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Development of a method for pressure-free volumetric dilatometry of polymer melts and solids

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Abstract

The tendency of polymers to shrink upon cooling and to expand upon heating strongly affects polymer processing operations. Therefore, quantifying these properties through dilatometry is crucial. Existing setups to measure dilatometry are, however, mostly limited to solid samples, or are expensive and impractical to use. Moreover, upcoming forms of polymer processing such as additive manufacturing techniques or more commonly named 3D-printing techniques require these properties to be measured under atmospheric pressure, which is not possible with most of the existing setups. Therefore, this paper describes a novel method for pressure-free volumetric dilatometry that is able to characterize samples in both liquid and solid phase, and during liquid-solid transitions. The principle of the method is based on the use of a highly viscous confining fluid that, in combination with a simple piston-die sample container, offers a cheap, easy-to-use and safe method to measure volumetric dilatometry on a variety of samples. The method is verified by comparison with standards and data from literature.

Keywords: Dilatometry, Thermal characterization, Additive manufacturing

1. Introduction, state-of-the-art

The ability to accurately characterize the specific volume v of a material as a function of temperature T and/or time t is critical in many engineering fields, as these volume changes affect both the processing and end-use performance of these materials. Full characterization of this material parameter is however complicated as there are a variety of physical phenomena that may result in dimensional changes. These include thermal expansion and shrinkage, thermal transitions such as crystallization, melting and glass transitions, and chemical shrinkage such as curing or crosslinking. Especially characterizing samples that exhibit both liquid-like and solid-like behavior within the temperature range of interest has proven to be difficult.

In order to characterize these properties, many dilatometric methods have been developed. These methods can be classified in three classes: methods to determine material density, direct dilatometric methods and indirect dilatometric methods.

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Methods to determine material density are usually designed to determine the density at one specific temperature, generally room temperature. The most relevant methods are density gradient columns [1,2] (see also ISO 1183-2), balance assemblies using buoyancy methods (Archimedes, ISO 1183-1), gas and liquid pycnometers (ISO 1183-1, ISO 1183-3) and titration methods (ISO 1183-1). In theory, these methods can be used to determine solid and liquid densities of a material at different temperatures and times, as demonstrated for example by Li et al. [3]. However, this is a very cumbersome and time-consuming method to determine $\nu(T,t)$ of a material, and only few of the mentioned techniques can be used to measure both liquids and solids.

Direct dilatometric methods directly measure dimensional changes of a sample as a function of temperature or time. Possible methods include linear dilatometers, such as push-rod, laser, capacitance and optical dilatometers, thermo-mechanical analyzers (TMA) and piston-die pressure-volume-temperature (PVT) techniques [4,5]. Linear dilatometers and TMAs are only suitable for measuring solid samples, as their measurement principles and cell designs are not adapted to liquids. In contrast, piston-die PVT techniques use a sample confined in a rigid die or cylinder equipped with a movable piston. This method can therefore measure both liquids and solids. However, to ensure continuous and complete contact between piston and sample, pressure needs to be applied by the piston, resulting in PVT data sets. Data at atmospheric pressure can only be obtained through extrapolation. A fundamental problem with this technique is that, especially for solid samples, the state of stress is not hydrostatic [6]. Further practical complications include the formation of voids when samples solidify from the outside, and leakage around the piston when the sample is in the molten state.

Indirect dilatometric methods use an auxiliary medium, for example a confining fluid, to measure dimensional changes of samples. Possible methods include dilatometer cells using particulate filling media such as fused quartz powder [7], mercury capillary dilatometers [8-12] and confining fluid PVT techniques [6, 13]. The problem with particulate filling media is that liquid samples will flow into the interstitial spaces of the filling medium, resulting in erroneous measurements on non-solid samples. This is not the case when a liquid filling medium is used. Therefore, the use of mercury as confining fluid in dilatometers is fairly widespread. Mercury can be used in combination with both liquid and solid samples, has well-known dilatometric properties, rarely interacts with polymer samples and its high surface tension allows accurate readings of the liquid surface for example in capillary columns. However, this high surface tension also limits the technique to samples with reasonably low surface area. Therefore, measurements on films, fibers and fine powders are not possible. Furthermore, an important disadvantage of mercury is its high toxicity to humans and to the environment.

Automated mercury dilatometers exist in several forms. US patent 6,718,281 [11] describes a mercury dilatometer in which an optical displacement sensor perpendicular to the liquid level is used to provide automatic readings of the level of the measuring capillary. Patent DE 102005001945 [12] describes a variation of this

setup, in which the liquid level is monitored by a laser, moving parallel to the capillary. However, one of the most widely used setups in academia and industry is a pressurized mercury dilatometer commercialized by Gnomix Inc. In this device, the sample and confining fluid are contained in a rigid sample cell of which one end is closed by a flexible bellows [6]. This cell assembly is placed in an electrically heated pressure vessel and by measuring the motion of the bellows, the PVT behavior of a sample is obtained. The advantage of applying pressure is that any outgassing either of the confining fluid or the sample does not affect the measurements. However, extrapolation to atmospheric pressure may lead to errors, especially in transition areas such as during crystallization, as these transitions can be strongly affected by pressure. However, the main disadvantage of this method is more of a practical nature, with very high measurement effort, high acquisition cost, and safety issues (mercury toxicity).

Hence, in this paper, a new indirect dilatometric method is proposed that provides an alternative for the toxic mercury. Moreover, the newly proposed technique will be able to directly measure the volume change as a function of temperature at ambient pressures.

2. Experimental work

2.1 New dilatometric setup

The dilatometric method described in this section addresses the above and other limitations associated with the current state-of-the-art. The novel method consists of two aspects. The first aspect considers the use of a highly viscous fluid as confining medium in order to replace mercury. The second aspect then consists of a novel dilatometer cell that allows the use of this fluid for dilatometric measurements in existing linear dilatometers. The combination of both aspects results in a cheap and safe setup that can measure volumetric changes in solids and liquids under atmospheric pressure.

2.1.1 Use of highly viscous fluid

The most innovative part of this new setup is the use of a highly viscous fluid as confining medium. This type of fluid allows indirect dilatometric measurements using regular piston-die dilatometer cells, as the high viscosity prevents leakage of the fluid within reasonable time spans. A fluid that is highly suitable for this application is silicon oil, but other fluids may be applicable as well. Figure 1 shows the zero shear viscosity versus temperature of a commercially available silicon oil that is used in this study. In this case, the viscosity does not drop below 20 Pa.s in the measured temperature range.

Figure 1: Zero shear viscosity as a function of temperature for a high-viscous silicon oil, trade name Rhodorsil® 47 V 1000000.

There are several aspects that make silicon oil a highly suitable confining medium. First of all, silicon oils are readily available, also at high viscosities. They are safe, non-flammable and non-toxic to humans and environment. They are also transparent, making visual observation of the sample during preparation and measurement possible. As a confining fluid, silicon oil is inert and does not react with most common materials. Moreover, unlike mercury, silicon oil does not react with metals, allowing the measurement of even low-melting metals or metal-filled polymers.

Other important advantages include the fact that silicon oil remains stable over a wide temperature range. The wetting and lubricating properties of the oil also prevent samples from sticking to the walls of the dilatometer cell. Therefore, the sample is always under uniform hydrostatic pressure, and the development of stresses in the sample due to adherence to cell walls is avoided. Finally, the density of silicon oil is slightly lower or comparable to many targeted materials such as polymers. This, in combination with the high viscosity of the fluid, allows easy suspension of samples, which prevents blockage of the piston by hardening samples, and allows the use of simple vertical cups instead of U-shaped dilatometer cells.

One of the few disadvantages is that silicon oil has a thermal expansion similar to most polymers. This leads to loss of accuracy when measurements are corrected for the contribution of the confining medium. Further inaccuracies result from the viscosity decrease at high temperatures, which sometimes leads to slight leakage of the oil. However, the problems related to these factors can be dealt with as will be further discussed in section 2.2.

2.1.2 Novel dilatometer cell

This section considers a novel dilatometer cell design, which makes it possible to perform pressure-free measurements on samples contained in a highly viscous fluid.

In principle, the high-viscous fluid could be used as a confining medium in any dilatometer cell that can hold liquids. However, as fluids like silicon oil adhere to glass, they are unsuitable for capillary or optical techniques, limiting their use mainly to piston-die or sealed cell designs. The dilatometer cell that is described in this section is a cheap and easy-to-use piston-die design that can be used in combination with practically any existing linear dilatometer or TMA.

The dilatometer cell, shown in Figure 2, consists of a cup containing the sample and filling medium, and a tight-fitting piston which moves linearly in response to volume changes. The fit between piston and sample cup is tight, but still allows free movement of the piston. For the cup dimensions, materials and test parameters used in this study, a gap of 0.02 mm between the outer surface of the piston and the inner surface of the cup is found to be optimum, but this may vary if other dimensions or materials are used. Additionally, the length of the piston that is contained within the cup should be as long as possible, and this length should be maintained over the entire measurement temperature range. In this study a minimum length of 7 mm is used. The tight fit in combination with the long path length prevents leakage of the highly viscous fluid within reasonable time frames, while still allowing free movement of the piston during measurements.

Figure 2: The new dilatometric setup, on the left a schematic representation, on the right the implementation in a commercial TMA-device (here a TMA Q400, TA Instruments), with transparent polymer pellets contained in high-viscous silicon oil.

Materials to manufacture the cup and piston are typically materials that are thermally stable and have low thermal expansion coefficients. This makes any contribution to the dilatometric measurement negligible, and avoids the piston from getting stuck due to thermal expansion. Good materials that meet these requirements are low-expansion glasses, such as fused quartz or borosilicate glass. Apart from their very low thermal expansion coefficients, these materials are also readily available and, when used in combination with a transparent confining fluid, also allow for visual observation of the sample. The cups and pistons required for the setup can easily be manufactured starting from glass tubes. Preferable, the tight fit between cup and piston is achieved by starting from tubes that already show this tight fit. Alternatively, a fit can be achieved by careful grinding of the piston side, but this is not recommended as this often disrupts the cylindrical shape of the piston, leading to leakage when the piston is moving upwards during measurements.

The setup consisting of the proposed dilatometer cell and the highly viscous fluid has several advantages over existing dilatometric setups. Samples of any size and shape, including pellets and powders, can directly be measured without premolding. In order to measure fine powders for example, these can be mixed manually with a certain amount of confining fluid, which after thorough degassing under vacuum conditions creates a high-viscous paste that can be immersed in pure confining fluid for the actual measurement. Samples can be measured under atmospheric pressure, and under heating, cooling or isothermal conditions. The applicable temperature range depends on the dilatometric device or TMA that is used for the measurement, and the fluid that is used as confining medium. When silicon oil is used, the applicable temperature range is from around -40 up to 300°C.

The setup can be used in combination with many existing linear dilatometers or TMAs. This expands the application range of these devices to volumetric dilatometry of both solid-like and liquid-like materials, and solid-liquid transitions. The dilatometer cell shape and size can easily be adapted to fit in any existing dilatometer. The size can also be changed, for example to increase measurement sensitivity, limit the required amount of sample, or reduce thermal gradients and inertia. A possible modification could be to use the cell design shown in Figure 2 upside-down in order to measure liquid samples with a density lower than the confining medium, which would otherwise leak around the piston.

The use of a transparent cup material such as low-expansion glass, in combination with a transparent viscous fluid such as silicon oil, allows visual observation of the sample before, during and after measurement. Therefore, possible issues including bubble formation, sample degradation, or other changes can easily be traced. Additionally, the suggested materials are safe, cheap and non-toxic to humans and environment, and the resulting setup is reusable and easy to operate.

2.2 Experimental method

The measuring principle is based on a known quantity of sample, and a known quantity of confining fluid, enclosed air-free in the dilatometer cell. The height of the piston is monitored as a function of time or temperature using a linear dilatometric device. From this linear signal, the specific volume of the sample as a function of time or temperature can then be calculated by using the volume change in combination with a reference density of the sample at 25°C and atmospheric pressure.

To obtain $v(T,t)$ of the sample, the signal has to be corrected for the volumetric changes of the confining fluid. This can be done in several ways: by using literature values for $v(T,t)$ of the fluid, by measuring $v(T,t)$ of the fluid with this or a different setup, or by applying a baseline correction. The latter is done by repeating the same measurement that was done on the sample, so with the same cup and exactly the same temperature profile (heating and cooling), but with only confining fluid in the cup. After correction for the different amount of fluid used in the baseline and actual

measurements, these data can be subtracted from the original signal to obtain $v(T,t)$ of the pure sample. Advantages of the baseline method are that possible contributions from the dilatometer cell, temperature inhomogeneities, and slight leakage (if present) of confining fluid is also being corrected for.

There are two ways to measure the specific volume of a sample as a function of temperature. This is demonstrated in Figure 3 for a sample of pure silicon oil, the confining fluid used in this work. The first possibility consists of a continuous measurement at a certain heating or cooling rate. Disadvantage of this method is that the temperature distribution within the sample may not be uniform or in equilibrium. This can be observed in Figure 3, as thermal inertia during the faster ramp result in a larger gap between heating and cooling curves. However, the heating and cooling curves measured at 0.5°C/min overlap perfectly. The second possibility consists of a step-wise approach, in which the sample is kept isothermally at each temperature until equilibrium is obtained. Disadvantage of this method is, however, that the heating or cooling rate during thermal transitions is not controlled. For a semi-crystalline polymer, for example, crystallization may occur very slowly or very rapidly depending on which temperature points are selected for the measurement, and this may result in different properties of the solid material.

Figure 3: Dilatometric measurement of silicon oil, trade name Rhodorsil® 47 V 1000000, using different measurement protocols on a TMA Q400 (TA Instruments).

In the following examples, borosilicate glass cups such as those shown in Figure 2 are used for the dilatometer cell. The inner diameter of the cup is 10 mm and Rhodorsil® 47 V 1000000 silicon oil is used as confining fluid. The dilatometer cell is used in combination with a commercial TMA Q400 (TA Instruments) equipped with a linear push-rod probe and an oven with nitrogen purge. Table 1 lists the polymer samples that are used for the examples. Each sample is thoroughly dried before measurement, and after addition of silicon oil, the immersed sample is further subjected to vacuum drying for at least 24 hours to remove any volatiles or entrapped gasses. Baseline corrections are applied to correct for the oil contribution,

and reference densities at 25°C are taken from material datasheets or measured using Archimedes' method (ISO 1183-1).

Table 1: Polymer materials used for the examples in this study.

Material		Trade name	Manufacturer
Poly(methyl methacrylate)	PMMA	Altuglas® V 825T	Arkema
Polybutene-1	PB-1	Koattro PB 0801M	Lyondellbasell
Poly(lactic acid)	PLA	Ingeo™ Biopolymer 3251D	NatureWorks
Thermoplastic polyurethane	TPU	Luvosint® TPU X92A-1	Lehmann & Voss

3. Results: calibration and verification of the new setup

3.1 Calibration of the new setup

Calibration of this measurement setup depends on the device that is used for the dimensional measurement. In general, the standard calibration protocol of the used device can be followed, with small adjustments that are required to accommodate the new setup. In this study, a thermo-mechanical analyzer (TMA) is used. Therefore, the proposed calibration steps apply to a TMA, but should be very similar for any other dilatometric device. The calibration consists of the following steps: force and probe calibration, temperature calibration and cell constant calibration.

The force and probe calibration calibrates the exerted force, the LVDT and the compliance of the probe. These parameters do not need adjustment for the new setup. The temperature and cell constant calibrations, on the other hand, do require adjustment, as the sample size and heating rates in the new setup are rather different from those used in regular TMA measurements.

Temperature calibration is done by measuring temperature standards and comparing the measured melting point to the theoretical value. Figure 4 shows the dilatometric measurement on an indium sample. In this example, the onset of melting almost perfectly corresponds to the theoretical value of 156.6°C, thus no correction is necessary. In general, the calibration should be redone when repositioning the thermocouple or when using different temperature ramps. In this study, however, it is found that calibration values did not need adjustment as long as low heating rates (between 0.5 and 1°C/min) or step procedures are used.

In this study, a three-point temperature calibration is used. This includes one measurement at room temperature, one indium and one tin measurement (theoretical melting point 232°C). The temperature is then corrected by a cubic spline fit between these points, with fixed offset values outside of the calibration window.

The next calibration step consists of determining the cell constant. This is a general correction factor for the linear displacement measured by the TMA. For this calibration, the measured expansion coefficient of a standard material is compared

to its theoretical value. Generally, metals such as aluminum are used. However, for this setup metals are not the best option, as they have low expansion coefficients compared to the confining oil. Therefore, a polymer standard is used of which the dilatometric data are measured accurately using a different technique, as will be demonstrated in the next section.

Figure 4: Dilatometric measurements of an indium metal standard (heating rate 0.5°C/min). The dashed line marks the melting onset.

3.2 Verification and examples

Figure 5 shows the measurement of an amorphous PMMA sample during step-wise heating. A clear glass transition is visible around 110°C, which is confirmed by differential scanning calorimetry (DSC).

Figure 5: Dilatometric measurement of an amorphous PMMA grade, compared to measurements with a Gnomix device [14] and with a regular TMA setup.

In order to verify its accuracy, the measurement is compared to data of the same PMMA grade, obtained using two other methods. One curve is obtained by

extrapolation from a PVT measurement on a Gnomix device. The other curve is determined from a regular linear TMA measurement on a solid sample, assuming that the volumetric expansion coefficient equals the linear expansion coefficient times three. In general, good agreement is found between the data. Only at higher temperatures, a slight deviation is found from the Gnomix data. There are several possible explanations for this. Most likely, these are related to inaccurate corrections for the confining fluids, or errors in volume or temperature calibration in either of the devices. In any case, if it is assumed that the Gnomix data are correct, a cell constant is determined with a value of 0.997, which is very close to the theoretical value of 1. However, to get optimum accuracy, a temperature-dependent cell constant should be used, as the signal deviation clearly depends on temperature.

A further example is displayed in Figure 6, which shows the measurement of a semi-crystalline PB-1 sample. A heating and cooling ramp is performed at 0.5°C/min. A clear melting expansion step is visible around 110°C, followed by crystallization at 80°C, which is in agreement with DSC measurements. The figure also shows literature data for another grade of PB-1. The match is not perfect, but this may be due to the fact that a different grade was measured, with possibly different crystallinity or added fillers. Nevertheless, the slopes of the curves show a good match.

Figure 6: Dilatometric measurement of a semi-crystalline PB-1 grade, compared to measurements on a Gnomix device [6].

This example also demonstrates an interesting application of the new dilatometric technique. The fact that crystallization and melting steps are not of the same size is because of the polymorphic behavior of this material, and this behavior can thus be studied using the setup. An example of this can be found in Van den Eynde et al. [15].

Figure 7 shows two further examples of measurements with the new setup, one PLA and one TPU. Heating and cooling ramps are performed at 0.5°C/min. Unlike the shown example of PB-1, this PLA example has more common semi-crystalline behavior, where the heating and cooling curves match both above the melting point

as well as below the crystallization point. However, what is less common here is the very large gap between melting and crystallization points, which is caused by the very slow crystallization kinetics of PLA. This large gap, in addition to the different expansion coefficients of the molten and solid phases, makes that the volumetric expansion step upon melting is very large (about 5.4%) in comparison to the shrinkage step upon crystallization (only about 2.6%). This example, together with the PB-1 example, shows the added value of having a setup in which both heating and cooling curves can be measured to allow full characterization of a material.

Finally, the other example in Figure 7 shows the cooling curve of a TPU material. Unlike the previous examples, this material was in fine powder form, as it is meant for use in laser sintering which is currently one of the most common additive manufacturing techniques. The crystallization step around 150°C is very small due to the very low number of crystallites present in this particular TPU. In any case, this example shows that unlike many of the existing techniques, the new dilatometric setup has no problem measuring fine powders. This, in addition to the fact that it operates under atmospheric pressure, makes this setup ideal for characterizing materials for 3D-printing techniques such as laser sintering. Further measurements on polyamide and TPU powders for laser sintering can be found in Verbelen et al. [16,17].

Figure 7: Dilatometric measurement of a semi-crystalline PLA grade and a TPU grade (TPU data taken from [17]).

4. Discussion and potential applications

In the first section, it was discussed that most existing dilatometric techniques are limited to measurements on solid samples and cannot be used above the softening point of a material. Those that can measure liquid-like samples mostly require elevated pressure and/or the use of hazardous substances like mercury. Moreover, these methods are often expensive and cumbersome to use.

Therefore, a new dilatometric setup is developed that deals with these limitations. Many advantages of this setup have been discussed. One of the main advantages is the fact that both solids and liquids can be measured, under atmospheric pressure. The cell design can easily be adapted depending on the dilatometer used and the intended application. In this study, only low heating and cooling rates were studied. But to improve thermal control at higher rates, the design could easily be scaled down. Finally, an important advantage compared to existing techniques is that this setup is practical, safe and cheap.

Some minor disadvantages of the setup are that correction for the used confining medium is required, and that leakage may occur at high temperatures. In this study, it is found that when using the suggested gap between piston and cup of 0.02 mm, and the minimum applicable force of 0.001 N in the TMA, measurements up to 250°C are possible without any leakage. At higher temperatures, some leakage occurs, which can partially be corrected for by a baseline correction as explained above. Any measurement above 280°C resulted in volatiles formation by either the sample or the oil, so this can be seen as the current upper limit of the setup.

In general, this setup can greatly expand the possibilities of existing TMAs or dilatometers. Using the new setup, thermal phenomena such as the glass, melt and crystallization transitions can be studied, in addition to the expansion or shrinkage behavior of both solid and liquid material. Also, any sample shape including pellets or powders can be measured directly, without preforming. Finally, the TMA used in this study does not require any modification in order to accommodate the setup.

Potential applications of the technique would include any measurements that benefit from the aforementioned advantages. An interesting application is the study of polymer shrinkage and expansion at atmospheric pressure. This is very useful information for any polymer processing technique that operates at ambient pressure, including all current 3D-printing techniques, and certain coating and rotomolding processes. But also for polymer processing at elevated pressures, this technique can give a first indication on the material behavior. Another application that was not covered in this paper would be the study of thermoset curing. The obtained density measurements can also be used to study polymorphism, for example in polymers, but also in food products or biomedical applications.

5. Conclusions

This paper discussed the development of a novel technique to measure dilatometry on solids and liquids. Among many advantages, this technique offers a practical, cheap and safe way to measure for example crystallization shrinkage of polymers under atmospheric conditions. The development of this technique thus allows easy evaluation of one of the important material parameters involved in many polymer processing methods and polymer applications.

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Highlights

- New dilatometric setup using highly viscous liquid as confining fluid is developed.
- This setup offers a safe, cheap and easy method to measure volume-temperature properties of polymers and other materials.
- Examples are given of measurements with PMMA, PB-1, PLA and TPU, and comparisons with literature data or other methods show good matches.