

DETERMINATION OF THE DEGREE OF GELATION OF PVC-U USING A DSC

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1 Introduction

For the last 10 years, several companies have used a DSC (Differential Scanning Calorimetry) technique in order to find optimum melt temperatures on PVC-U products (pipes and profiles).

The benefits with this test are accurate melt temperature measurement as well as the possibility of finding temperature variations in local areas of the product, due to the fact that only a small sample is required.

Moreover, systematic investigations of the relation between melt temperature in a pipe, the hoop stress at 60°C and the DMCT values, has been carried out.

The results clearly indicate an optimum melt temperature for the specified S-PVC resin/formulation.

The correlation to the current standardised gelation test was found by testing the same pipes according to the DMCT method, ISO 9852.

The method is very accurate and is environmental safer, compared to the DMCT method. This new test method has been introduced recently in ISO as a New Work Item Proposal.

2 Determination of the degree of gelation by Differential Scanning Calorimetry

Differential scanning calorimetry [1] measures the heat flow between a sample and its surroundings when the sample is subjected to a temperature program (heating or cooling), i.e. the heat absorbed (endotherm) or liberated (exotherm) by the sample. The physical and chemical processes that occur on heating are coupled with a loss or gain in energy or with a change of the specific heat capacity of the sample. Such processes are therefore shown as peaks or steps in the measurement curve. The integration of a peak (peak area) yields the transition energy or the heat of reaction.

Figure 1 shows the DSC curve of a PVC profile at a heating rate of 10 K/min. under nitrogen (70 ml/min). Four consecutive effects are apparent:

- The glass transition with the relaxation peak. This depends on the thermal history of the sample. Plasticizer-free PVC typically has a glass transition temperature (T_g) of about 80°C.
- A broad endothermic effect with an area 'A' between the glass transition and about 190°C. This temperature corresponds to the processing temperature. According to [2], the endothermic peak corresponds to the melting of the partially gelled PVC.

- A further broad endothermic effect with an area 'B' between 190 °C and 240 °C. According to [3], this corresponds to the melting of the previously non-gelled part during measurement.
 - Above 250 °C, the beginning of degradation of the PVC. The reaction of the hydrogen chloride formed and the aluminium crucible could be the reason why degradation almost always begins exothermally. The measured onset temperature is in good agreement with the temperature determined by thermogravimetry.
- The degree of gelation of the PVC is calculated as the ration of 'A' to the total area 'A + B'.

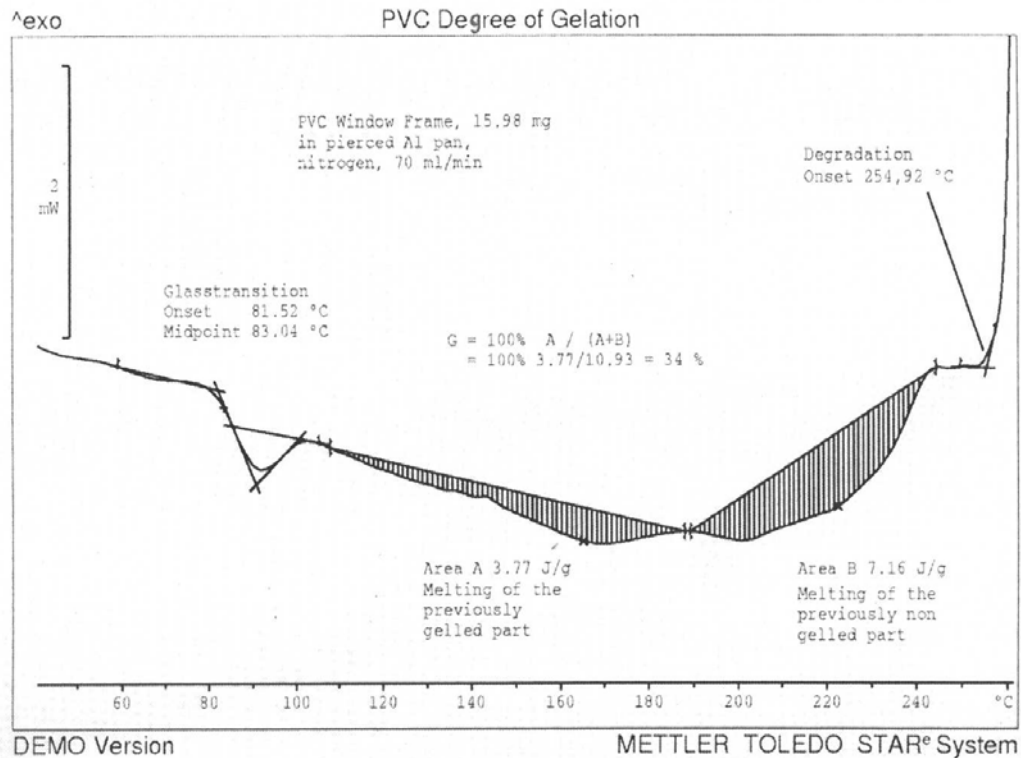


Fig. 1

Example of DSC analysis on PVC-U pipe

Test conditions :

- start temperature : 40 °C
- test stopped at 220 °C
- heating rate : 10 °C/h
- right limit of the surface of curve B taken at 210 °C

1. Example of a DSC analysis of a PVC-U pipe $\varnothing 90\text{mm}$ which showed a brittle failure at 350h during the hydraulic pressure test with test conditions 60°C- $\sigma 12,5\text{MPa}$. See table 1 and figures 4, 5 and 6 for test results.
2. Example of a DSC analysis of a PVC-U pipe $\varnothing 90\text{mm}$ which showed no failure during the hydraulic pressure test with test conditions 60°C- $\sigma 12,5\text{MPa}$. See table 2 and figure 7 for test results.

Table 1 : PVC-U pipe with brittle failure during pressure test

Graph, see figure	Sampling position (see fig. 3)	Place (*)	Weight of sample (mg)	Glass transition temperature Tg (°C)	Degree of gelation (%)
4	2	a	20,9	85	91
		b	21,5	84	78
		c	18,8	84	96
5	4	a	20,0	84	93
		b	20,2	86	70
		c	20,4	84	88
6	6	a	20,5	84	97
		b	19,6	77	67
		c	21,5	79	98

(*) with a: inner side, b: middle, c: outer side of the wall thickness

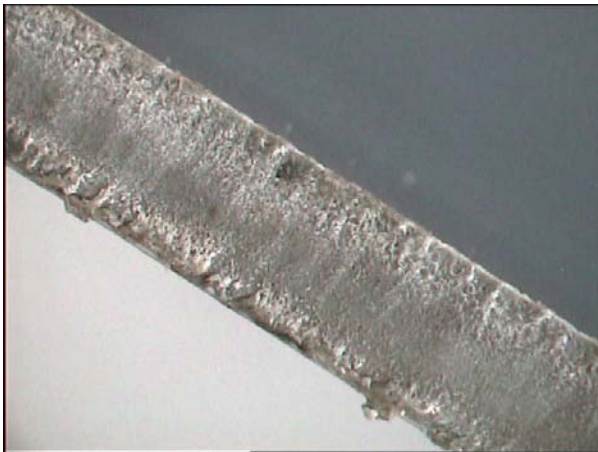


Fig. 2 : surface of a brittle failure of a PVC pipe $\phi 90$ mm

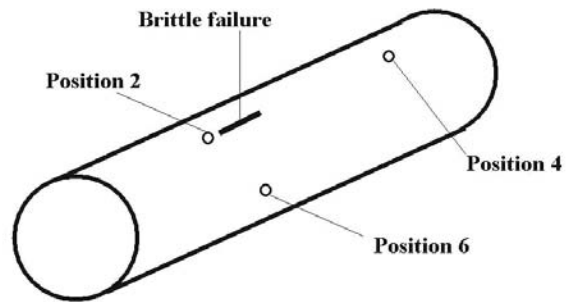
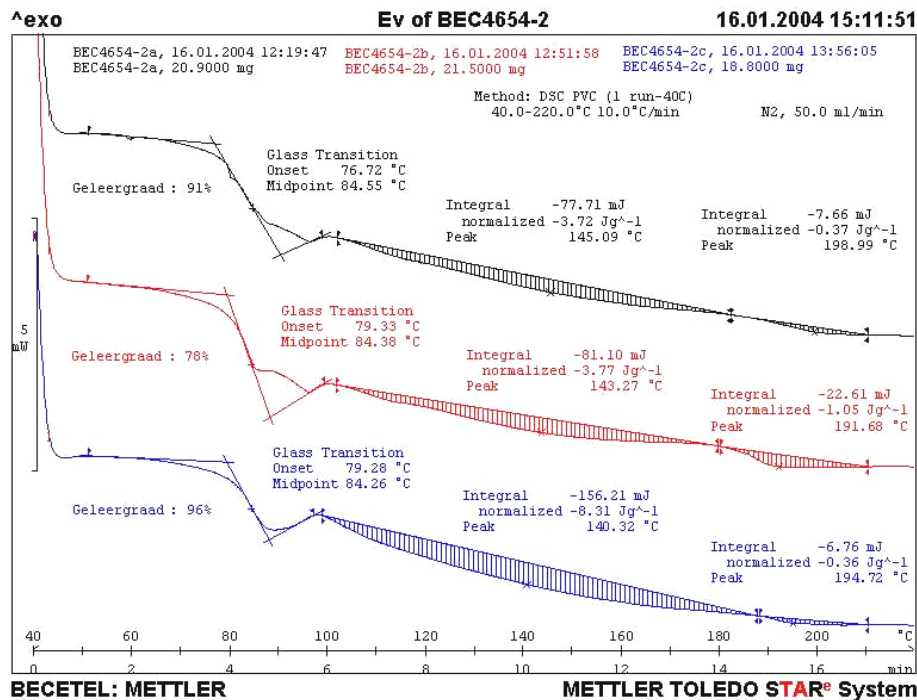


Fig. 3 : position of sampling

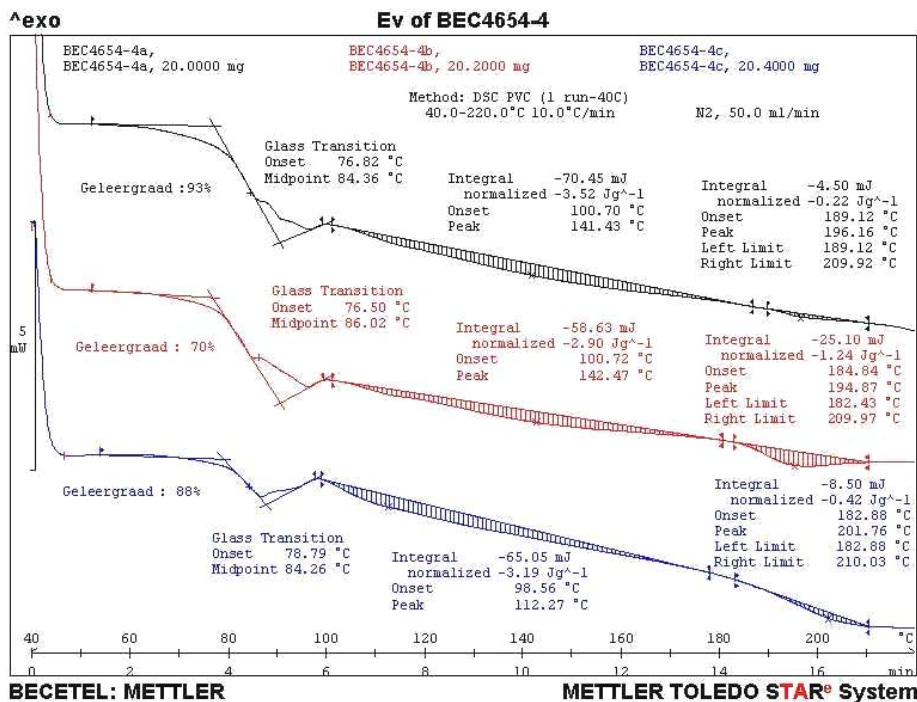
Table 2 : PVC-U pipe without failure during pressure test

Graph, see figure	Sampling position	Position (*)	Weight of sample (mg)	Glass transition temperature Tg (°C)	Degree of gelation (%)
7	random	a	20,9	84	92
		b	21,5	84	99
		c	18,8	84	84

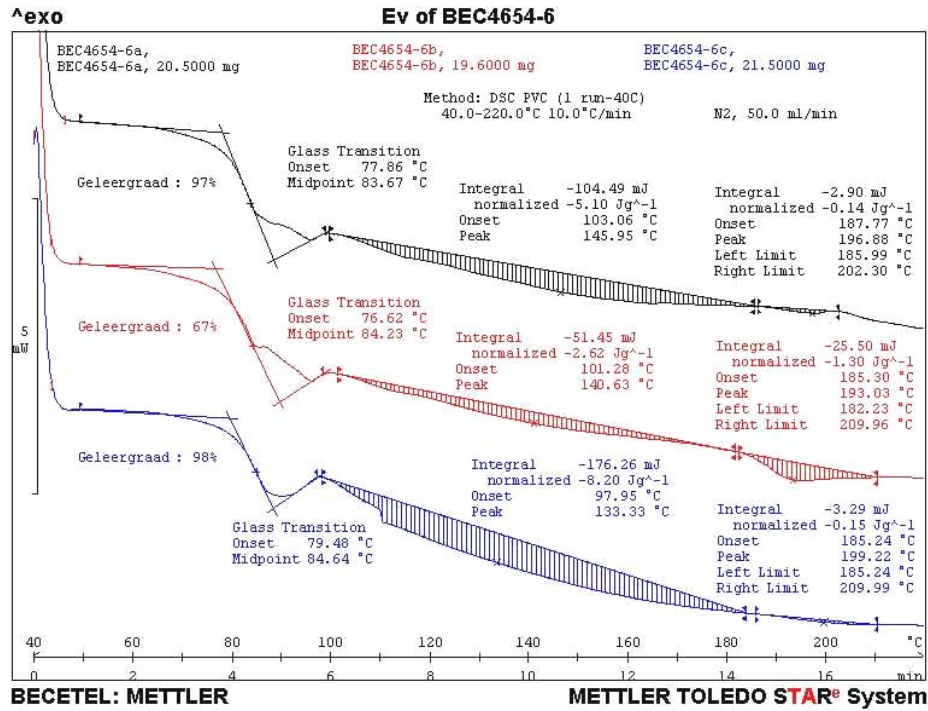
(*) with a: inner side, b: middle, c: outer side of the wall thickness



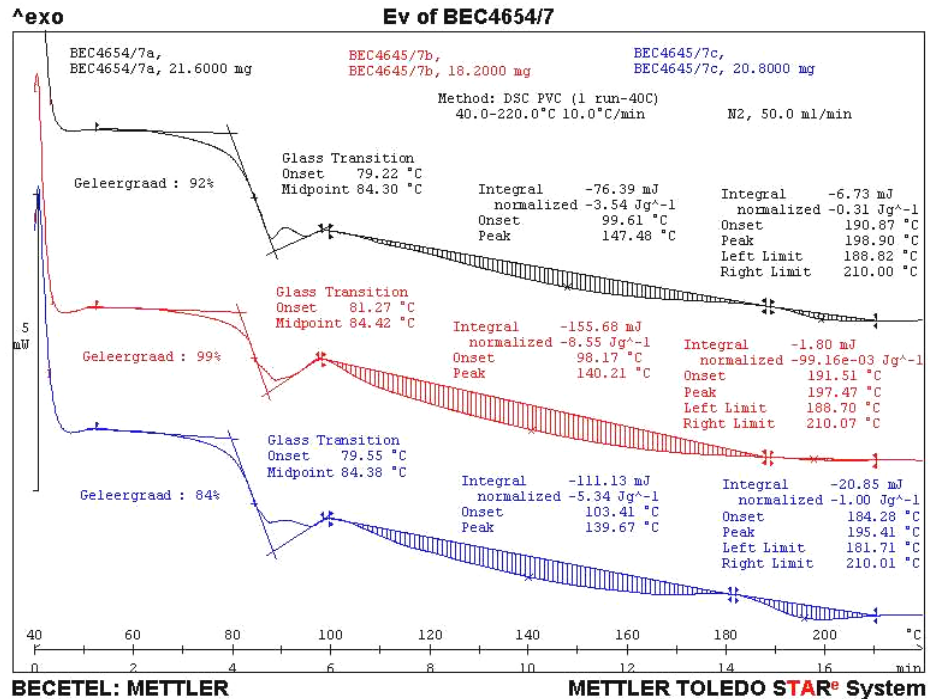
*Fig. 4 : PVC-pipe with brittle failure,
sample taken next to the brittle failure (position 2 of fig. 3)
(with a: inner side, b: middle, c: outer side of the wall thickness)*



*Fig. 5 : PVC-pipe with brittle failure,
sample taken on the same level of the brittle failure (position 4 of fig.3)
(with a: inner side, b: middle, c: outer side of the wall thickness)*



*Fig. 6 : PVC-pipe with brittle failure,
sample taken at 90° of the brittle failure (position 6 of fig. 3)
(with a: inner side, b: middle, c: outer side of the wall thickness)*



*Fig. 7 : PVC- without failure, random place of sample
(with a: inner side, b: middle, c: outer side of the wall thickness)*

3 Determination of the optimum melt temperature by DSC versus MCT and internal pressure test.

For the last 10 years, Hydro Polymers [4] has been using a DSC (Differential Scanning Calometry) technique in order to find optimum melt temperatures on PVC-U products (pipes and profiles).

DSC is a well established method for testing the melt temperature in PVC products, originally described by M. Gilbert and J. Vyvoda [5].

The benefits with this test are accurate melt temperature measurement as well as the possibility of finding temperature variations in local areas of the product, due to the fact that only a small size of sample is required. Typically approx. 15 mg is used. As an example this enables the operator to cut three different samples through the pipe wall of a 110 x 5,3 mm pipe (samples from outer - mid- and inner layer). Thus temperature variations in the pipe wall may be tested.

The cutting procedure is delicate and is accurately described in Annex 1.

A systematic investigation of the relation between melt temperature in a pipe, the hoop stress and the MCT values have been carried out.

The test was based on Norvinyl S-PVC with K-value 68 in a lead stabilised pipe formulation. Pipes were produced in dimension 50 x 3,7 mm, in a CM 45 extruder.

Different melt temperatures, ranging from 165 °C to 200 °C, were obtained by varying the extruder parameters as well as a minor tuning of the hydrocarbon wax (melting point 100 °C – 105 °C) in the formulation. The output rate was kept nearly constant at 75 - 78 kg/hour in the extruder.

Due to the specific wall thickness of this pipe the melt temperature was measured in the mid layer of the pipe wall by DSC.

Hoop stress test, according to ISO 1167, was carried out on the different pipes at 60 °C and 14 MPa.

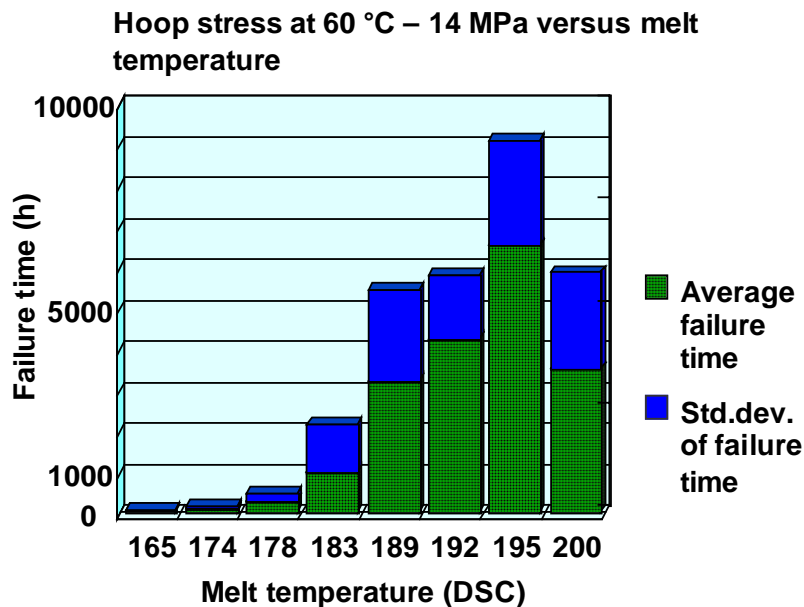


Fig. 7. Hoop stress versus melt temperature on pipes based on Norvinyl S-PVC with K-value 68

These results clearly indicate that the optimum melt temperature for the specified S-PVC resin/formulation is 195 °C.

The correlation to the current standardised gelation test was found by testing the same pipes according to the MCT method, ISO 9852.

The pipes were chamfered to an angle of 10° (approx. 17 mm band width). The Methylene Chloride was conditioned to the temperatures 15 °C to 35 °C with 5 °C intervals.

The result is presented in Fig 2. where the black graph (full line), shows the MCT result on the chamfered surface. The area to the left of the black graph means not passing the MCT test (>50 % attack) and the area to the right of the graph means passing (no, or <50 %, attack).

Hoop stress at 60 °C – 14 MPa and MCT versus melt temperature

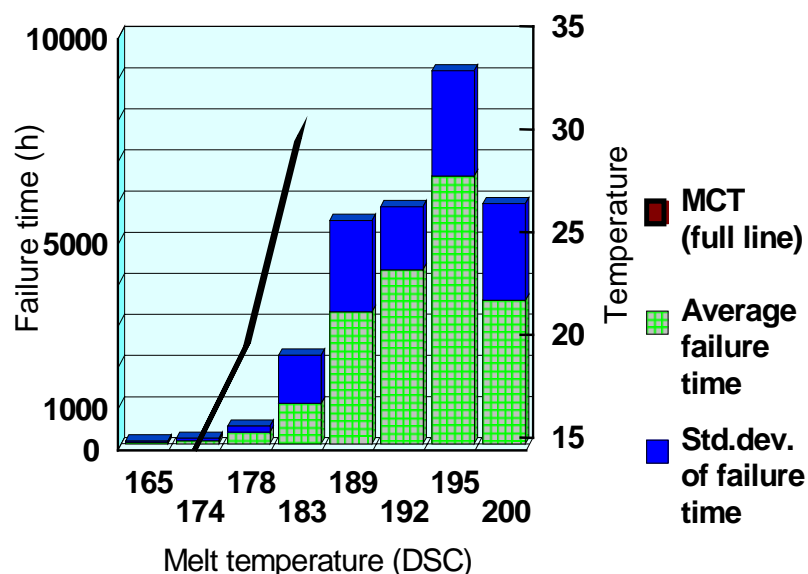


Fig. 8. Hoop stress and MCT versus melt temperature on pipes based on Norvinyl S-PVC with K-value 68.

Surprisingly the MCT values were much lower on the melt temperature axis than expected. However, the hoop stress is probably much more test to be much more precise in describing the required pipe quality than the MCT test.

4 Reference list

- [1] DIN 53765: Prüfung von Kunststoffen und Elastomeren , Thermische Analyse von Polymeren, Dynamische Differenzkalorimetrie (DDK)
- [2] H. Potente, S.M. Schultheid: Kunststoff 77 (1987) 401 - 404
- [3] J.W. The, A.A. Cooper, A. Rudin, J.L.H. Batiste: Interpretation of DSC. Measurements of the Degree of Fusion of Rigid PVC; Journal of Vinyl Technology, 11, 1, March 1989, pgs. 33 to 41.
- [4] O.K. Hagen, Hydro Polymers, Norway.
- [5] M. Gilbert and J. Vyvoda, Polymer, Vol 22, 1134-1136 (August 1981).

ANNEX 1

Cutting of rigid PVC materials for DSC-analysis using ISOMET low speed saw.

Apparatus

Buehler Isomet low speed saw (11-1180) with diamond wafering blades

Accessories

- High diamond concentration wafering blade, 7.6cmx0.15mm or 10.2cmx0.3mm
- Chuck, double hold-down saddle-type (other chucks are available).

Chemicals

Water, for cooling of the material (other liquids can also be used).

Samples

Rigid PVC materials (nearly all materials can be sectioned).

References

- Instructions from Buehler of operating, maintenance and available accessories and for correct use of the Isomet Low speed saw.
- Instrument procedure no. PVC-476-1

Principles of low speed saw sectioning

The basic concept of the low speed saw is illustrated in fig.1.

A sample (A) is held in a suitable chuck and is introduced through gravity by a known load (B), to a rotating wafering blade (C), which is coated with a film of lubricant picked up during its rotation through the cooling tank D.

The choice of operating conditions is dependent upon knowledge of the sample material.

Sample size and shape require selection of a suitable chuck, to hold the sample in a rigid position, and a correct blade for the cutting operation.

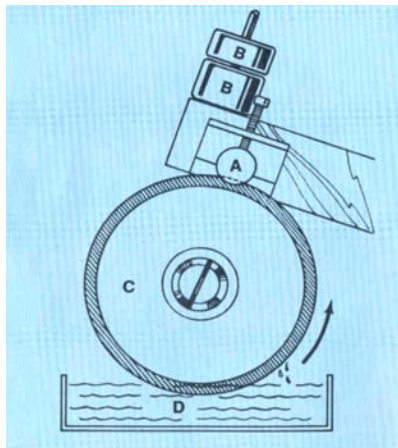


Fig. 1

Operating

The wafering blade is the heart of the Low speed Saw. It consists of a thin metal matrix rim. The effect of rotational speed is a significant factor. Moderate speed is effective for most applications and minimizes the damage.

-For sectioned PVC-materials, speed 5 on speed-controller normally is used.

The sample chuck holds the sample firmly in position to prevent inaccurate cuts and damage to the blade due to movement during sectioning.

-The most used chuck for PVC-materials is a double hold-down saddle-type.

Orientation of the sample in the chuck is important in order to effect cutting time and Prevent flanges from interfering (by vertically orientation).

A rectangular shape of the sample is preferred. This is achieved by horizontal orientation of the sample. See bottom of fig.2.

A micrometer cross-feed is a valuable aid in accurately locating a specific sectioning plane, or in producing samples of an exact thickness.

-Generally the thickness of PVC samples are about 0.5-0.7mm.

To obtain a correct load between sample and blade, four different weights are available.

-For rigid PVC-materials, all four weights are used (total 300g).

Adjustment of a "cut-off Switch" shut off the saw at the completion of the cut.

The cooling tank with water is placed under the blade.

The water minimizes the blade loading, and cleans the sample as well as the blade surface.

-Cold water is used for cooling of PVC samples and to clean the blade.

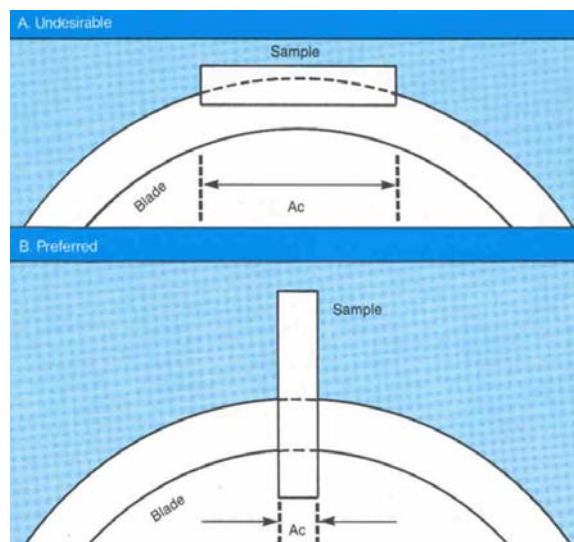


Fig.2

Cleaning the Saw

The saw is easy to clean. After use empty and wash the lubricant pan (cooling tank). Wash and dry the blade to prevent corrosive attack.

Wafering blades do not break down significantly, but they may become dull due to glazing, which coats the abrasive grains and reduce their cutting efficiency.

To dress the wafering blades, place a dressing stick into a sample chuck and cut off a thin slice, by a very low speed (2-3rpm). Repeat this 3-4 times.

New wafering blades should be dressed 5-7 times before any sample is cut.