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Identification of blowing agents in cellular PVC compounds by DSC.
Part 2. The detection and identification of azodicarbonamide

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Abstract

The determination by DSC of azodicarbonamide concentrations in PVC cellular powder formulations revealed a linear relationship between concentration and the decomposition enthalpy of the compound. Both the detection limits and the sensitivity of the method are reported. Furthermore, it has been shown that the enthalpy of azodicarbonamide decomposition is affected by cellular PVC compound formulation. This effect has produced an artificially high detection limit and lowered the sensitivity of the method in respect of the detection of azodicarbonamide in the polymer blend. As a result, the quantitative DSC method described herein is limited to azodicarbonamide concentrations above 0.5 wt.% in cellular PVC formulations.

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 formulation. 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 [1].

The identity and the amount of blowing agent determine the physical nature of the cellular structure and thereby the properties of the final

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product. A method for the qualitative and quantitative determination of blowing agents in the cellular PVC powder formulation before processing is therefore desirable, especially for quality control purposes.

The analysis of low levels (≈1–2%) of the blowing agent sodium bicarbonate in cellular PVC powder formulations has been achieved by DSC [2].

The work described here is concerned with the development of a method for the detection and quantitative analysis of azodicarbonamide (ADA), a common organic blowing agent in cellular PVC powder formulations, using DSC.

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 (13.5, 35 and 85 mg) were contained in boat shaped aluminium pans (supplied by Mettler) with crimped lids which had two holes pierced through. The reference consisted of an empty pan, again with a crimped lid with two holes pierced through. The temperature range for each analysis was 100–400°C.

Sample materials

The ADA used (Fig. 1) was a Genitron grade supplied by Schering Industrial Chemicals [3]. A range of cellular PVC mixture having different concentrations of ADA (0%, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 1.2% and 1.4%) was made, based upon a typical formulation as given in Table 1. Each of the above mixtures was prepared by weighing into a large pan, followed by mixing in a small Henschel high speed mixer of 3 kg capacity.

In addition, samples were made which consisted of different concentrations of ADA (0.6%, 0.8%, 1.0%, and 1.2%) in PVC resin.

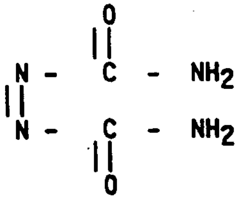

Fig. 1. Azodicarbonamide.

TABLE 1

Typical composition of cellular formulation containing ADA

Material	Composition (%)
Resin	76.5
Process aid	9.6
Impact modifier	2.9
Filler	2.9
Lubricant	1.2
Stabiliser	3.7
Pigment	2.8
Blowing agent (azodicarbonamide)	0.4

RESULTS AND DISCUSSION

Determination of detection limit and sensitivity

Each individual mixture containing ADA was analysed five times by DSC to obtain a mean value for the "blowing enthalpy" ΔH_B (Table 2). Similar measurements were performed on the mixture without ADA in order to confirm the absence of any competing thermal event near to that produced by the blowing agent.

The exothermic peak at 172°C seen in the DSC curves of the mixtures (Fig. 2) is due to ADA decomposition; the enthalpy ΔH_B, of this peak increases with increasing concentration of ADA (Table 2). The exothermic peak at 225°C is a constant feature of the PVC formulation (Table 1).

It is known that certain catalysts will reduce the decomposition temperature of ADA from around 200 to 170–190°C, with an increase in the rate of decomposition. These catalysts include zinc, cadmium and lead compounds, such as stearates and octoates, present as stabilisers in PVC formulations [3–5]. Hence the lowering of the decomposition temperature of ADA from 219°C (for pure ADA) [6] to 172°C in the mixtures is thought to be due to a catalytic effect caused by the heavy metal stabiliser present in the polymer.

A plot of mean ΔH_B against ADA concentration (%) in PVC cellular mixtures 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; error bars were drawn based upon the percentage relative standard deviation (%RSD), as given in Table 2. The regression plot (illustrated in Fig. 3) also shows the 95% confidence limits around the line. These errors are thought to be due to the non-homogeneity of the mixtures.

The linear relationship was found to be

$$y = 4.6715x - 1.8850$$

TABLE 2

Variation of enthalpy with ADA concentration in PVC cellular mixture, using small sample pans (sample mass 13.5 mg)

Conc. (%)	Blowing enthalpy ΔH_B (J g^{-1})				Peak temperature T_p (°C)		
	x_i	$\bar{x}$	S_x	%RSD	x_i	$\bar{x}$	S_x
0.6	0.7783				ND		
0.6	0.7792	0.6470	0.2626	40.6	ND		
0.6	0.9396				ND		
0.6	0.3478				ND		
0.6	0.3902				ND		
0.8	1.3046				175.2		
0.8	1.7305	2.0079	0.4961	24.7	173.2	173.2	1.2
0.8	2.2875				172.8		
0.8	2.1475				172.8		
0.8	2.5695				172.2		
1.0	2.3638				173.3		
1.0	3.1388	3.0838	0.4125	13.4	170.6	171.5	1.2
1.0	3.2171				170.8		
1.0	3.3546				170.6		
1.0	3.3446				172.3		
1.2	3.7466				173.8		
1.2	3.3662	3.7420	0.6979	18.7	173.0	173.2	0.6
1.2	4.9295				172.2		
1.2	3.5121				173.7		
1.2	3.1555				173.3		
1.4	4.6526				170.6		
1.4	4.2751	4.4514	0.1620	3.6	170.7	171.2	0.6
1.4	4.4379				171.7		
1.4	4.3171				171.8		
1.4	4.5745				171.3		

Key: ND, not determined because of the broad flat peak.

where y = enthalpy of decomposition for the blowing agent (J g^{-1}) and x = concentration of the blowing agent (%). The calculated statistical parameters are given in Table 3.

The above equation was used to obtain the detection limit and sensitivity of the method. However, an estimate of the random errors [7] associated with the slope and intercept is of interest, and these values are given in Table 3. These errors are large for both the slope b (%RSD = 7.0%) and the intercept a (%RSD = 80.6%). This is most probably due to the fact that the linear equation was determined from values which were obtained in the region of the instrumental detection limit, where errors are more likely to be large, especially in a.

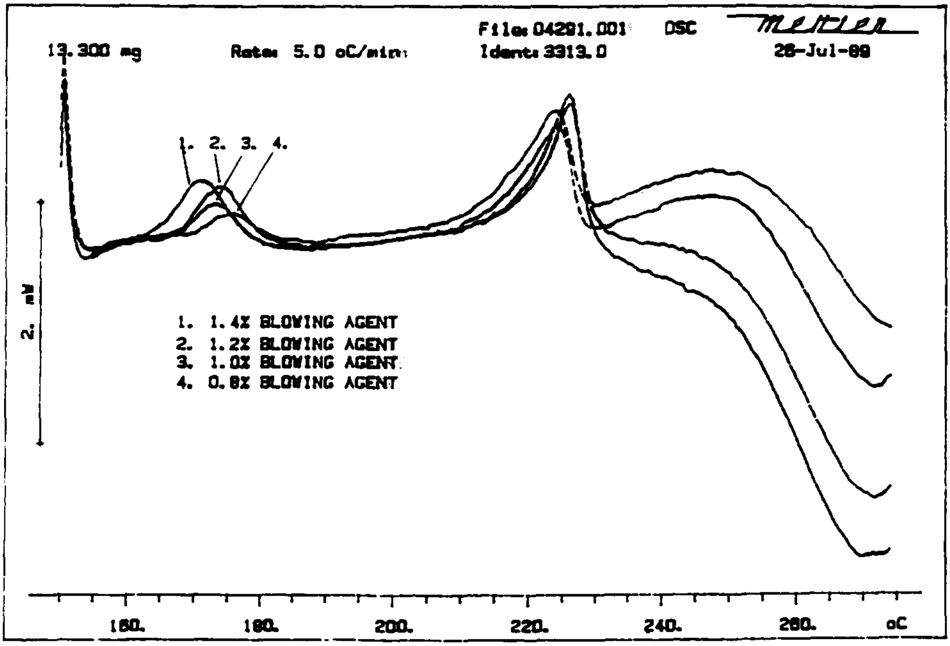

Fig. 2. DSC curves of 0.8%, 1.0%, 1.2% and 1.4% ADA in PVC cellular mixture (sample mass 13.5 mg).

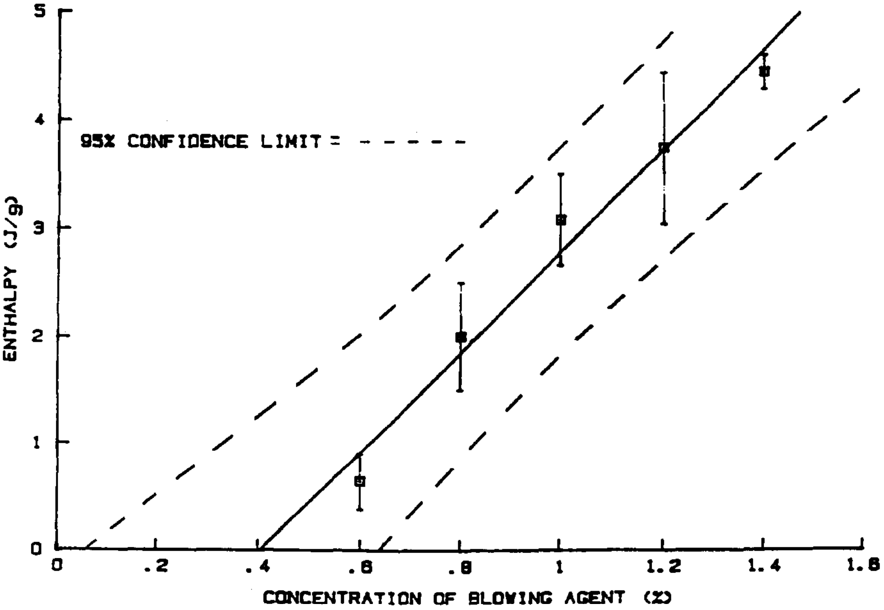

Fig. 3. Calibration curve for ADA in PVC cellular mixture using small sample pans (sample mass 13.5 mg).

TABLE 3

Statistical values obtained from the ADA data using small sample pans (sample mass 13.5 mg)

Statistical function [6]	Calculated value
Number of measurements n	25
Intercept a on y axis	−1.89
Standard deviation S_a of the intercept a	0.73
Slope b	4.67
Standard deviation S_b of the slope b	0.16
Correlation coefficient r	0.9459

The detection limit for ADA in the PVC cellular mixture studied was determined [8, 9] as 0.7% (95% confidence), and the method's sensitivity, i.e. the slope of the calibration graph, as 4.67 J $g^{-1}\%^{-1}$. This detection limit is above the 0.4% ADA concentration found in typical cellular PVC formulations (Table 1). Furthermore, according to the calculated sensitivity, 1.0% ADA should produce a decomposition enthalpy of 4.67 J g^{-1}. However, in practice a mean value of 3.08 J g^{-1} was measured (Table 2). This seems to suggest the possibility of a chemical reaction between ADA and a component of the mixture which effectively suppresses the ADA decomposition enthalpy. This suppression of ADA causes the calibration line to be shifted downwards to lower enthalpy levels, without affecting the slope of the line but producing a negative intercept. This effect is highlighted when comparing the calibration curves of ADA–PVC cellular mixes and ADA–PVC resin mixes (see discussion below).

A possible reason for the above effect may be ligation of ADA, via the lone pair electrons on the azo nitrogens [10], with one of the metals in the mixture, such as copper, which is present as the phthalocyanine complex

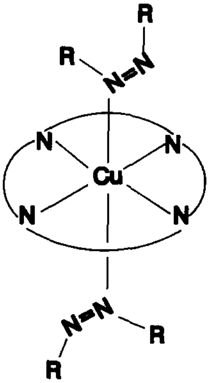

Fig. 4. Octahedral structure of ADA and copper phthalocyanine complex.

at low levels as a pigment. There are two possible sites for ADA to form an octahedral complex with copper phthalocyanine (Fig. 4). This makes the copper phthalocyanine pigment most favourable for the apparent reduction of ADA concentration in the mixture. Consequent upon ADA decomposition, only the non-ligated ADA contributes to the decomposition enthalpy, causing a reduction in the expected enthalpy.

In order to confirm this effect and improve the limit of detection, two procedures were carried out: (i) comparison of the results obtained for ADA decomposition in cellular PVC mixes with the results obtained for ADA in PVC resin, in the absence of metals; and (ii) increasing the sample mass by using larger sample pans.

Investigation into improving the detection limit

Because the detection limit of 0.7% (determined above) is rather high, larger sample masses (85 mg) were used to try and improve this. Again, as with the smaller sample masses, each mixture was analysed five times on the DSC. The results are tabulated in Table 4.

By increasing the sample mass from 13.5 to 85 mg the sensitivity was seen to improve (see discussion below) and a concentration of 0.4% of ADA was detected. However, concentrations of 0.2% and below were not detectable, and the suppression of enthalpy was still apparent, giving a negative intercept (Fig. 5) on the y axis.

The linear relationship for the larger samples was found to be

$$y = 5.9617x - 2.2888$$

where y = enthalpy of the decomposition for the blowing agent ($\mathrm{J\ g^{-1}}$) and x = concentration of the blowing agent (%); the calculated statistical parameters are given in Table 5.

These results again show large random errors for the slope b and the intercept a, although there is an overall improvement in precision when compared with the analysis at smaller mass, as indicated by the respective %RSD values. For the slope b, the large mass %RSD was 5.7%, and the small mass %RSD was 7.0%. For the intercept a, the large mass %RSD was 13.6%, and the small mass %RSD was 80.6%.

The detection limit using the larger mass was found to be 0.16% of ADA (95% confidence). However, a study of the curve (Fig. 5) suggests that the calculated detection limit of 0.16% is not realistic, as the results indicate that a concentration of 0.2% cannot be detected! This detection limit appears to be low because of a large negative intercept in the detection limit equation [7, 8]. Therefore, for this particular method, a more sensible definition of detection limit is required than that used above.

TABLE 4

Variation of enthalpy with ADA concentration in PVC cellular mixture, using large sample pans (sample mass 85 mg)

Conc. (%)	Blowing enthalpy ΔH_B (J g^{-1})				Peak temperature T_p (°C)		
	x_i	$\bar{x}$	S_x	%RSD	x_i	$\bar{x}$	S_x
0.4	0.2733				183.9		
0.4	0.1885	0.2400	0.0459	19.1	184.1	183.8	1.0
0.4	0.2158				182.3		
0.4	0.3010				183.7		
0.4	0.2213				185.0		
0.6	0.9414				178.7		
0.6	0.8000	0.9698	0.1479	15.3	180.4	179.4	0.6
0.6	1.1613				179.0		
0.6	1.0759				179.5		
0.6	0.8703				179.3		
0.8	2.6644				173.7		
0.8	2.3515	2.5093	0.1261	5.0	174.1	173.7	0.4
0.8	2.5943				173.1		
0.8	2.5133				173.8		
0.8	2.4230				173.9		
1.0	4.4376				171.1		
1.0	3.5365	3.9269	0.3433	8.7	172.7	171.9	0.6
1.0	3.6982				172.1		
1.0	3.9786				171.8		
1.0	3.9836				171.6		
1.2	4.6969				173.1		
1.2	5.1907	4.8240	0.2500	5.2	173.3	173.5	0.3
1.2	4.5685				173.8		
1.2	4.9623				173.6		
1.2	4.7015				173.7		
1.4	6.0767				171.0		
1.4	5.7179	5.9903	0.3789	6.3	171.2	171.0	0.2
1.4	5.7578				170.7		
1.4	6.6184				170.9		
1.4	5.7806				171.1		

It may be more sensible [9] to use the x intercept value, instead of the y intercept value, in calculating the detection limit. Then, by adding two standard deviations ($2S_a$) [7] to this intercept, the detection limit can be expressed with 95% confidence. This definition is illustrated in Fig. 6. Using this definition, the limit of detection becomes 0.49% of ADA (95% confidence).

The sensitivity of this method using large sample masses has been improved to 5.96 J g^{-1} $\%^{-1}$. This suggests that a 1.0% ADA concentration

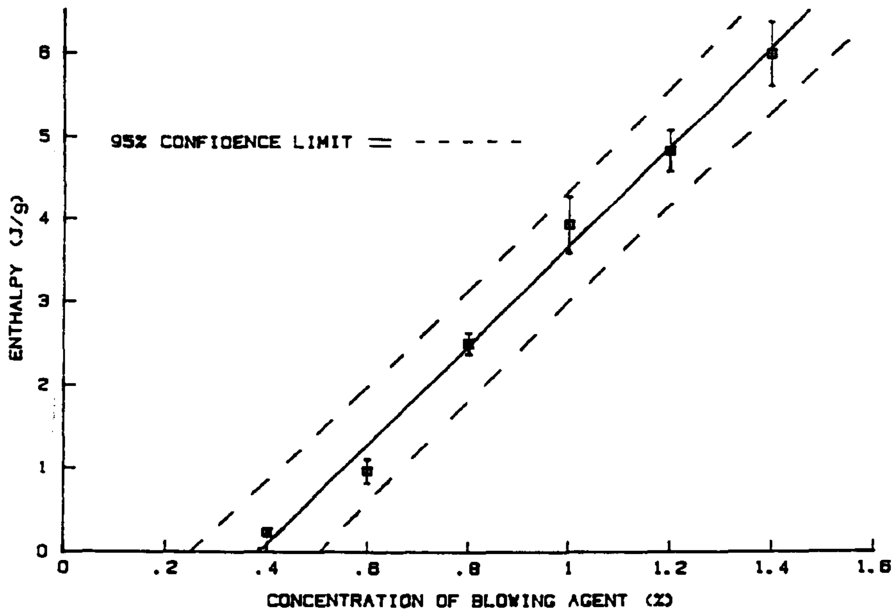

Fig. 5. Calibration curve for ADA in PVC cellular mixture using large sample pans (sample mass 85 mg).

should produce an enthalpy of 5.96 J g^{-1}. However, the results obtained for the 1.0% concentration level gave a mean value of 3.93 J g^{-1} (Table 4). This suppression in the enthalpy, equal to 2.03 J g^{-1}, indicates that ADA is still suppressed to the same degree for the large sample masses as for the smaller samples (Table 6).

In order to support the idea that suppression of ADA is due to a chemical reaction between a non-resinous component of the mixture, samples with various ADA concentrations were made in PVC resin, which represents the simplest possible formulation. These results are discussed below.

TABLE 5

Statistical values obtained from the ADA data using large sample pans (sample mass 85 mg)

Statistical function [6]	Calculated value
Number of measurements n	30
Intercept a on y axis	−2.29
Standard deviation S_a of the intercept a	0.15
Slope b	5.96
Standard deviation S_b of the slope b	0.16
Correlation coefficient r	0.9904

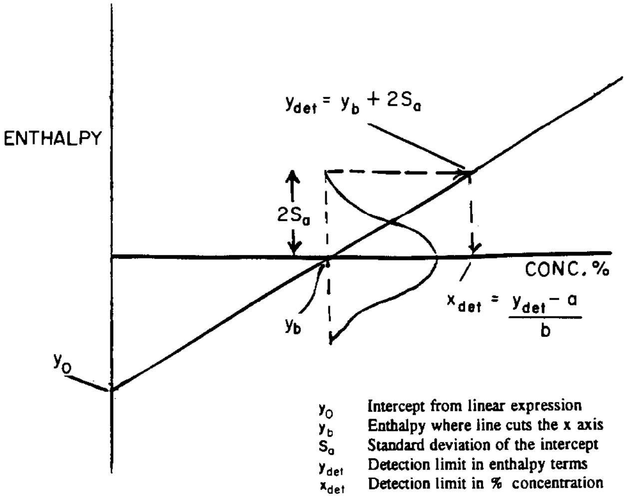

Fig. 6. Derivation of detection limit for ADA in cellular PVC mixture.

TABLE 6

Suppression in ethalpy. Sensitivity for 1% ADA concentration (enthalpy, J g^{-1})

	Small mass	Large mass
Expected enthalpy (i)	4.67	5.96
Actual enthalpy (ii)	3.08	3.93
Difference (i) – (ii)	1.59	2.03
Percentage difference	34.05	34.06

TABLE 7

Variation of enthalpy with ADA concentration in PVC resin

Conc. (%)	Blowing enthalpy ΔH_B (J g^{-1})				Peak temperature T_p (°C)		
	x_i	$\bar{x}$	S_x	%RSD	x_i	$\bar{x}$	S_x
0.6	4.8064	4.6726	0.1892	4.0	213.1	211.1	2.8
0.6	4.5388				209.1		
0.8	5.5171	5.9385	0.5959	10.0	210.1	210.0	0.2
0.8	6.3598				209.8		
1.0	6.4911	6.9305	0.6214	9.0	210.7	210.5	0.3
1.0	7.3699				210.3		
1.2	8.3873	8.5208	0.1888	2.2	210.3	210.5	0.2
1.2	8.6543				210.6		

Investigation into the suppression of enthalpy

Four concentrations of ADA (0.6%, 0.8%, 1.0%, and 1.2%) in PVC resin were prepared and analysed twice by DSC. These results are given in Table 7.

It is noteworthy that the samples in Table 7, involving PVC resin and ADA only, all gave approximately the same peak temperature T_p, for ADA decomposition: 210°C, the same as that expected for pure ADA decomposition [6].

The linear relationship for these results was found to be

$$y = 6.2683x + 0.8741$$

where y = enthalpy of decomposition for the blowing agent (J g^{-1}), and x = concentration of the blowing agent (%). The sensitivity for this method is 6.27 J $g^{-1}\%^{-1}$. Consequently a 1.0% ADA concentration should give an enthalpy of 6.27 J g^{-1}. The results show a difference of 0.66 J g^{-1} (9.5% difference) between the experimental and the theoretical value for a 1.0% ADA concentration in PVC resin, which is fairly good agreement; this small difference is most likely due to the non-homogeneity of the sample material. The suppression of ADA is clearly evident when comparing the calibration curve for ADA in cellular PVC mixture with that of ADA in PVC resin (Fig. 7). These results confirm the influence which a non-resinous component in the sample exerts on the decomposition enthalpy of ADA.

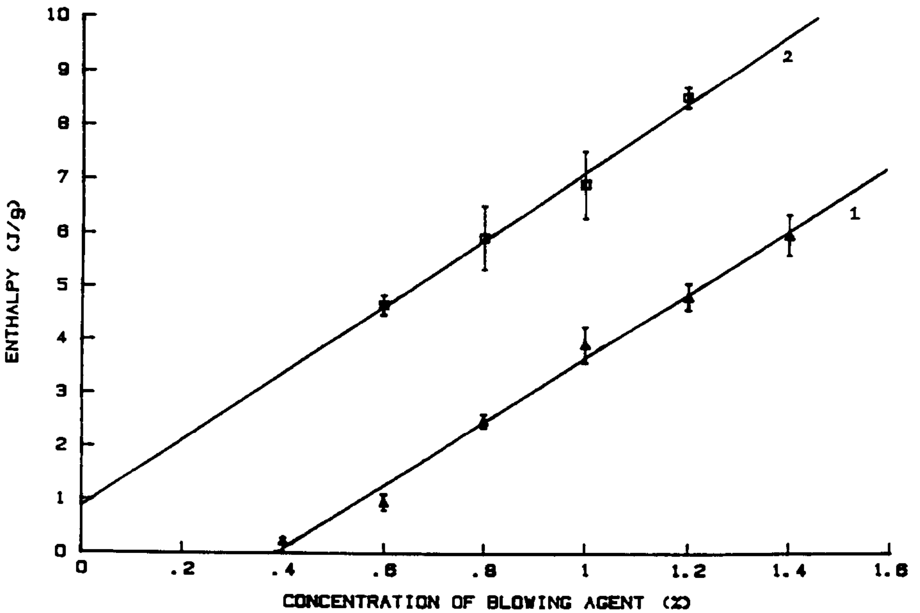

Fig. 7. Comparison of calibration curves for ADA in cellular PVC mixture (curve 1) and in PVC resin (curve 2).

CONCLUSIONS

The DSC examination of mixtures of PVC cellular formulations with various levels of ADA showed the expected linear relationship between ADA concentration and decomposition enthalpy, with a detection limit of 0.49% of ADA (95% confidence) using a sample mass of 85 mg. The sensitivity was expected to be 5.96 J g^{-1} $\%^{-1}$ but was found to be 3.93 J g^{-1} $\%^{-1}$, a difference of 34.0%. This discrepancy is attributed to the suppression of the ADA decomposition enthalpy, probably resulting from the ligation of ADA with a non-resinous component of the mixture, such as copper phthalocyanine. This reduces the effective ADA concentration so that only the unligated ADA contributes to the decomposition enthalpy, thus producing an artificially high detection limit.

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