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Test Method

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.

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.

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 $v(T,t)$ 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

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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. Fig. 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.

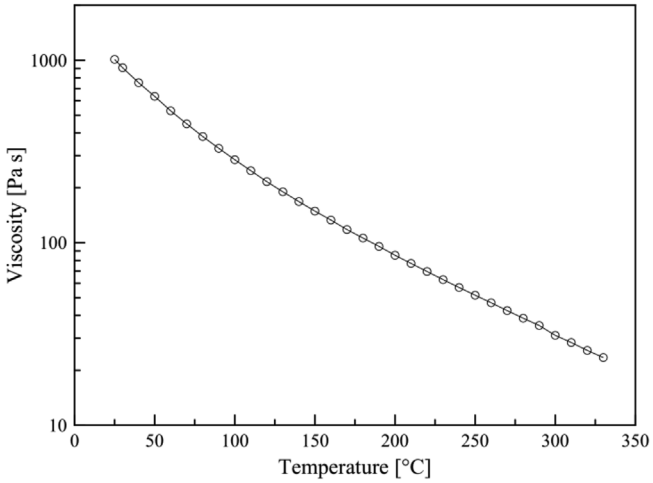

Fig. 1. Zero shear viscosity as a function of temperature for a high-viscous silicon oil, trade name Rhodorsil® 47 V 1000000.

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 Fig. 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