Using Differential Scanning Calorimetry to Determine the Quality of a PVC Part

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Abstract

Failure of unplasticized poly(vinyl chloride) (PVC-U) pipes and fittings may be related to many factors, such as, design, installation, abuse and/or manufacturing. A successful failure investigation may require detailed analysis of all these factors to determine the primary cause of failure. This paper will review current techniques that use aggressive chemicals to qualitatively assess the quality of the PVC pipe or fitting. The paper will also review a technique that utilizes differential scanning calorimetry (DSC). This technique can accurately determine the temperature at which the part was manufactured. It is also able to determine the percent gelation of the PVC material, which is directly related to the mechanical properties of the part.

Poly(vinyl chloride) - PVC

Plastic is a popular alternative to copper, steel, aluminum and other materials for pipes and fittings. The most widely used plastic for pipes is PVC, which comprises 66 percent of the water distribution market and 75 percent of the sanitary sewer market in the US [1]. This material has distinct advantages over metal piping.

In light of skyrocketing copper costs, plastic can be significantly less expensive. Labor costs can be as much as 50 percent lower, due in large part to the use of easy to apply solvent cements that eliminate the need to solder. Noise reduction with plastic can be as much as four times over copper of comparable size. Further, there are fewer problems associated with condensation. Corrosion resistance of PVC is typically much greater than steel. It is estimated that 700 water main breaks occur in North America with 2.2 trillion gallons of water lost annually in the US. This results in a $2.98 billion loss in revenue [1]. Possibly the most important advantage of plastic is that it may eliminate the risk of contamination that can come from copper and other metals. Medical studies have shown a direct correlation between copper ingestion and a number of birth defects, digestive disorders and even Alzheimer's disease [2].

Failure of Plastic Piping and Fittings

Failure of a piping system can result in large monetary damages. Water leaks can quickly create substantial damage, and clean-up cost can be significant due to issues related to mold. PVC fails for many of the same reasons that other plastics fail, including:

- Chemical Attack
- Product or System Design
- Installation
- Manufacturing
- Abuse

PVC is considered to have relatively good chemical resistance. However, like all plastics it can be attacked by a host of foreign chemicals. Chemicals such as ketones, aromatic and chlorinated hydrocarbons, esters and benzene can be very aggressive to a PVC part. Figure 1 shows a pipe that swelled and cracked as a result of contact with a phthalate ester. Failure as a result of installation can occur for many different reasons including: overbelling of the pipe's bell during insertion of the male, incorrect adhesive, improper joining technique, wrong climate, and inadequate support.

Plastic pipe is manufactured using an extrusion process. Fittings are primarily produced by injection molding. Like most plastic manufacturing operations, the processing conditions determine the quality of the product. Of particular importance is the temperature of the PVC during manufacturing. The temperature during processing influences the degree of PVC gelation. If the processing temperature is too low, the degree of gelation, or fusion, will be reduced. If the processing temperature is too high, degradation of the PVC will occur. Both of these situations will result in lower than optimal material properties (e.g. strength, chemical resistance) and may result in product failure while in the field. Figure 2 shows a crack in a pipe prior to installation. Such a failure is a direct result of poor manufacturing techniques. As this paper will show, inadequate fusion of the PVC was more than likely the cause of this defect. This paper will investigate common techniques used to determine if the correct processing conditions were used during manufacturing.

Chemical Immersion Techniques to Determine Degree of PVC Gelation

The degree of gelation of PVC during the manufacturing process is critical to ensure proper mechanical strength. Two widely used techniques currently exist to qualitatively determine the level of gelation. These techniques follow the standards ASTM D2152 Acetone Immersion Test [3] and ISO 9852 Dichloromethane Test [4]. These techniques involve aggressive chemicals and give a pass/fail result. The part fails if the chemical is able to attack the PVC. This attack will result in the lifting of polymer from the surface.

Acetone Immersion Test (AT)

This technique follows ASTM D2152 [3] and is used to determine the adequacy of PVC gelation of extruded PVC pipes and injection-molded fittings. Samples that are taken from the pipe or fitting must be removed without modifying the structure of the PVC. A mechanical saw should not be used since the friction generated could substantially increase the temperature of the plastic. This may change the degree of gelation and give erroneous results. A knife or Buehler Isomet low speed saw are two methods that can be used to ensure that the degree of gelation is not altered.

High quality acetone with a low level of moisture should be used for the test. The prepared samples are completely immersed in the acetone for 20 minutes. The samples are then examined for lifting, raising or removal of any PVC material from the surfaces. The standard states that "at least 50% attack of the inside, outside, or mid-wall surface or at least 10% attack on more than one surface shall be considered indicative of inadequate fusion."

It is important to note that this test only detects inadequate gelation and does not determine the over-all quality of the PVC pipe or fitting. This test cannot differentiate between thermally degraded and adequately fused PVC. This technique cannot be used to give actual physical properties, such as burst and impact strength.

Dichloromethane Immersion Test (DCMT)

This technique follows ISO 9852 [4]. This technique is very similar to the acetone immersion test to determine the adequacy of gelation. As with the AT test, sample preparation should ensure excessive heat is not generated and the degree of gelation is not modified. Again, a knife or Buehler Isomet low speed saw are two recommended methods.

The samples should be immersed in high quality dichloromethane for 30 minutes. After removal from the test apparatus, the sample should be examined for signs of attack which may involve lifting, raising or removal of material from its surface.

Using DSC to Examine the Quality of PVC

The acetone immersion test and the dichloromethane test may provide some insight into whether the PVC had proper gelation. However, these techniques require the use of aggressive and toxic chemicals, give a subjective pass/fail result, and do not give information on the processing history of the PVC.

During processing of a PVC part, as the material is heated, the smaller "grains" (crystallites) melt first. During melting, the grains fuse together forming a partially-gelled state. The level of gelation is dependent on the processing temperature, with higher temperatures yielding a higher degree of gelation.

Information on these events can be captured using DSC. According to Gilbert and Vyvoda [5], and Vanspeybroeck and Dewilde [6], the degree of gelation and the processing temperature of a PVC part can be determined using DSC.

Gilbert and Vyvoda processed PVC compounds at various temperatures using controlled conditions. Thermal analyses using DSC were conducted on the processed samples. The samples were heated from room temperature to 240^{o}C at 20^{o}C per minute. Figure 3 shows several DSC thermograms of PVC processed at various temperatures.

The first transition observed between 80-85^{o}C represents the glass transition temperature (T_g) of the PVC. Area "A", which is an endothermic response, represents the melting of the partially gelled crystallites or the level gelation that was present in the part. Area "B" represents the melting of crystallites that did not gel during the processing of the PVC part.

As stated above, the degree of gelation is dependent on the processing temperature, which can also be seen in Figure 3 [7]. The inflection point found between areas A and B indicates the processing temperature. The DSC thermogram shows good correlation between the processing temperature stated in [5] and the inflection point.

The degree of gelation can be estimated as [6]:

$$Degree\ of\ Gelation = \frac{Area\ A}{Area\ A + Area\ B}$$

The mechanical properties such as impact strength, tensile strength and relative elongation of the PVC part are related to the degree of gelation [6, 8, 9].

The authors conducted a study to understand how well DSC can predict the processing temperature of PVC. Samples of PVC parts were heated and cooled in the DSC cell at controlled conditions. Figure 4 shows the results of a sample heated at 10^{O}C/min to a temperature of 190^{o}C and then slowly cooled. The sample was then reheated at a rate of 10°C/min. The figure illustrates that the inflection point between Area A and Area B is the same as the temperature that the sample was raised to (190°C) during first heat. This would represent the processing temperature of a PVC part during manufacturing. Similar runs were conducted in which the part was heated to various temperatures during first heat. These runs also showed that DSC was able to accurately determine the "processing" temperature.

Trials were also run using a faster cooling rate, which would represent more realistic manufacturing conditions. Figure 5 shows the DSC thermogram during first heat to 195°C. Also shown is the DSC thermogram of the second heat after cooling at a rate of 40°C/min. Again, the DSC accurately shows the maximum temperature (195°C) during first heat.

Understanding the level of gelation and its relation to the final mechanical properties of PVC can be a powerful tool to evaluate the quality of parts, and for failure analysis.

A study of a PVC pipe failure (Pipe #1), which exhibited a circumferential crack on its interior surface (Figure 2), utilized the DCM chemical test, as well as, DSC. Figure 6 shows the coupon after the DCMT. Severe lifting of the PVC is seen. According to the ISO Standard 9852[4] the PVC failed the test and is considered to be inadequately fused. A sample from the same cracked location of the pipe was analyzed using DSC. The sample was heated at a rate of 10°C/min to approximately 230°C. Figure 7 shows the DSC thermogram of this sample with gelled (Area A) and ungelled (Area B) indicated. The T_g was found to be 84.8°C and the processing temperature 177°C. The degree of gelation was calculated to be 55.9%.

A pipe that cracked axially while in service was also examined (Pipe #2). The sample after the DCM chemical test is shown in Figure 8. Again, severe lifting is observed in this photograph. The DSC thermogram of a sample taken near the crack is shown in Figure 9. The T_g was found to be 84.7°C and the processing temperature 177°C. The degree of gelation was calculated to be 53.9%.

An exemplar (not cracked) PVC pipe[1] (Pipe #3) was also analyzed. No lifting of the PVC was observed during the DCM chemical test. Figure 10 shows the DSC thermogram for this pipe. The T_g was 84.9°C and the processing temperature during manufacturing of the pipe was found to be 195°C. The degree of gelation was calculated to be 97.1%.

Though this is not an exhaustive study on the comparison of the DCMT and DSC methods, nor the validity of the DSC method, it does show that the cracked pipes have a lower degree of gelation than the uncracked exemplar and this may have contributed to failure. There are clear benefits of using DSC to analyze PVC, including:

- Controlled conditions
- Small sample size
- Localized/specific sample selection
- Ability to determine degree of gelation
- Ability to determine the processing temperature
- Does not use aggressive chemicals
- Quantitative results (instead of pass/fail)

Additional research will focus on determining how Area B should be measured and the relationship between the degree of gelation to mechanical properties.

Conclusion

This paper reviews a technique that utilizes DSC to determine the quality of unplasticized PVC parts. This technique allows one to accurately determine the temperature at which the part was manufactured. It is also able to determine the percent gelation of the PVC material, which is related to the mechanical properties of the part. This technique has clear advantages over commonly used methods that use aggressive chemicals. Further research needs to be completed to relate the degree of gelation to mechanical properties in the PVC parts.

References

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[1] 6" Charlotte PVC Pipe. Type 1. Sch 40.

Figures

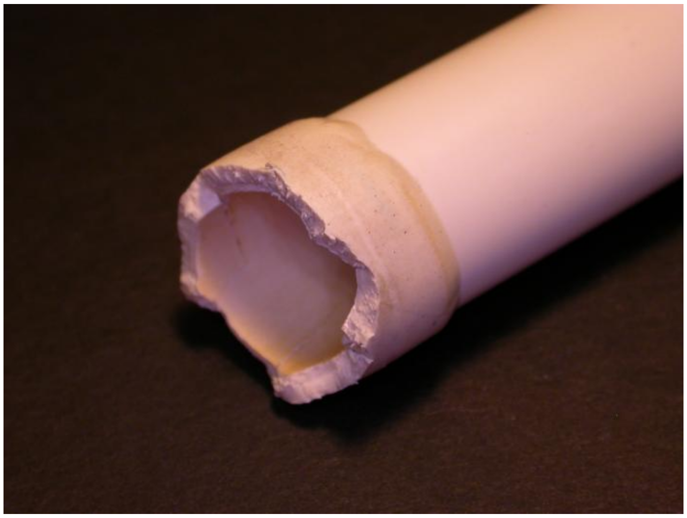

Figure 1 – Chemical attack of a plastic pipe.

Figure 2 – Circumferential crack in PVC pipe prior to installation.

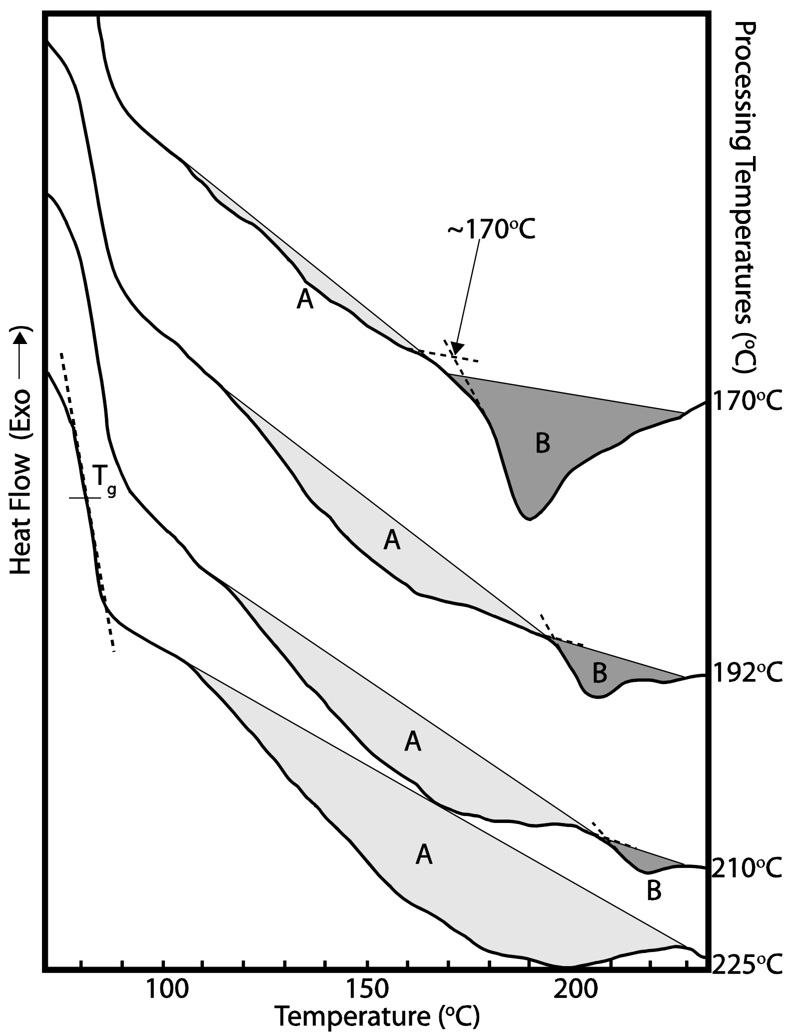

Figure 3 – DSC thermograms of PVC samples manufactured at various temperatures.

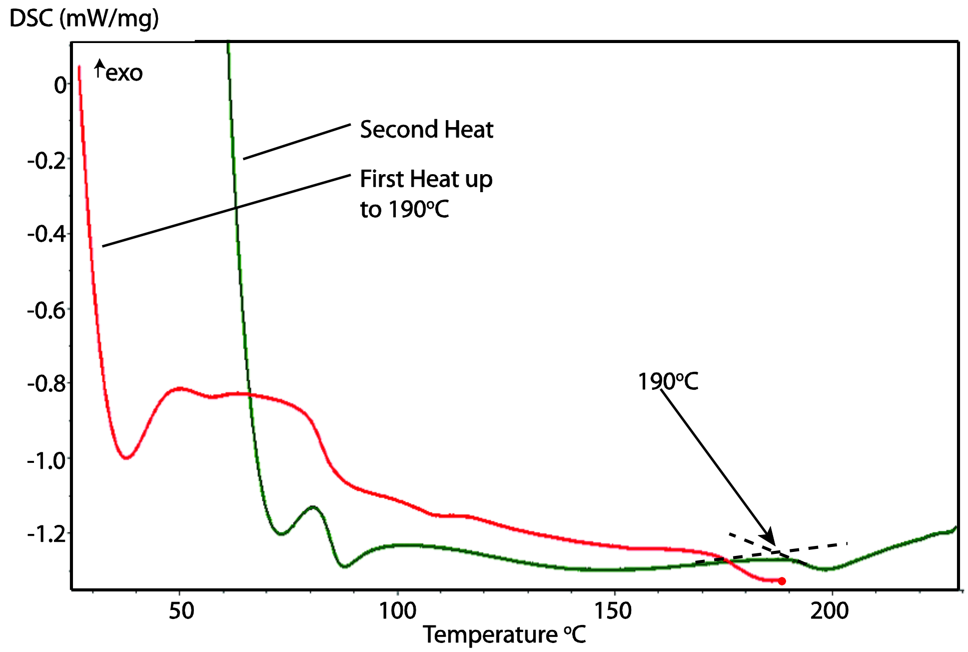

Figure 4 – DSC thermogram of a PVC sample heated to 190ºC and then cooled slowly.

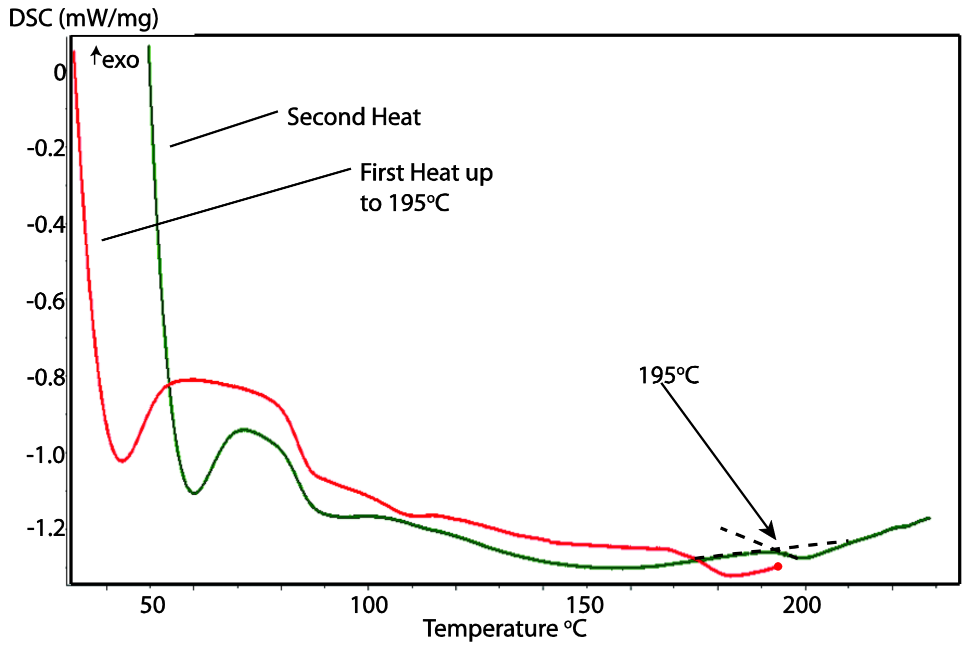

Figure 5 – DSC thermogram of a PVC sample heated to 195ºC and then cooled quickly at 40ºC/min.

Figure 6 – PVC sample of failed Pipe #1 after immersion in dichloromethane.

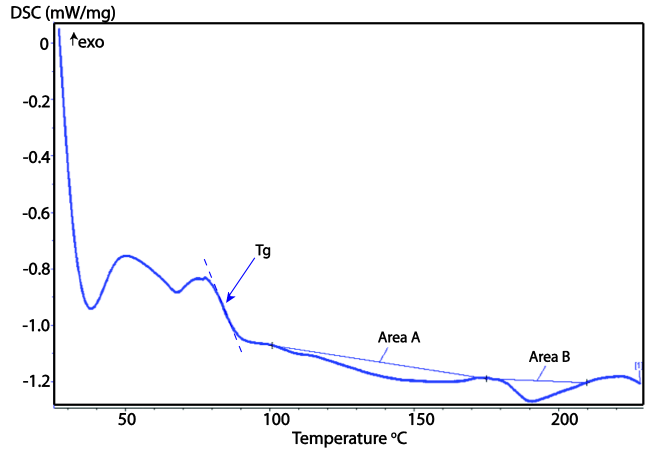

Figure 7 – DSC thermogram of failed Pipe #1.

Figure 8 – PVC sample of failed Pipe #2 after immersion in dichloromethane.

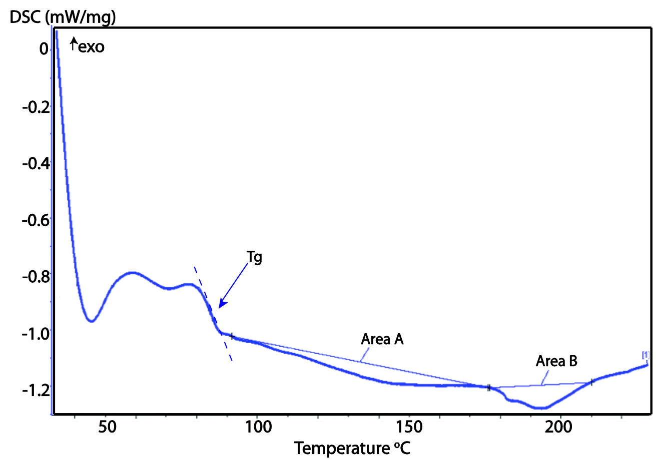

Figure 9 – DSC thermogram of failed Pipe #2.

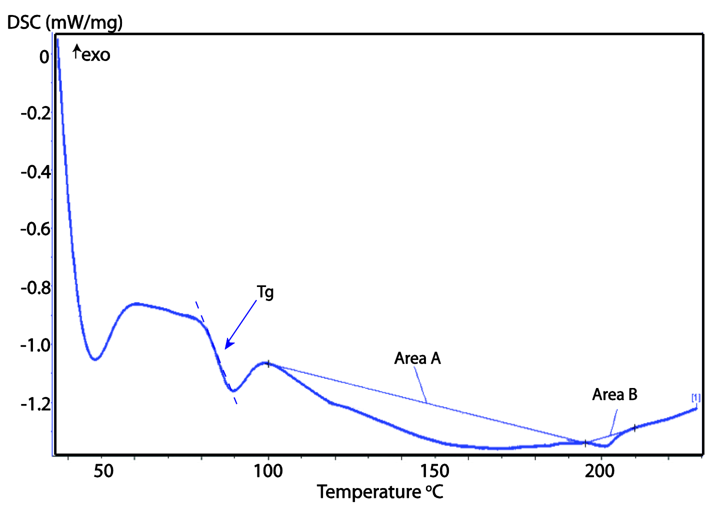

Figure 10 – DSC thermogram of Exemplar Pipe #3.