Shrinkage and CTE of Resins by Volume Dilatometry

Y. Chowdhury, D. Dietrich, A. Bauer

Motivation

Changes in specific volume occur e.g. during the curing of thermosets (volume shrinkage) or due to any thermal impact on resins (thermal expansion etc.).

Therefore reliable information on volume shrinkage and coefficient of thermal expansion (CTE) is important for resin's application and simulation of resin containing components.

Exact (time and temperature resolved) volume change information from resin curing and its successive temperature cycles can be provided by **capillary volume dilatometry**.

InnoMat runs several volume dilatometer setups in its application lab and performs volume dilatometry of diverse materials at client's request.

Method

A capillary volume dilatometer consists of a glass bulb into which the sample is placed, and a glass capillary connected to the bulb. For measurement, this assembly is filled with a "confining" fluid. The confining fluid surrounds the sample and transfers its volume changes into a rising or falling meniscus in the capillary, read by a moving light barrier.

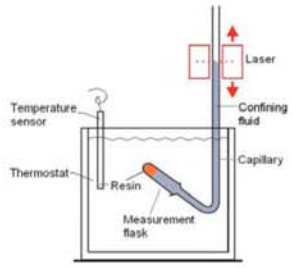


Fig. 1: Setup of a capillary volume dilatometer for thermal curing resins

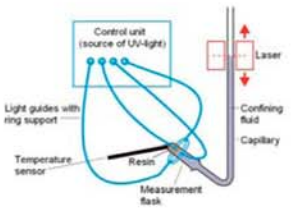


Fig. 2: Setup of a capillary volume dilatometer for light curing resins

These setups makes continuous automated recording of the volume-temperature-time function during curing possible.

Equipment capability:
- Temperature range 25 °C to 250 °C
- Individual temperature profiles according to customer's needs / application process
- Normal pressure
- Small sample quantities (0.5 to 1 g)

Results

Volume dilatometry enables determination of:
- Specific volume (reciprocal density) over temperature and time
- Volume shrinkage of polymerization processes (e.g. curing of a reactive thermoset)
- Coefficient of thermal volume expansion of cured resins or other solid resin materials
- Glass temperature

Sample Results

Figure 3 shows the specific volume over time for the curing of a cyanate ester at 180 °C for 210 min. The shrinkage starts at 180 °C and continues during the isothermal phase. At heating and cooling the specific volume follows the temperature gradient.

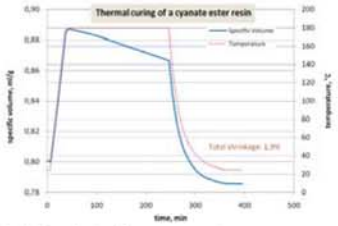


Fig. 3: Thermal curing of a cyanate ester resin

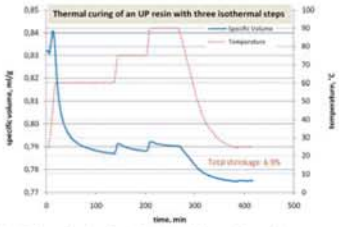


Fig. 4: Thermal curing of an UP resin with three isothermal steps

Figure 4 represents the gradient of the specific volume for a curing cycle of a hot-curing UP resin. Shortly after reaching 60 °C the resin starts to shrink. The shrinkage is not finished after the first isothermal step. In every isothermal step a continuing shrinkage is detectable.

Figure 5 displays an example of a light induced shrinkage measurement. At the first UV-light exposure of the material, a considerable shrinkage occurs. To insure that all reactive species have reacted, a second UV-light exposure is performed. The exothermal nature of polymerization is clearly detectable.

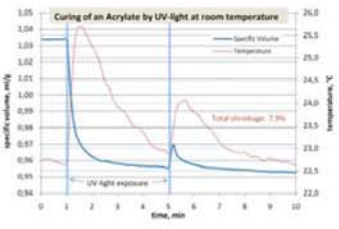


Fig. 5: Curing of an Acrylate by UV-light at room temperature

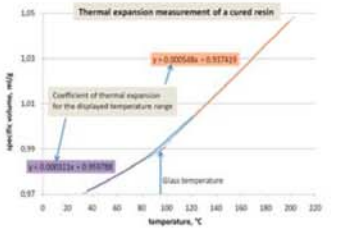
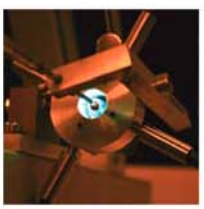


Fig. 6: Volume dilatometric measurement of thermal expansion

Figure 6 gives an example for a measurement of the volumetric thermal expansion coefficient. These measurements are usually performed on cured resins with a heating rate of 1 K/min. The graph displays different volumetric coefficients of thermal expansion below and above the glass transition temperature.

To compare the volumetric CTE determined by volume dilatometry with the linear CTE gained by thermo-mechanical analysis (TMA) a cured cyanate ester resin was measured. The results display very well the correlation between linear and volumetric CTE by a factor of 3.

T = (30 to 90) °C	Linear CTE, ppm/K	Volumetric CTE, ppm/K
Volume dilatometry	54 (calc.)	**164**
TMA	**53**	159 (calc.)



Contact

InnoMat GmbH
Yvonne Chowdhury
Kantstr. 55
14513 Teltow, Germany
y.chowdhury@innomat-gmbh.de
http://www.innomat-gmbh.de

Shrinkage and CTE of Resins by Volume Dilatometry

Yvonne Chowdhury, D. Dietrich, A. Bauer
InnoMat GmbH, Teltow, Germany

Motivation

Volume shrinkage during the curing of thermosets causes problems in many applications, e.g. molding compounds, filling materials and adhesives. During their curing and lifetime thermosets run through different temperature cycles, accompanied by changes in specific volume. But for development of new materials and for process control, a reliable material characterization (volume-temperature-time function of the resin being cured) is very important for scientists and engineers.
Nowadays, increased reliability requirements on components often demand lifetime predictions from simulation methods. Therefore exact volume change information from resin curing and its successive temperature cycles is required. An appropriate measurement device providing time and temperature resolved volume change information has already been developed – a capillary volume dilatometer.
InnoMat runs several volume dilatometer setups in its application lab and performs volume dilatometry of diverse materials at the client's request.

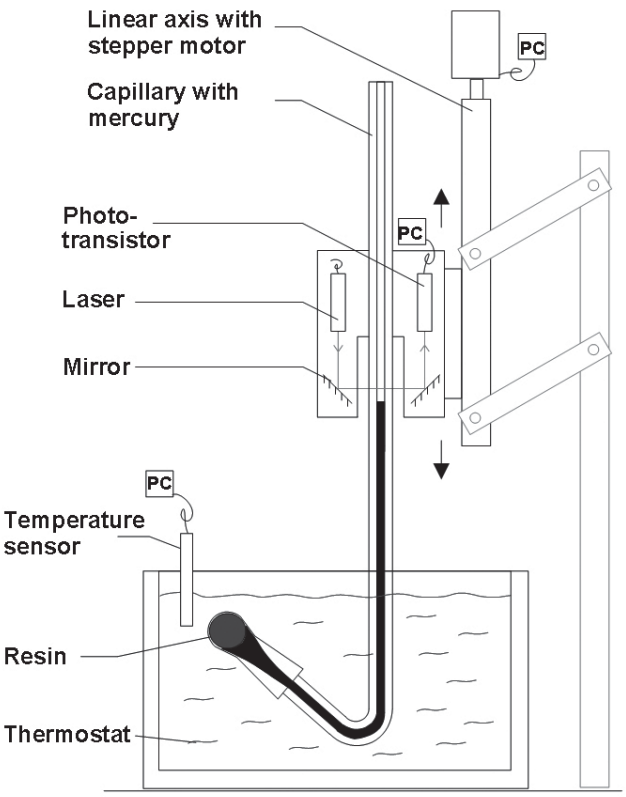


Figure 1: *Set-up of a capillary volume dilatometer*

Method

A capillary volume dilatometer consists of a glass bulb into which the sample is placed, and a glass capillary connected to the bulb. For measurement, this assembly is filled with a "confining" fluid (mercury, Galinstan or silicon oil – chosen according to the nature of sample material). The confining fluid surrounds the sample and transfers its volume changes into a rising or falling meniscus in the capillary, read by a moving light barrier. This setup makes continuous automated recording of the volume-temperature-time function during curing possible.
In InnoMat's application lab for volume dilatometry different curing methods can be realized:

- Thermal curing via oil bath
- Light curing by blue or UV-light

Sample Results

Volume dilatometry enables determination of:

- Specific volume (reciprocal density) over temperature and time
- Volume shrinkage of polymerization processes (e.g. curing of a reactive thermoset)
- Coefficient of thermal volume expansion of cured resins or other solid resin materials
- Glass temperature

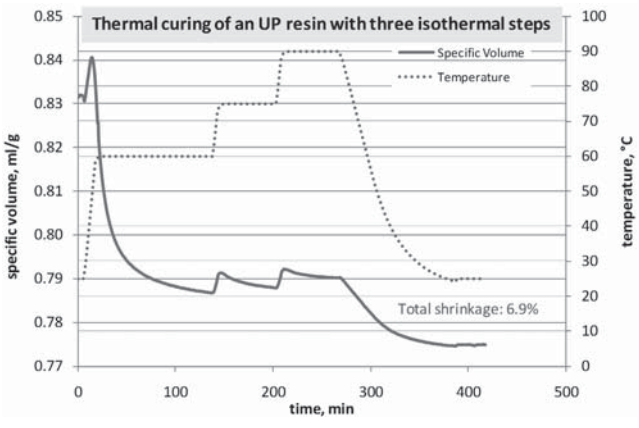


Figure 2: *Thermal curing of an UP resin with three isothermal steps*

Figure 2 represents the gradient of the specific volume for a curing cycle of a hot-curing UP resin. Shortly after reaching 60 °C the resin starts to shrink. The shrinkage is not finished after the first isothermal step. In every isothermal step a continuing shrinkage is detectable.

Figure 3 displays an example of a light induced shrinkage measurement.At the first UV-light exposure of the material, a considerable shrinkage occurs. To insure that all reactive species have reacted, a second UV-light exposure is performed. The exothermal nature of polymerization is clearly detectable.

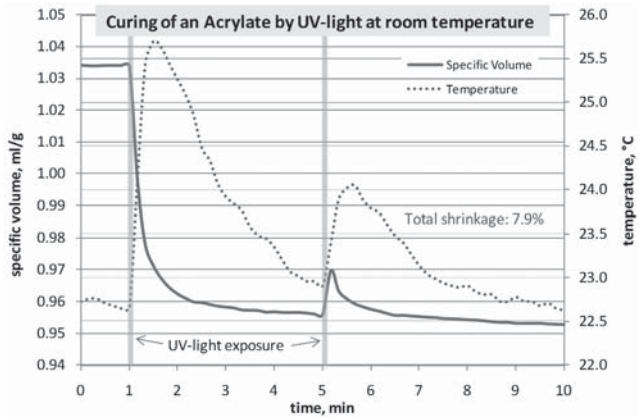


Figure 3: *Curing of an Acrylate by UV-light at room temperature*

Figure 4 gives an example for a measurement of the volumetric thermal expansion coefficient. These measurements are usually performed on cured resins with a heating rate of 1 K/min. As expected, the graph displays different volumetric coefficients of thermal expansion below and above the glass transition temperature.

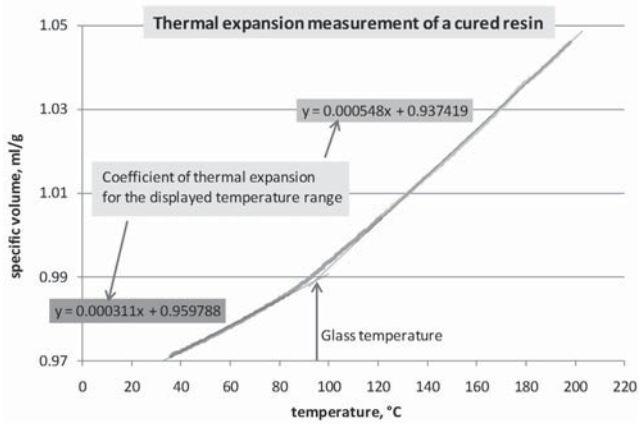


Figure 4: *Volume dilatometric measurement of thermal expansion*

Contact

Yvonne Chowdhury
InnoMat GmbH
Kantstrasse 55
14513 Teltow, Germany
y.chowdhury@innomat-gmbh.de
http://www.innomat-gmbh.de