 5	2 2279				156.2		
0.5	2 2541	2 4030	0 1708	7 1	158 7	158 0	1.1
0.5	2.4362				158.2		
0.5	2.6494				157 6		
0.5	2 4476				159 1		
1.0	5 1495				154 6		
1.0	3 4540	3 9217	1 2390	31.6	154 7	154 8	0.8
1.0	5 3440				155.5		
1.0	2.7607				155 6		
1 0	2.9004				153 7		
1 3	4.1079				146 0		
1 3	5 2198	4 4862	0 4752	10 6	147 8	148.1	1.3
1 3	4 5513				148 3		
1 3	4 0218				148.9		
1 3	4 5303				149.3		
1 5	5 7372				151 8		
1.5	6.1315	6.1331	0 2480	4 0	151.1	151 7	1 0
1 5	6.4143				151.7		
1.5	6 2331				153 2		
1.5	6.1485				150.5		
2.0	7.7470				146 5		
2 0	6.4185	7 3603	0.7172	9.7	147 0	147.2	0 5
2 0	6 8911				147 3		
2 0	7 5006				147.2		
2 0	8 2441				147 8		

The major endothermic peak was identified as the sodium bicarbonate decomposition in the cellular compound, as the enthalpy, ΔH_B, of this peak increases with increasing concentration of sodium bicarbonate (see Table 2 and Fig. 1).

Because activators have no influence on sodium bicarbonate [2], the peak temperature, T_p, for pure sodium bicarbonate should be approximately the same as that for sodium bicarbonate in the cellular compound [3]. However, the results show that T_p exhibits a 14°C shift to a higher temperature, for the 0.5% sodium bicarbonate concentration, compared to that of the pure sodium bicarbonate. This shift is most likely due to the low concentration of sodium bicarbonate in the compound and to the fact that the thermal event is diffusion controlled. Consequently, as the concentration of sodium bicarbonate is increased, T_p approaches the value for pure sodium bicarbonate, 144°C; and at the 2.0% level, the mean T_p shift is only 3°C (147.2°C, Table 2). Therefore, the T_p shift is thought to be a dilution effect and not due to the presence of activators.

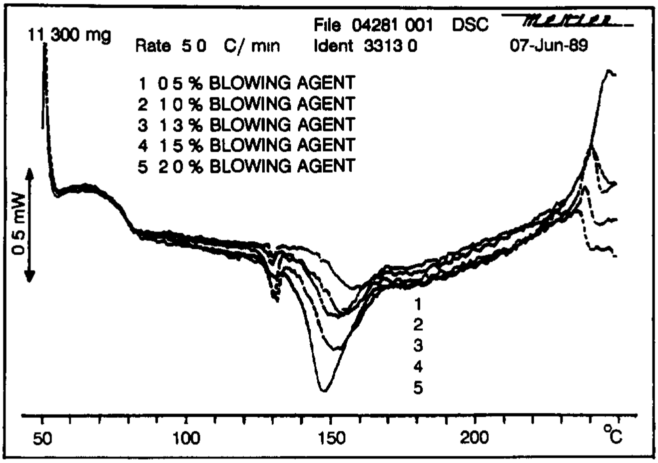

Fig. 1. DSC curves of 0 5, 1 0, 1.3, 1.5 and 2.0% sodium bicarbonate in PVC cellular compound

A plot of mean ΔH_B against % concentration of sodium bicarbonate in PVC cellular compound was obtained using a computer graphics program and all of the experimental data in Table 2. This gave a best line-fit through the plotted points, and error bars were drawn based on the % relative standard deviation (%RSD), given in Table 2. The regression plot also shows a 95% confidence limit around the line (illustrated in Fig. 2). These errors are thought to be due to the non-homogeneity of the mixed compound.

The linear relationship was found to be

$$y = 0.5817 + 3.3962x \qquad (1)$$

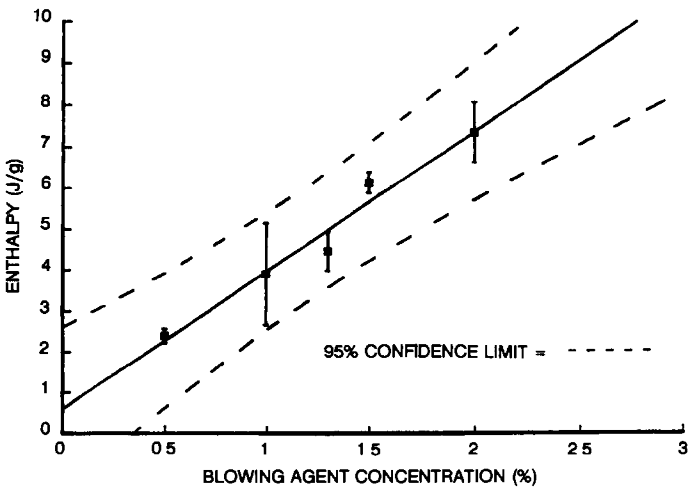

Fig 2 Calibration curve for sodium bicarbonate in PVC cellular compound

TABLE 3

Statistical values obtained from the sodium bicarbonate data

Statistical function [4]	Calculated value
n, number of measurements	25
Intercept, a, on y-axis	0.58
Standard deviation of the intercept, S_a	0.38
Slope, b	3.40
Standard deviation of the slope, S_b	0 29
Correlation coefficient, r	0.9265

where y is the enthalpy of the decomposition for the blowing agent (J g^{-1}) and x is the concentration of the blowing agent (%); the calculated statistical parameters are given in Table 3. This equation was used to obtain the limit of detection, and to determine the concentration of the blowing agent in a production sample by interpolation (see text below). However, an estimate of the random errors [4] associated with the slope and intercept is of interest, and these values are given in Table 3.

These results show that the random errors are large for both the slope, b (% RSD = 17.5%), and intercept, a (% RSD = 136.1%). This is most probably due to the fact that the linear equation was determined from values obtained around the instrumental limit of detection where errors are likely to be large, especially in a.

The detection limits for sodium bicarbonate in the PVC cellular compound were determined [5,6] as 0.7% (99.7% confidence) and 0.5% (95%

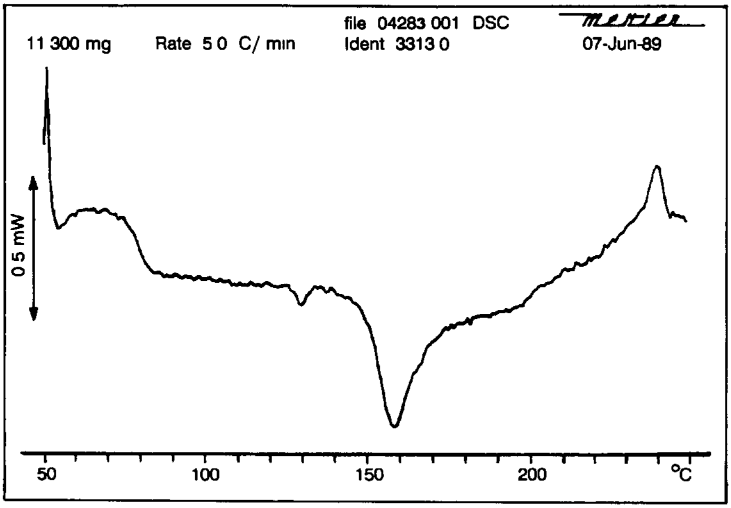

Fig. 3. DSC curve for sodium bicarbonate in production PVC cellular compound.

TABLE 4

Blowing enthalpy values, ΔH_B (J g^{-1}), of sodium bicarbonate in production PVC cellular compound

Measured	Mean	Standard deviation
5 44 5 74	5.59	±0.21

confidence) and the method's sensitivity, i.e. the slope of the calibration graph, was found to be 3.40 J g^{-1} $\%^{-1}$.

This limit of detection, even at the 95% confidence level, is well below the sodium bicarbonate concentration expected in typical cellular PVC compound formulations (1.3%, given in Table 1). However, confirmation of this and the practicality of the method was determined by the analysis of a production sample.

Determination of sodium bicarbonate in a production sample of PVC cellular compound

A typical production sample was analysed twice using this method and the DSC curve is illustrated in Fig. 3. Tables 4 and 5 present the results of these analyses. The obtained value of 1.50% sodium bicarbonate is in good agreement with the expected formulation value of 1.3% for a typical cellular compound formulation. The relative error of 15.4% is most likely due to the inaccuracies associated in weighing and mixing the formulation.

FINAL COMMENTS

The DSC examination of a PVC cellular compound showed the expected linear relationship between concentration of sodium bicarbonate (Hydrocerol) and enthalpy of decomposition, with a detection limit of 0.5% and sensitivity of 3.40 J g^{-1} $\%^{-1}$ (using 95% confidence).

The peak temperature, T_p, value for the decomposition varied according to the concentration of sodium bicarbonate in the cellular compound.

TABLE 5

Concentration of sodium bicarbonate found in production PVC cellular compound

Expected conc (%)	Conc. found (%)	Standard deviation [7] (%)	Relative error (%)
1 3	1.50	0.22	15 4

Therefore, in an unknown cellular compound only tentative identification of sodium bicarbonate is possible using T_p alone; additional confirmation must be obtained from the enthalpy of decomposition.

The results show that a DSC method can be established using the conditions given in the experimental section above, for the quantitative and qualitative analysis of sodium bicarbonate in cellular compounds.

The detection limit of 0.5% (95% confidence) is significantly below the level known to be present in typical cellular compound (i.e. 1.3%). Therefore, this DSC method could be used for quality control of batches of compound before release to customers, and for the examination of any material supplied by customers for investigation.

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