APPLICATION NOTE

Differential Scanning Calorimetry

Author

Phil Robinson

Ruston Services Ltd.
Cheddleton, UK

Effect of Processing Temperature on the Analysis of PVC Samples for Gelation using the DSC 4000

Introduction

PVC Gelation Analysis by DSC has been described by a number of workers over the years, and has become an accepted method for analysis of processed PVC. What might not be well known, is the manner in which this analysis is made valid, which is discussed in this work.

Most errors in the analysis results from sample preparation, and some data will need to be discarded. The reproducibility can be significantly improved by observing a few simple points.

Samples Submitted

Four samples of extruded PVC section were submitted for testing by DSC to determine the degree of gelation. The samples provided were;

1. Sample A63: Extruder Temperature = 198.5 °C
2. Sample A65: Extruder Temperature = 198.5 °C
3. Sample B70: Extruder Temperature = 201 °C
4. Sample B72: Extruder Temperature = 201 °C

Sample Presentation and Analysis

Calibration

The DSC was calibrated using the recommended procedure by PerkinElmer, using indium (In melting point =156.60 °C) and lead (Pb melting point = 327.47 °C). Peak area (energy) was calibrated using the heat of fusion of indium. (28.45 J/g).

PerkinElmer®
For the Better

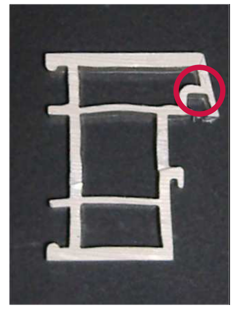
Sample Preparation

The sample under test was an extruded box section which is shown in the photograph to the right. Very thin flat samples are necessary for this work, because the DSC is measuring heat-flow differences in response to sample shape changes caused by the various relaxations, seen up to 240 °C.

Samples were therefore cut from the sections of PVC extrusion in the area shown for all four samples. The cuts were made using a low-speed diamond saw which does not produce any stresses in the sample during preparation, and produces very smooth samples, which allow good thermal contact with the DSC sample pan.

Using a knife to cut samples produces distortions in the material (curling) during cutting, resulting in poor thermal contact with the sample pan at the start of the test. When such a sample is heated subsequently, these stresses are released and produce distortion of the baseline as the glass transition is passed, causing changes in thermal contact and leading to errors in the determination of gelation.

The following cutting using the diamond saw produced thin sheets sample material about 0.5 mm to 0.7 mm thick and these were cut to size to suit the DSC sample pan using a circular "punch". The flattest side following the "punching" process was laid downwards in the open aluminium sample pan used for the test to ensure the best possible thermal contact. Sample masses of around 20 mg were used for this testing.



Samples taken from circled area of the extrusion.

The sample pan was left open during testing since it is the sample shape changing. Producing the baseline, shifts the measured gelation effect to produce the evaluation. Because each sample changes in a slightly different way, there is some variability in the data from each test, requiring that a number of tests on each sample are made to confirm reproducibility.

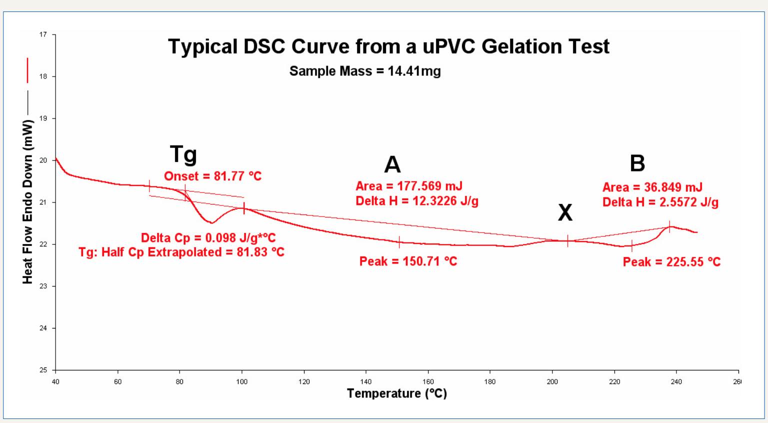
Method

The method used in the DSC was to heat from ambient to 240 °C at 10 °C/min under a nitrogen atmosphere flowing at 40 mL/min. The sample pans used were PerkinElmer standard aluminium sample pans (0219-0041), which are about 6 mm diameter. The DSC was water cooled, with a water circulator/chiller set at 5 °C.

NOTE: The sample pan is not crimped, allowing the sample freedom to move and distort in the pan during heating.

Background

The background of this method is based on that developed by Dr. M. Gilbert and Dr. J. Vyvoda and published in Polymer, produced August 1981. Other workers include those from Norsk Hydro Polymers, and Becetel.



This curve shows a typical DSC curve for this type of analysis. The features seen are;

- Tg The glass transition of unplasticized PVC, seen at about 82 °C, followed immediately by a small relaxation phenomenon.
- A A broad endotherm with a peak area "A" which it is proposed (Potente and Schultheid, 1987) to be related to the melting of partly gelled PVC.
- X A peak at about 204 °C which is proposed to be the processing temperature.
- B A broad endotherm which is proposed (JWThe, AACooper, ARudin, JHLBatiste – Measurements of the degree of fusion of Rigid PVC, March 1989) to be the melting of the previously non-gelled part of the PVC.

Calculation of Results

The degree of gelation of the PVC is calculated as the ratio of A to the total area A+B as follows:

$$\% \, Gelation = \frac{Area\ A}{(Area\ A + Area\ B)}$$

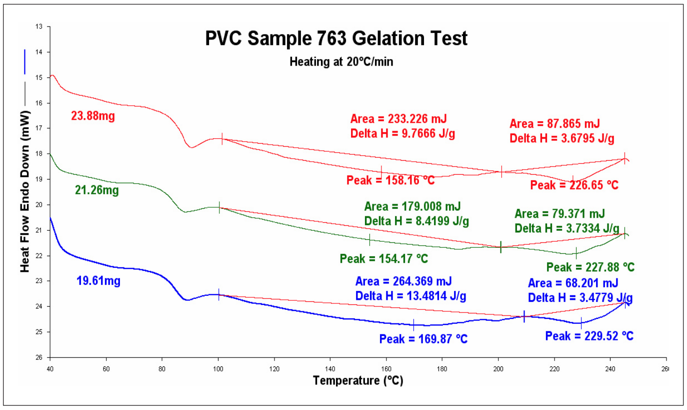
Results and Discussion

From the data shown in Curves #1 to #4, it can be seen that the processing temperature does influence the degree of gelation determined by this method. The results, based on averaging of the three values obtained, indicates that the lower extrusion temperature (198.5 °C) has resulted in a lower degree of gelation (73.6% – 73.8%) than material extruded at 201 °C. This 201 °C material demonstrated a degree of gelation calculated to be 85.1% - 85.3%.

Single Furnace DSC such as the DSC 4000 allows PVC processors to monitor the degree of gelation of the PVC in their extruders.

Extruded PVC Material in which the gelation is too low has been shown to have poor impact properties, and single furnace DSC can provide a simple method of examining this property of the material. Variation in extruder characteristics can be easily identified, with the result that the PVC sections being produced will be more dimensionally stable and have better impact resistance when given the correct level of gelation. Single Furnace DSC therefore allows PVC processors to have better control of the extrusion process, which will enhance the quality of their products.

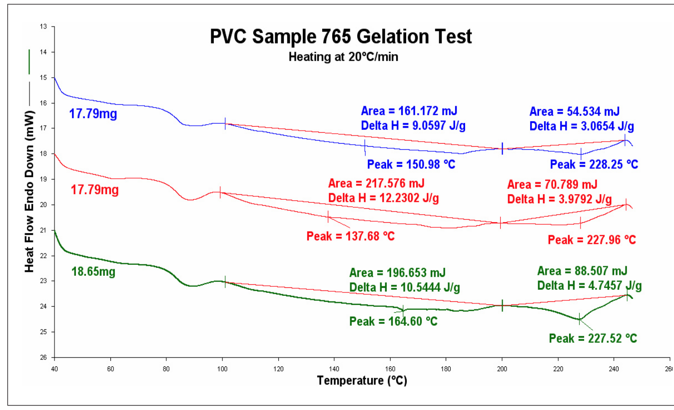
Curve #1 - PVC Sample A63



The three data sets in Curve #1 above have the following calculated degrees of gelation:

Peak A	Peak B	Gelation	Average
9.7666	3.6795	72.6%	
8.4199	3.7334	69.3%	73.8%
13.4814	3.4779	79.5%	

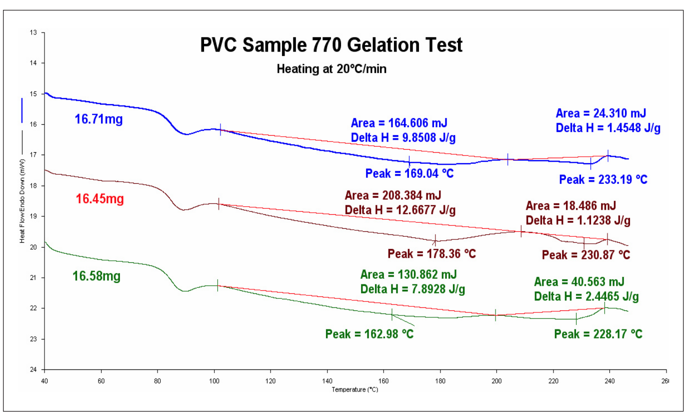
Curve #2 – PVC Sample A65



The three data sets in Curve #2 above have the following calculated degrees of gelation:

Peak A	Peak B	Gelation	Average
9.9057	3.0654	76.4%	
12.2302	3.9792	75.5%	73.6%
10.5444	4.7457	69.0%	

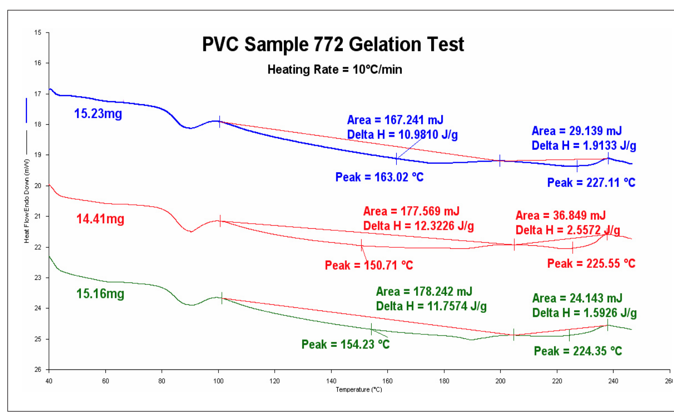
Curve #3 – PVC Sample B70



The three data sets in Curve #3 above have the following calculated degrees of gelation:

Peak A	Peak B	Gelation	Average
9.8508	1.4548	87.1%	
12.6677	1.1238	91.9%	85.1%
7.8928	2.4465	76.3%	

Curve #4 – PVC Sample B72



The three data sets in Curve #4 above have the following calculated degrees of gelation:

Peak A	Peak B	Gelation	Average
10.9810	1.9133	85.2%	
12.3226	2.5572	82.8%	85.3%
11.7574	1.5926	88.1%	

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

011615_01