VOLUME DILATOMETRY – ONLINE INVESTIGATION OF SHRINKAGE DURING THERMAL OR RADIATION CURE

Yvonne Chowdhury, Dirk Dietrich, Annette Bauer

InnoMat GmbH, Teltow, Germany

Motivation

Volume shrinkage during cure of thermosets causes problems in many applications, e.g. molding compounds, filling materials as well as adhesives.

During cure and lifetime thermosets run through different temperature cycles accompanied by changes in specific volume. But for development of new materials or process control a reliable material characterization (volume-temperature-time function of a curing resin) is very important for scientists and engineers.

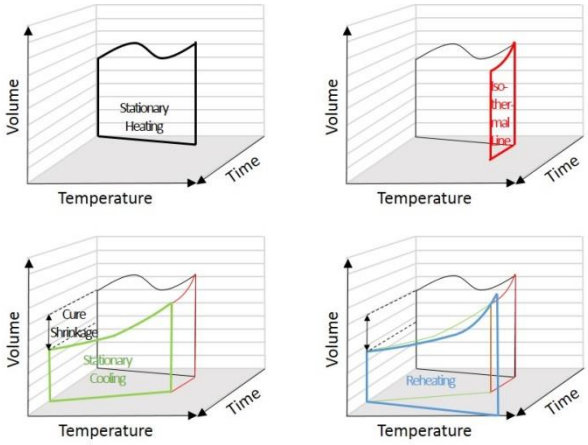

Figure 1: *Exemplary gradient of the volume-temperature-time function of a reactive resin during and after curing.*

Increased reliability requirements on components demand nowadays often lifetime prediction with simulation methods. Therefore exact volume change information from resin cure and succeeding temperature cycles is needed.

An appropriate measurement device providing time and temperature resolved volume change information has already been developed – a capillary volume dilatometer.

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

Method

A capillary volume dilatometer consists of a glass bulb where the sample material is filled in and a glass capillary connected with the bulb. For measurement this assembly will be filled up with a "confining" fluid (mercury). The confining fluid surrounds the sample material to be investigated and transfers its volume changes into a rising or falling meniscus of a liquid column readable by a moving light barrier.

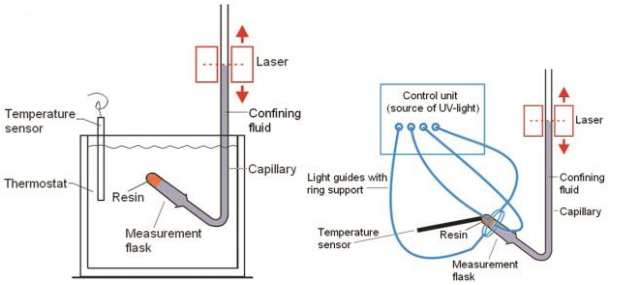

Figure 2: *Set-up of a capillary volume dilatometer with oil bath (left) and with UV-light curing unit (right).*

By this setup a continuous automated recording of the volume-temperature-time function during curing is possible.

In InnoMat's application lab for volume dilatometry different curing methods can be realized:

- Thermal curing via oil bath (from room temperature up to max. 250 °C)
- Light curing by blue or UV-light

Results

Volume dilatometry enables determination of

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

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.

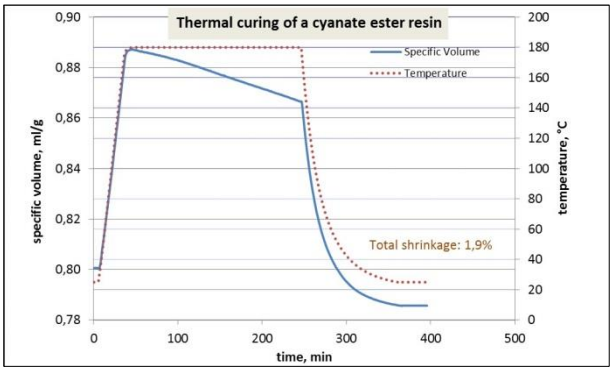

Figure 3: *Thermal curing of a cyanate ester resin.*

Figure 4 represents the gradient of the specific volume for a curing cycle of a hot curing UP resins. 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.

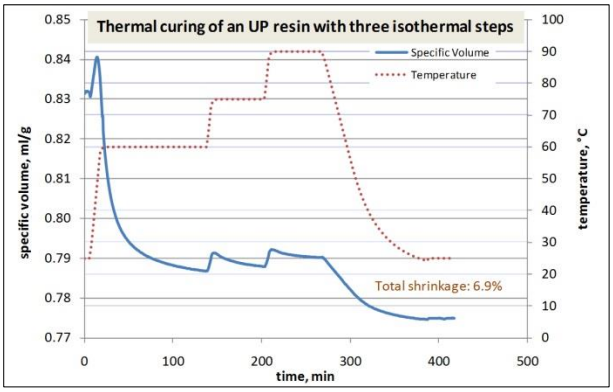

Figure 4: *Thermal curing of an UP resins with three isothermal steps.*

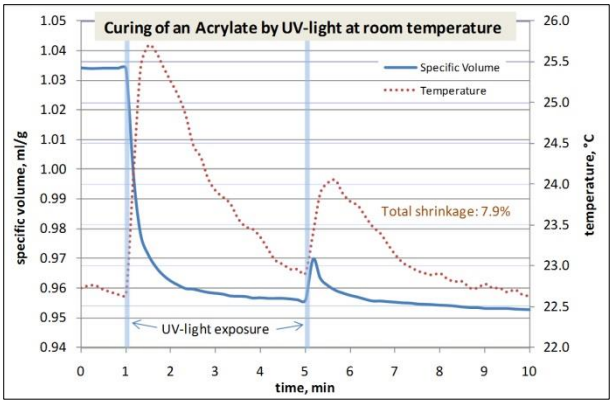

Figure 5: *Curing of an acrylate by UV-light at room temperature.*

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 ensure that all reactive species have reacted, a second UV-light exposure is performed. The exothermal nature of polymerization is clearly detectable.

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.

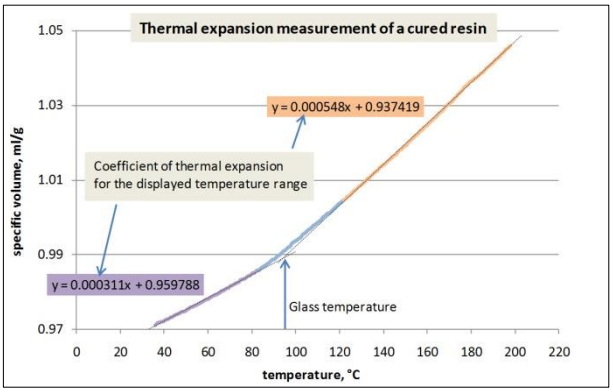

Figure 6: *Volume dilatometric measurement of thermal expansion.*

Contact

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