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Test method

Determination of volumetric shrinkage of thermally cured thermosets using video-imaging

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ABSTRACT

Video-imaging is one method of analyzing the shrinkage of resins. For the measurement, a drop of resin is placed near an illumination source and its contour is imaged from the front with a camera. This paper presents a further development, detailed investigation and verification of this technique to analyze the chemical shrinkage of thermally cured epoxy resins during cure. A new cylindrical sample holder was developed which enables the automated detection of the baseline, as well as defining the scale within the pictures. In a test series, the resin's volume was varied, as well as its contour. The findings confirm that the measured volume shrinkage is independent of the drop shape.

Finally, the obtained shrinkage results were verified and evaluated in comparison with values measured by a mercury dilatometer and a rheometer. The shrinkage results of the investigated new method are in good accordance with the more established methods.

1. Introduction

Temperature cured thermosets show volumetric changes during the curing process. These changes can be separated into thermal and chemical shrinkage. Thermal shrinkage, on the one hand, is relevant whenever the curing temperature is changed and, therefore, mainly in heating up and cooling down processes. Temperature changes thus cause thermal shrinkage. The amount of volumetric change is determined by the temperature change and the coefficient of thermal expansion. Chemical shrinkage, on the other hand, is caused by the crosslinking of the thermoset during cure. The reaction of the resin induces volume contraction due to the conversion of Van-der-Waals interactions to covalent bonding. This reaction increases the density of the resin.

The shrinkage leads to many problems in the application fields, such as process-induced distortions of angled fiber reinforced plastics [1,2] or uneven surfaces due to shrinkage marks [3]. Therefore, good understanding of thermal and chemical shrinkage during the curing process of thermosets is required for the production of high-quality composite parts.

In the past, numerous different measuring devices have been developed [4,5]. There are some reliable methods to determine thermal shrinkage, for example by thermal mechanical analysis. In contrast, measuring chemical shrinkage is more difficult. The major difficulty is the need for an unhindered and isothermal cure of the resin. In practice, many methods have an effect on the volumetric shrinkage of the resin. The sticky resin is in contact with the walls of the measuring device, which causes internal stress and affects the volume contraction. In addition, the exothermic reaction of the resin can cause temperature gradients, which accelerate the polymerization speed and lead to a mixture of chemical and thermal volumetric changes.

Video-imaging is a method with little resin–device interaction and with small sample sizes. This method avoids overheating and has been used for many years to analyze UV-cured resins. The optical method is established for dental materials in particular. A frequently used, commercially available measuring device is the AcuVol (Bisco Inc., USA) [6–10] but some other experimental setups are also known [11,12]. The method usually follows one basic setup. A light source is placed near to a drop of resin. The sample is imaged from the front by a charge-coupled device (CCD) camera. From the

Abbreviations: CCD, charge-coupled device.

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digital images, the drop shape is analyzed and the volume of the resin is calculated. For UV-cured resins, the lamp itself might be used as a source to initiate the polymerization. In other cases, an additional light-curing unit is placed a distance from the top of the resin. To ensure a symmetrical drop shape, the resin is normally placed on a pedestal made of polytetrafluoroethylene [6,11]. Other authors [12] do not use a pedestal and also obtain meaningful results, although this might not be true for all drop shapes.

In general, the imaging of the drop shape can be divided into single and multi-view modes. In the single-view mode, the drop volume is only analyzed from one direction, while in the multi-view mode the drop is rotating. Rotating the drop enables camera shots to be taken from different angles. The advantage of this method is that an asymmetric drop shape is taken into account when calculating the resin's volume [7]. Nevertheless, Sharp et al. [8] showed good agreement between the results of single and multi-view measurements. These results are explained by the fact that only the ratio between two volumes is calculated for shrinkage. Asymmetric drops cause problems for the accurate calculation of the drop's volume, but not for the calculation of shrinkage. Therefore, the single-view mode is the faster and simpler option, without a negative influence on measurement accuracy.

Currently, video-imaging techniques are reliable measuring devices with which to determine the chemical shrinkage of resins, but which are limited to light cured adhesives. In the presented study, the method is extended to include hot curing epoxy resins. For this purpose, an oven and an automated scale and base-line detector were integrated into the measuring device. The influence of the experimental setup was analyzed in a series of experiments. Finally, the shrinkage results from the video-imaging technique were compared and evaluated against results taken from a mercury dilatometer and a rheometer.

2. Experiment

2.1. Test setup

The contour analysis system OCA-20 by DataPhysics Instruments Ltd. was used as an experimental setup. The analysis system consists of an illumination source, an electrically heated sample table and a video measuring system. The illumination source is an LED light, which is software controlled for adjustable and homogenous back lighting. The measuring platform consists of a lower and an upper electrical heating plate between which the sample can be placed. The temperature of the oven is controlled by two thermocouples. One is placed in the lower heating plate and the other in the air between the plates. The complete heating chamber has a glass housing to enable the visual analysis of the sample in situ. The video is recorded by a monochrome CCD camera with a resolution of 768 × 576 pixels and an objective lens with a zoom factor of 0.7–4.5. Camera and measuring stage are both adjustable in height to ensure the horizontal alignment of light, sample and camera. The experimental setup is depicted in Fig. 1.

For measuring, a drop of liquid resin with a defined volume is placed on a cylindrical sample holder. To obtain drops with defined dimensions, the automated dosing unit of the contour analysis system was used. The dosing unit consists of a syringe which operates automatically and is computational controlled. The formed drop can be laid on the sample holder, as demonstrated in Fig. 2.

The sample holder consists of aluminum object slides with milled cylinders. Aluminum was chosen due to the high thermal conductivity of the metal. In this way, fast heating and homogenous temperature distribution within the drop is ensured. The surface of the aluminum was treated with the release agent Chemlease (Chem-Trend L. P.). This means that the resin does not bond to the metal surface after cure and the sample holder can be reused. The cylindrical shape of the sample holder ensures a defined base area and a rotational symmetry of the drop. The validity of assumptions is confirmed by the results of Sharp et al. [8].

The study focuses on the verification of the video-imaging technique to measure the volume shrinkage of thermosets during cure. A serial examination was carried out to analyze the influence of the drop volume and the diameter of the cylindrical sample holder on the experimental results. Drop volumes of 5 μl, 10 μl and 15 μl were chosen and the diameter of the sample holder was varied between 2 mm, 3 mm and 5 mm.

The material used in this study was a commercially available resin RTM6 (Hexcel), which is an epoxy resin cured by amines. RTM6 was purchased as a one-component system, which means that the resin and hardener have already been mixed by the supplier. This assures a constant ratio of components for all experiments.

Before starting the shrinkage measurements, the resin was heated for 30 min at 80 °C to decrease the viscosity. Afterwards, the resin was degassed at 5 mbar for 10 min to remove remains of air.

The resin was cooled down to room temperature and applied to the different measuring equipment.

For curing, the resin was heated from 25 °C to 180 °C at a rate of 3 K/min. Isothermal curing at 180 °C was applied for 90 min. Afterwards, the sample was cooled down to 25 °C. No defined cooling rate was used since the cooling was conducted with only ambient air. During the whole curing cycle, the sample was monitored with the camera which takes a picture every second.

The presented results are average values based on at least three experiments.

2.2. Evaluation method

The volume of the resin sample was calculated by analyzing the video pictures. To calculate the correct resin volume from the pictures, two major challenges need to be solved. One problem is the identification of the correct image resolution at any zoom adjustment or recording distance. The image resolution was used for size calculation, and dominates the procedure accuracy. The other difficulty is the visual identification of the interface between the resin

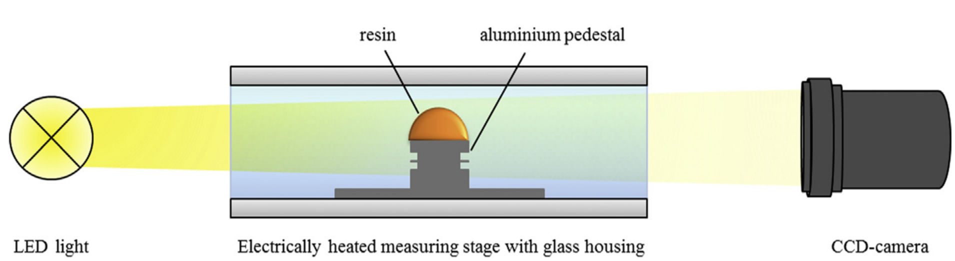

Fig. 1. Experimental setup of a video-imaging device.