NON-DESTRUCTIVE AND IN-SITU DETERMINATION OF THE DEGREE OF GELATION OF PVC PIPES

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Abstract

Various non-destructive methods, based on different physical principles, were investigated for their ability to differentiate between uPVC pipes having various levels of gelation. It was found that the micro-hardness method was not able to differentiate between uPVC samples of different levels of gelation. A possible explanation is that the affected volume under the indentation does not reach the centre of the pipe wall where differences in the level of gelation are most pronounced. The laser scattering and laser microscopy methods fail because the surface roughness is not only determined by processing temperature (which is related to the level of gelation), but also by other factors in the production process. The Profile NMR-MOUSE is able to scan through the thickness of the pipe wall. However, the amounts and relaxation rates show no significant differences between uPVC samples of different levels of gelation. The NMR results can be explained from DSC measurements, where no detectable differences in crystallinity have been observed for the different ways of processing.

Keywords: pipe, PVC, gelation, non-destructive.

INTRODUCTION

The level of gelation (or fusion level) is a measure for the initial quality of PVC pipes after processing, Hermkens et al. (1). In the beginning of the production of PVC pipes, the extrusion process was not fully under control, leading to a variation in levels of gelation amongst the pipes produced. As a consequence, uPVC pipes with variations in quality were installed. Studies have shown that an insufficient level of gelation has a negative effect on the impact properties of uPVC gas and water pipes, Hermkens et al. (1), Benjamin (2), Meijering (3). As a consequence, the pipes with an insufficient level of gelation form a potential source of (dangerous) brittle failure when impacted. Therefore, a non-destructive and in-situ determination (i.e. without taken out pipes from the grid) of the level of gelation of PVC pipe networks would be a very helpful tool. In this paper various experimental methods have been applied in an attempt to differentiate between uPVC pipes of different levels of gelation. The methods were chosen for their possible ability to determine the level of gelation, but also for their non-destructive character and potential in-situ implementation in uPVC pipe networks.

SELECTION OF TECHNIQUES

An overview of techniques that were considered in this work is given in Table I. The arguments to select the listed techniques are described in the dedicated sections.

Table I: Techniques that were considered for the determination of the level of gelation of uPVC pipes.

Technique	Physical quantity	NDT	In-situ
Micro-hardness	Inhomogeneity of properties.	+	+
Micro-MC	MC resistance	+/-	+
Laser surface scattering	Surface roughness	++	++
Laser microscopy	Surface roughness	++	+
X-Ray	Detection of crystallinity	+/-	o
Single-sided NMR	Molecular mobility	++	o

NDT: ++ fully non-destructive, + non-destructive on macroscopic scale, +/- safety issues regarding PVC degradation.
In-situ: ++ small device, simple apparatus, + small device, more sophisticated apparatus, o relatively large device

A possible relation between the micro-hardness and the level of gelation is based on the relation between gelation and inhomogeneous properties within the extruded product. As the particulate structure after extrusion is partially intact for a product with a low level of gelation, Benjamin (2), inhomogeneity of local mechanical properties is expected. Hence, variations in local hardness can be expected and may give an indication of the level of gelation. Micro-hardness determination can be considered as a non-destructive technique on a macroscopic scale, because the indentations can be made small as compared to surface defects (e.g. scratches) present on the (inner) surface of the pipe. Micro-hardness determination has potential to be implemented as the indenter systems can be compact devices that can to be fitted onto internal pipe inspection systems. Based on these arguments, this surface-based method will be further investigated.

The Micro-MC approach, which is based on an adaptation of the Methylene Chloride (MC) test, was developed in this study. Small holes are milled into the inner surface of the pipe and brought in contact with MC. After a certain contact time the holes are inspected visually for attack. This method is considered to be a little more destructive than the micro-hardness method, because of a potential risk of PVC degradation. Several measurements on PVC, with a range of levels of gelation, showed that this method can only differentiate between samples of low levels of gelation of around 30 %. Because of the poor sensitivity to the level of gelation and the potential risk of PVC degradation, the Micro-MC method is discarded as a potential technique for in-situ determination of the level of gelation. However, this method can give an indication of the level of gelation over the thickness of the pipe wall. This will be presented in the discussion part of his paper.

Visual differences in the surface roughness of uPVC pipes of different levels of gelation can be observed with the naked eye, Hermkens et al. (1), Benjamin (2).

Therefore, surface characterisation methods could be able to determine the level of gelation. Therefore, two different surface characterisation methods are selected for further investigation: laser surface scattering and laser microscopy. Both methods are non-destructive if the power of the laser is such that it does not cause significant degradation of the PVC pipes. Relatively small lasers and cameras are available that could be relatively easily be implemented into equipment for inspection of PVC pipes.

Although crystallinity is affected by the processing of PVC, only indications of changes in crystallinity for different processing conditions are found using X-Ray scattering, Gilbert (5). No clear relation between X-ray scattering measurements and the level of gelation has been established, Diego (6), Fillot (7). Therefore, the method is discarded as a potential technique.

The Profile Nuclear Magnetic Resonance MObile Universal Surface Explorer (Profile NMR-MOUSE) is a relatively novel technique developed at RWTH Aachen University for material characterisation, Perlo (8). The Profile NMR-MOUSE is a form of single-sided NMR, hence the measurement takes place at one side of the pipe wall and can thus be applied as an in-situ technique. This non-destructive method can penetrate inside the bulk and measures molecular mobility through the wall thickness. The potential of this method will be investigated in this work.

EXPERIMENTAL

The codes of the pipes and corresponding levels of gelation are displayed in Table II.

Table II: New “N” and excavated “EX” uPVC pipes used in this work.

N-pipe	Level of gelation MCT	DSC (%)	EX-pipe	Level of gelation MCT
N-0	Under	19	EX-0	Under
N-1	Intermediate	48	EX-1	Under
N-2	Good	73	EX-2	Intermediate
N-3	Over	91	EX-3	Good
			EX-4	Over
			EX-5	Over

A set of pipes, coded by ‘N’, were extruded at different processing temperatures, with the same formulation and were extruded on the same machine. The pipes coded by ‘EX’ are excavated pipes taken from different parts of the PVC gas grid in The Netherlands and are expected to be processed under different conditions, with different formulations and different extruders. The levels of gelation were determined by the Methylene Chloride Temperature (MCT) test and Differential Scanning Calorimetry (DSC).

MICRO-HARDNESS

A possible relation between the hardness and the level of gelation is based on the homogeneity of the extruded product. A high level of gelation would imply a more homogeneous structure, Benjamin (2). In that case, the local hardness at the product surface is expected to have minor variations and the average hardness would be relatively high. For lower levels of gelation, the product would contain an increasing number of local mechanically weak regions as the particulate structure is still intact. During indentation, the indenter would penetrate deeper into the regions where fusion is less pronounced, resulting in a decrease of the local hardness value. Therefore, the variation in local hardness is expected to increase for lower levels of gelation, whereas the average hardness is expected to show only a minor decrease for lower levels of gelation.

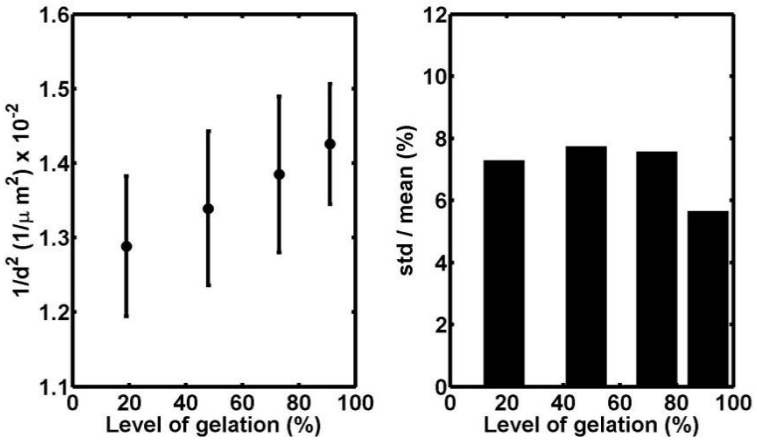
The hardness of polymers is ill defined as the stress field under the indenter and the deformation behaviour of glassy polymers are quite complex. As a consequence, many empirical relations to relate hardness to mechanical properties have been proposed, Pelletier (9). A measure of the hardness in this work is defined as $1/d^2$ where d is the indent depth. The relation clearly does not incorporate the complex behaviour of indentation on polymers, but is given only as a measure for determining relative differences between samples which are indented at equal conditions.

Indentations with a Vickers indenter were carried out on the bottom of the curved inner surface of the N-type samples of different levels of gelation using a LECO AMH 43 Micro-indenter. A mass of 200 g and a dwell time of 15 s were applied for each indentation. The samples were supported by a layer of clay on a fixed metal sheet. The samples were left for at least 30 minutes at the test temperature of 23 °C for the samples to equilibrate before indentation. The micro-indenter is not capable of determining the depth of the indents because this system is based on visual image determination of the diagonals of a Vickers indent. Therefore, a Keyence VK-9700 Laser Scanning Microscope was used for measuring the height profile of the indented surfaces. The indent depth was determined by analysis of a Matlab program applied to the height profiles of the indented surfaces. The time between indentation and surface measurements is taken to be at least three days, to ensure that no significant recovery of the indents takes place during the height profile measurements. The noise in the microscopic data was filtered out by applying a 5x5 median filter. The tilt, which is caused by misalignment of the sample with respect to the reference plane of the microscope sample table, is removed after filtering.

The micro-hardness data of the N-type samples are shown in Figure 1. An increasing trend of the average hardness with increasing level of gelation is observed, which confirms the hypothesis. However, the spread in the measurements is such that the difference cannot be considered to be significant. The variation in the local hardness, Figure 1 (right), is fairly independent of the level of gelation. This observation does not confirm the hypothesis. Based on these results, the micro-hardness method is

regarded to be insufficiently distinctive for reliable determination of the level of gelation.

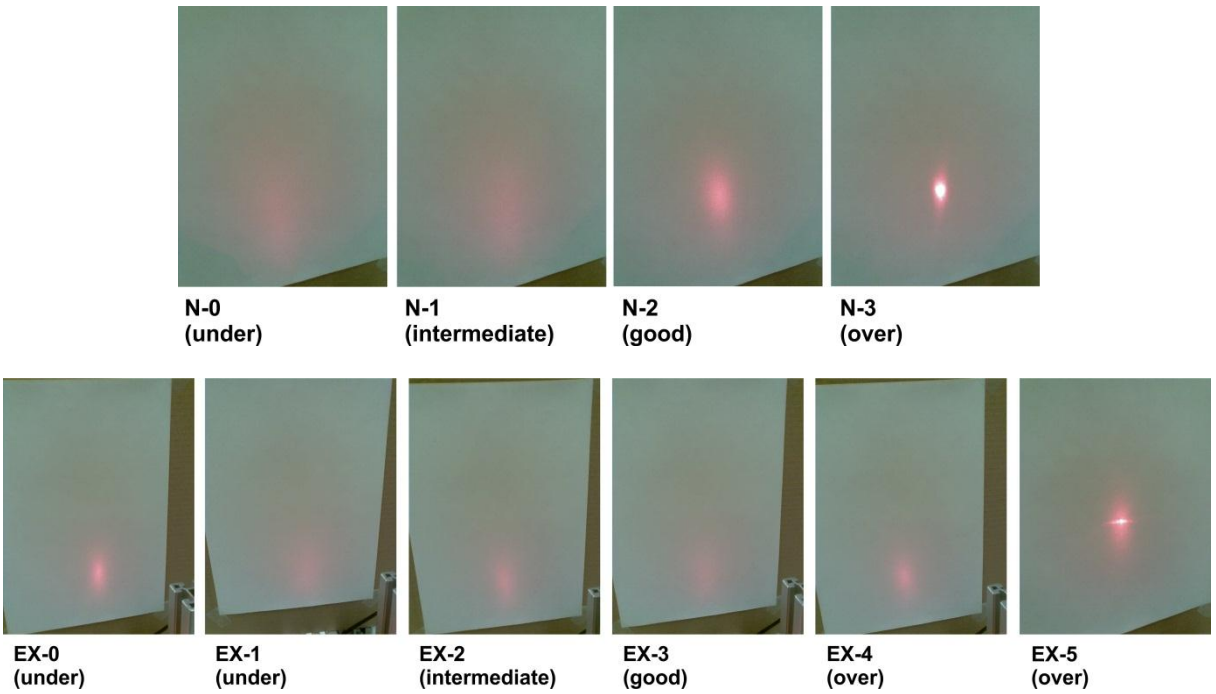
Figure 1: *Left:* the hardness $1/d^2$ plotted versus the level of gelation for N-samples. Each error bar presents one standard deviation based on at least 26 indentations. *Right:* relative scatter of the hardness $1/d^2$ plotted versus the level of gelation for the N-samples.



LASER SURFACE SCATTERING

Differences in visual appearance of the inner surface of uPVC pipes can be observed with the naked eye. For increasing levels of gelation, the N-pipes show a monotonic increase from dull (or matt) to a more shiny appearance. This effect can be easily seen by comparing projections of laser scattering measurements of the pipe's inner surface, see Figure 2 top.

Figure 2: Laser scattering projections of N-pipes (top) and EX-pipes (bottom) for different levels of gelation.

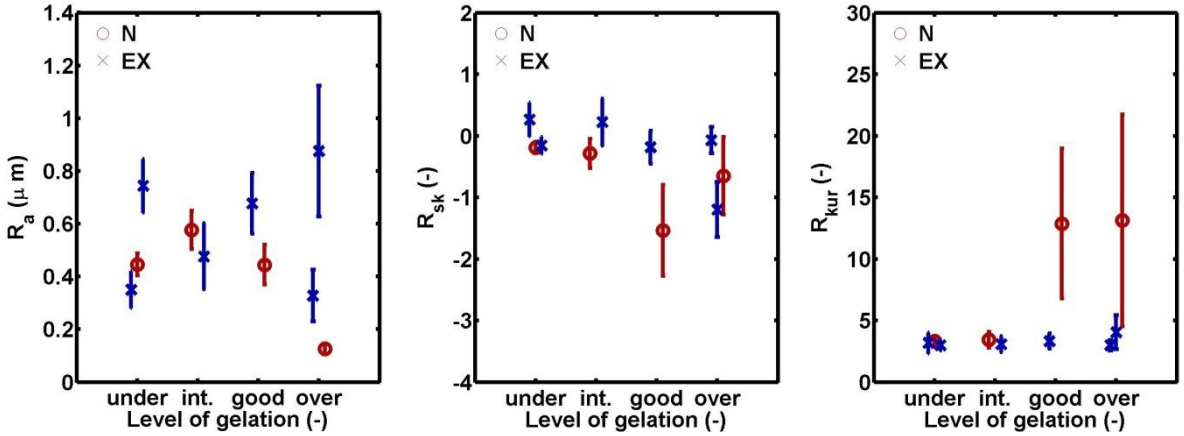


This effect is believed to originate from interaction between the PVC melt and the extruder wall. During extrusion at relatively low processing temperatures the primary particles are more intact resulting in a more diffused scattering. At higher processing temperatures the primary particles are more fused together resulting in a smoother, more shiny surface, Summers (4). Because the surface scattering behaviour from a light source (e.g. laser) is related to surface roughness (polished samples of various levels of gelation showed equal scattering), laser scattering could be a useful non-destructive method to determine the level of gelation. For laser scattering to be implemented into equipment for inspecting an existing PVC grid, laser scatter projections of uPVC pipes from different parts of the network having different levels of gelation must be compared. Figure 2 (bottom) shows laser scatter projections of excavated pipes having different levels of gelation. It is clear that these laser projections of excavated pipes do not show a clear relation with the level of gelation as was found for the N-pipes. This means that the proposed laser scattering method has potential to be able to determine the level of gelation of newly produced uPVC pipes from the same batch, but not for excavated uPVC pipes produced from different batches.

LASER MICROSCOPY

Another way of surface characterisation is by determination of surface roughness parameters by laser microscopy. Surface roughness parameters on the inner surface of pipes were determined using a Keyence VK-9700 Laser Scanning Microscope. The roughness parameters for the N- and EX-samples are displayed in Figure 3.

Figure 3: The surface roughness parameters of the inner surface of N- and EX-samples plotted against the level of gelation. The error bars represent one standard deviation of ten measurement performed consecutively in axial direction of the pipes.



The arithmetical mean roughness (R_a) of the N-samples for the highest level of gelation is significantly lower than for the other levels of gelation. This corresponds to a relatively smooth surface which results in a more specular reflection by laser light, as observed in Figure 2 (top). The skewness roughness (R_{sk}) shows a small decrease for the N-sample of “good” level of gelation which corresponds to a relative

increasing number of holes in the surface which can be seen by microscopy (not shown in this work). Hence, reference curves of only the R_a and the R_{sk} are enough to differentiate between samples of levels of gelation of “under/intermediate”, “good”, and ”over” produced with the same formulation and extruder, but different processing temperatures. The kurtosis roughness (R_{kur}), a measure for the “peakedness” of the surface height distribution, of N-samples has a step-like behaviour in the levels of gelation between intermediate level and good level of gelation and could be an additional indicator to differentiate between levels of gelation in the ranges “under/intermediate” and “good/over”. Although the roughness parameters indicate to have some potential to determine the level of gelation, more measurements and more sets of pipes must be tested to confirm this. For determining the level of gelation of PVC pipes in the grid, however, no reference curves can be determined. For the proposed method to work, various pipe samples of different sources must show a significantly clear relation to the level of gelation. The roughness parameters for the EX-samples are shown in Figure 3. The R_a for the EX-samples shows large variations for the same level of gelation. This means that measurements of R_a for various parts of the uPVC gas grid do not give a direct indication of the level of gelation. The R_{sk} and R_{kur} for the EX-samples do not show direct indication with the level of gelation either. Therefore, it can be concluded that this technique is not suitable for in-situ determination of the level of gelation of buried PVC pipes.

SINGLE-SIDED NUCLEAR MAGNETIC RESONANCE

Single-sided NMR is capable of detecting differences in crystallinity for PE pipes that originate from different annealing treatments above the glass transition temperature, Buda (10). Although no clear relation between crystallinity and different processing temperatures (which is related to the level of gelation) has been established in PVC, Gilbert (5), single-sided NMR provides a potential alternative for determination of crystallinity as NMR determines crystallinity by the molecular mobility and not by the state of order as in X-ray scattering, Blümich (11). The capability of single-sided NMR to differentiate between uPVC samples of different levels of gelation was therefore investigated. The NMR decay signals of semi-crystalline polymers can be approximated by using a bi-exponential function, Buda (10),

$$I = A_{shrt}e^{\left(-t/T_{short}\right)} + A_{long}e^{\left(-t/T_{long}\right)}, \qquad (1)$$

where I is the measured intensity and t is time. The hypothesis proposed in this work is that the measures $1/T_{short}$ and $1/T_{long}$ are assumed to be the characteristic relaxation rates of the crystalline and the amorphous phases in uPVC, respectively. The measures $A_{short}/(A_{short}+A_{long})$ and $A_{\text{long}}/(A_{short}+A_{long})$ are assumed to be measures for the amounts of NMR crystallinity and amorphous phase in uPVC, respectively. The transverse magnetization decays were measured for the N-samples using a Profile NMR-MOUSE. The decay signals were acquired through the thickness of the

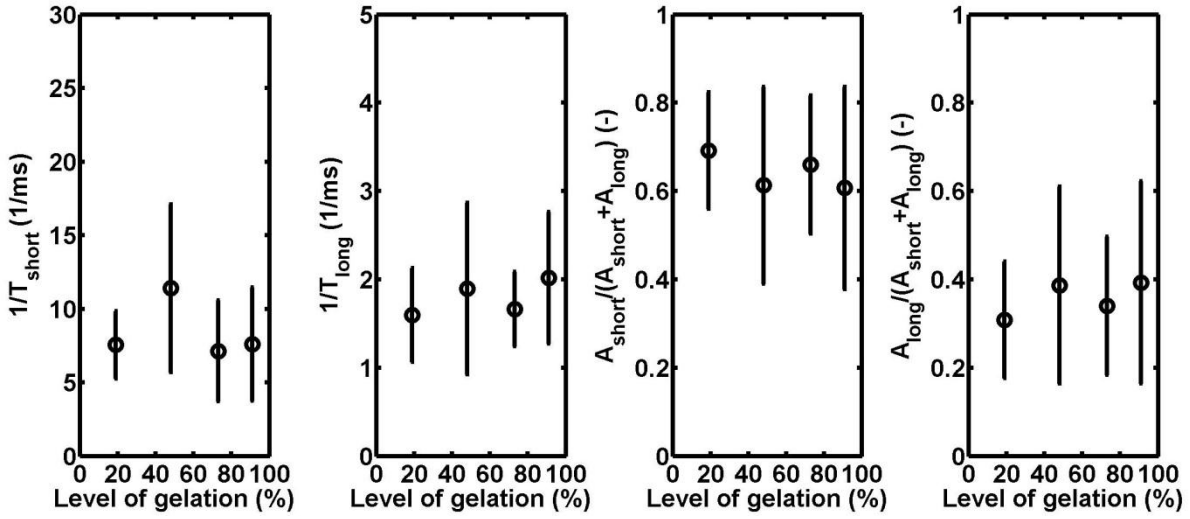
sample with a step width of 200 µm up to a depth of 2 mm using the Radio Frequency (RF) Carr-Purcell-Meiboom-Gill (CPMG) sequence. A number of 256 scans were recorded per step. The settings used for the NMR measurement are displayed in Table III.

Table III: Settings of the NMR measurement used in this study.

Parameter	Value
RF frequency	29.3 MHz
RF pulse length	2.2 µs (9/4 dB)
CPMG Echo time	0.0218 ms
CPMG No. of echo's	200
Receiver gain	90 dB
Acquisition time	0.003 ms

Figure 4 shows the relaxation rates and amount of the crystalline and amorphous phases in PVC. Neither significant changes in the relaxation rates nor in the amount of crystallinity are observed. These results show that NMR is not able to differentiate between uPVC samples of different levels of gelation.

Figure 4: *Two graphs on the left:* the relaxation rates of the crystalline and the amorphous phases in uPVC for different levels of gelation, respectively. *Two graphs on the right:* the amount of NMR crystallinity and amount of the amorphous phase in uPVC for different levels of gelation, respectively. All error bars represent one standard deviation of nine measurements made through the thickness of the sample.

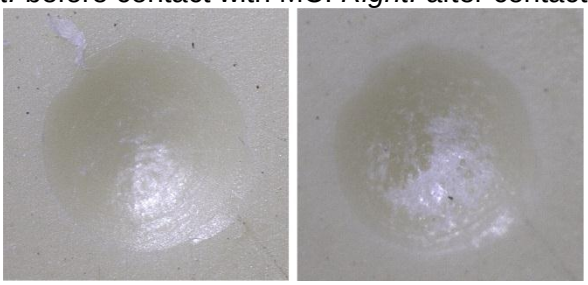


DISCUSSION OF APPLIED TECHNIQUES AND CONCLUSIONS

A possible explanation of the disability of the micro-indentation method to differentiate between different levels of gelation is that it is a surface measurement. It is however known that the level of gelation varies through the thickness of the pipe

and is highest at the pipe walls and lowest at the centre, Choi (12). Therefore, the differences in the level of gelation at the inner surface of the N-type pipe section might not be that high. The micro-MC method was applied to test this. Holes of different depths were milled using a manual power tool. The holes are brought in contact with MC after a few seconds of milling at room temperature. For a uPVC sample of low level of gelation no attack could be observed unless the depth of the holes was larger than 0.35 mm. Figure 5 shows a hole of 0.35 mm depth before and after MC contact.

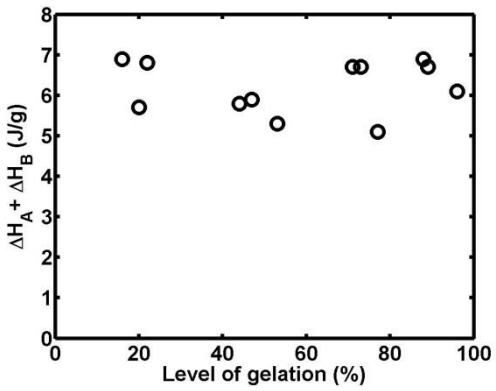
Figure 5: Surface of N-sample of 19% level of gelation, milled with a hole of about 0.35 mm deep. *Left:* before contact with MC. *Right:* after contact with MC.



Only the centre of the hole, thus at largest depth, is affected by the MC. This confirms that the level of gelation is higher at the surface than in the middle of the pipe wall. A preliminary comparison between the indentation results in this study and numerical indentation simulations presented in Visser (13) shows that the volume affected by the indentation in this study only reaches the order of depth of ~0.3-0.4 mm. Therefore, the variations in level of gelation are too deep below the surface to be picked up by the micro-hardness method used here. This gives a possible explanation why the micro-indentation method is not sensitive to the level of gelation of PVC pipes.

The laser scattering and laser microscopy methods show potential to determine the level of gelation for uPVC samples produced on the same machine and from the same formulation, but fail for random excavated PVC pipes. The surface roughness is probably not only determined by the level of gelation but also by other factors in the production process.

Figure 6: The sum of the amount of heat to melt the primary (ΔH_B) and secundairy crystallinity (ΔH_A) of N-samples of different levels of gelation as determined by DSC.



A possible explanation for the disability of the NMR measurements to differentiate between uPVC samples of different levels of gelation is that the total crystallinity changes due to different processing temperatures are negligible. The total amount of crystallinity can be determined by adding the areas of the two endotherms in DSC measurements. Figure 6 shows that the total crystallinity is independent on the level of gelation. Therefore, the total crystallinity cannot be taken as a measure for the level of gelation. This observation might explain why NMR does not show significant differences in NMR crystallinity. As no significant changes occur in crystallinity under different processing conditions, relaxation times, as measured by NMR, are not expected to change with the level of gelation as well.

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