Comparison of the Curing Process of Epoxy and Acrylate Resins for Stereolithography by Means of Experimental Investigations and FEM-Simulation

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Abstract

An improved method of investigating the mechanical properties of stereolithography resins during the curing process is described. With this method a typical acrylate material and a common epoxy resin are compared. An example of a finite element analysis shows the suitability of a material model (Burger) to simulate the mechanical stress due to polymerisation stress.

1 Introduction:

There have been many investigations into the curing process of stereolithography resins to determine the reaction rate or shrinkage. Both are crucial for the building process, especially the delay, building time or the accuracy. Previously shrinkage has been regarded as the direct and only reason for warpage. FEM simulation of the curing process, mainly the mechanics, is an attempt to enhance the accuracy of parts built with acrylic resins which showed reasonable curl.
The IKP developed a testing method for stereolithography resins to determine the linear shrinkage, the resulting mechanical stress (which cause warpage) as well as the progression of the mechanical properties from the liquid resin till the green part. This data can then be used for FEM simulation.

2 Measuring method

With the measuring device shown in figure 1 the most important influences of the building process on part accuracy can be determined directly in the stereolithography system. A Stereos Desktop system manufactured by EOS GmbH was used. This system is quite similar to others using a HeCd- Laser. The measuring equipment device has been constructed and optimized for several time intervals especially for these investigations.

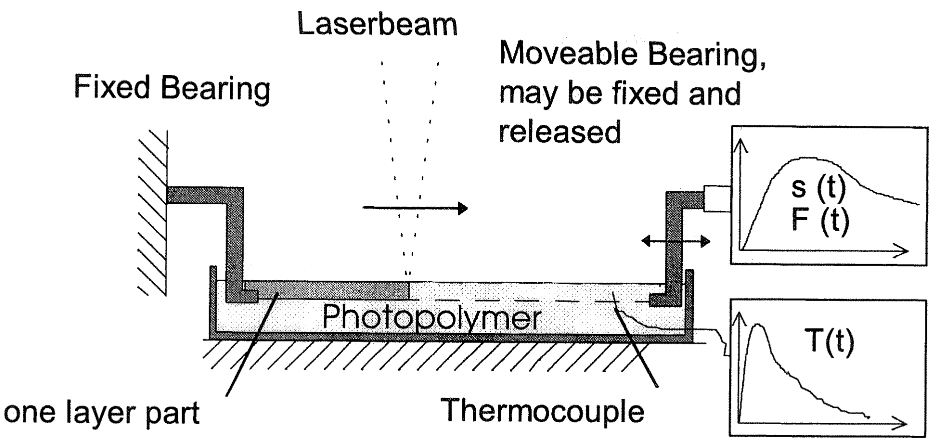

Figure 1: Measuring apparatus

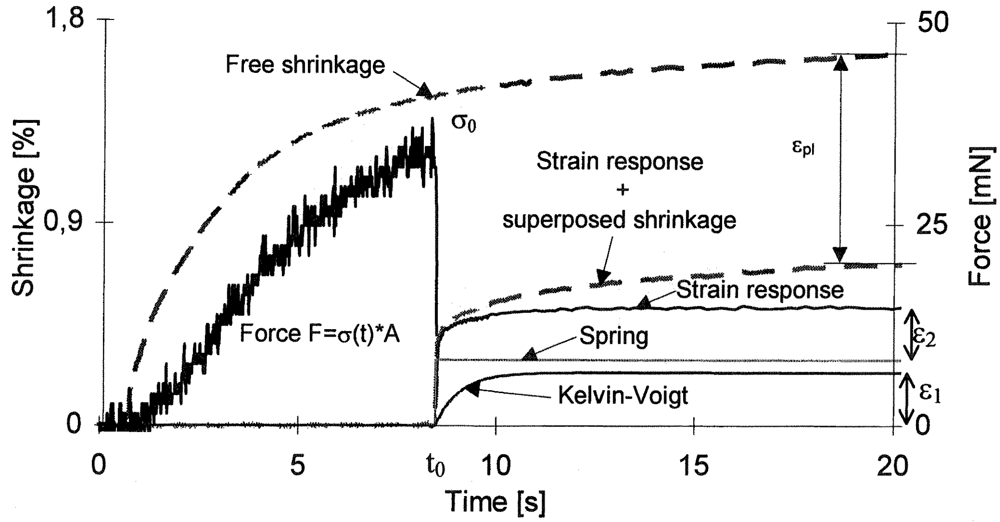

Figure 2: Measuring curves of shrinkage- and force. The response at the end of force measuring leads to the material parameters.

The geometry of the test parts were determined by the structure elements of the stereolithography process. These are single lines but also the hatching of plates (single layers) with a typical length of 10 mm. They are scanned so that they stick immediately with both ends to the measuring device, thus clamping is not necessary. The experiments may be performed in a variety of modes. In one case only one end of the specimen is fixed and the movement due to the shrinkage of the other end is measured. This is called the free shrinkage. With a stepping drive it is also possible to control the length of the part. When it is kept constantly, as it is the case when curing a layer on top of a part, the necessary force is measured. This measurement is called force test or hindered shrinkage. From the force and the cross section of the part the stress can be calculated as one reason for curl. As a combination of both tests one can start with measuring the force and release the bearing at a certain time (Figure 2). This experiment then leads to the mechanical material properties.

3 Determination of the mechanical material behavior –curing dependent creep law

The standard tests to determine the mechanical material properties are the tensile test, dynamic mechanical analysis or creep and relaxation tests. Tensile tests can be done but the Youngs modulus does not describe the material completely. With stereolithography resins where the material properties vary from liquid to brittle depending on their respective times for the curing state, these tests are problematic. For example the creep test: Shortly after the irradiation very small forces will cause high strain. However after a few seconds with the progression of the reaction, the material becomes harder and the applied force leads to only small strains which are not measurable.

To avoid these problems the following method is used:

Firstly the free shrinkage is measured. This is required as it is superimposed to all measurements and has to be eliminated afterwards. Then the length of the specimen is kept constant. The polymerization shrinkage now induces strain and according to the strength of the material stress which also is measured. At a specific starting time t_0 one bearing will be released. The force drops to zero and the part becomes shorter. The elimination of the superposed shrinkage gives the strain response. This experiment is similar to a "reverse relaxation" test. The strain response can be divided into the elastic strain ε_1 and the time dependent retardation part ε_2. The elastic strain ε_1 leads to the young's modulus E_1. The course of ε_2 can be described with one, or if necessary, several Kelvin-Voigt models (E_2, η_2).

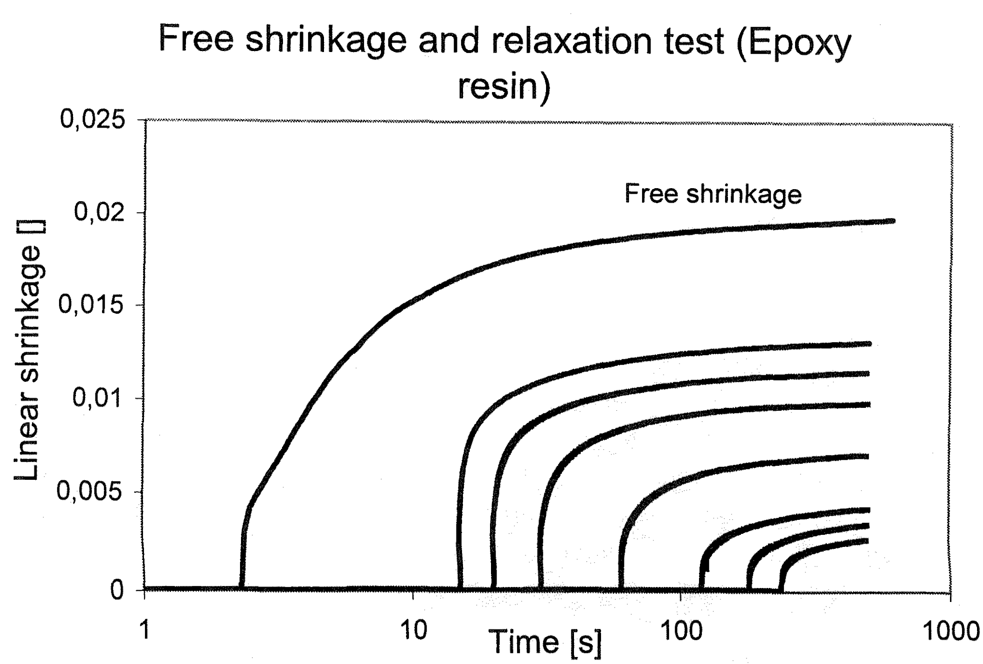

Figure 3: Measurements of free shrinkage and relaxation tests

This experiment can be repeated for several starting times t_i (Figure 3). The later the part is released, the lower are the strain responses due to plastic deformation ε_{pl}. This behavior is modeled (Figure 4) with one more damping element η_{pl}. It is stepwise determined (Boltzmann Superposition) through Equation 1.

Equation 1:

$$\varepsilon_{pl}(t) = \int_0^t \frac{\sigma(\tau)}{\eta_{pl}(\tau)} d\tau$$

The complete model together with typical courses of the parameters is shown in Figure 4. Other tests showed that for the obtained strains (smaller than 5 %) linear visco-elastic material laws may be used.

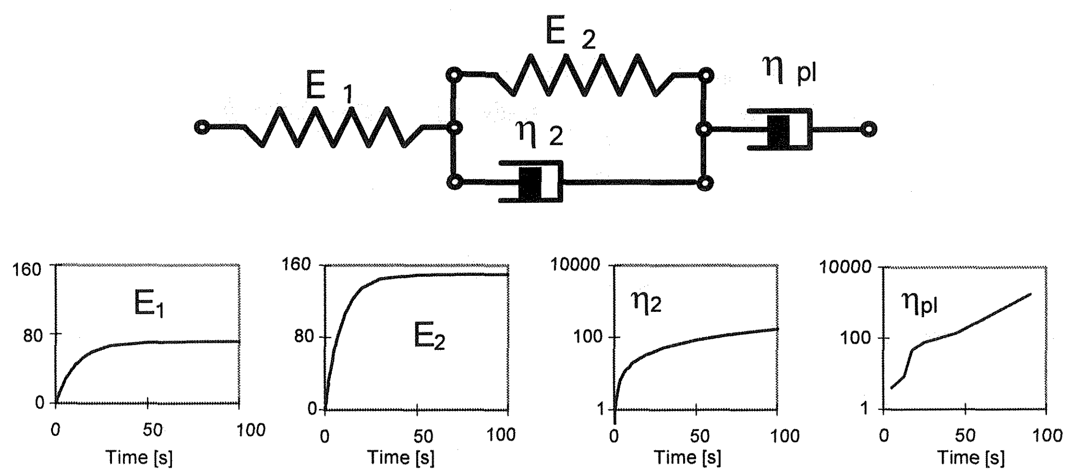

Figure 4: Burger model with its time dependent parameters (acrylate material)

4 Comparison of acrylate and epoxy resins

There already have been many comparisons of both material classes. The most important difference is that the degree of polymerization of the acrylates which can only be influenced by the duration of exposure of UV light. This is due to initiation by radicals and the inhibition by oxygen. The oxygen in the material and from the environment stops the reaction quickly. Thermal curing has only little effect. Only by increasing the number of exposures and the total amount of used UV energy, the degree of polymerization can be raised /1/. Contrary the epoxies, which are initiated by cations, once exposed with enough UV- light to start the reaction properly, cure by themselves with time. This is also called dark reaction. Heating accelerates the reaction /2/.

The investigated materials are Silacure 1485 from Siemens /3/, one of the latest acrylate materials developed which shows good accuracy. And on the other hand the well known Somos 6110 from DSM (former DuPont) which is a hybrid resin of mainly epoxy and acrylate. Both are cured with the HeCd- laser. The comparison was made on parts (length 10 mm, width 3 mm) with the same

cure depth c_d of 0,4 mm. This is a typically used when building parts with a layer thickness of 0,2 mm and is most suited for the measurements. With less cure depth the stress is to small to be measured properly. The parts were scanned with a laser power of 18 mW on the vat, a hatching distance of 0,05 mm at a temperature of 27 °C. For the acrylate material an exposure of 100 mJ/cm^2 was used, for the epoxy 144 mJ/cm^2.
Figure 5 and Figure 6 show the course of the four parameters that can be calculated from the relaxation tests using the Burger model. As explained below, for the epoxy resin a material model with 7 parameters should be applied, but comparing only four parameters is far more practical. Again the much slower reaction of the epoxy can be seen. However, the increase of strength of the acrylate material stops at about 60 seconds, whereas the properties of the epoxy resin seem to increase still after 240 seconds. Further experiments have to be done to investigate the final values. Of course in simple tensile test (also done in this apparatus) it was observed, that the young's modulus rises for more than two hours /1/.

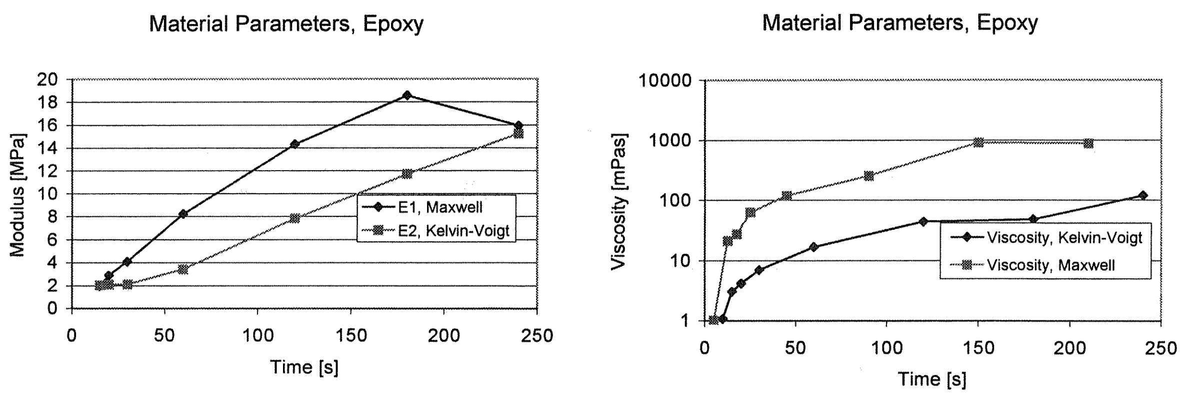

Figure 5: Material Parameters of Epoxy resin (4 Parameter Approximation)

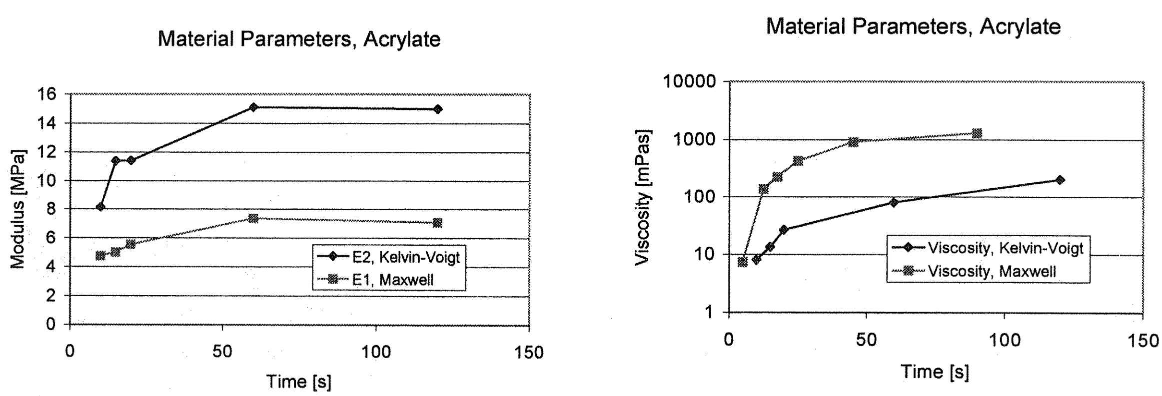

Figure 6: Material Parameters of Acrylate resin (4 Parameter Approximation)

It has to be considered that the epoxy material has, in contrast to the acrylate, reasonable reaction energy (exothermy). So that the part becomes warm during the first seconds. Accordingly the increase of strength partly is caused by the temperature change while cooling. This effect lasts for about 50 seconds /4/. It has to considered that the overall Modulus E is calculated with Equation 2. So the total modulus is always smaller than the single ones. For the acrylate as example E_1 , keeps below 8 MPa, E reaches a value of about 5 MPa, whereas the Modulus of the epoxy resin at the end of the measurement is about 8 MPa .

Equation 2:

$$E = \frac{1}{\frac{1}{E_1} + \frac{1}{E_2}}$$

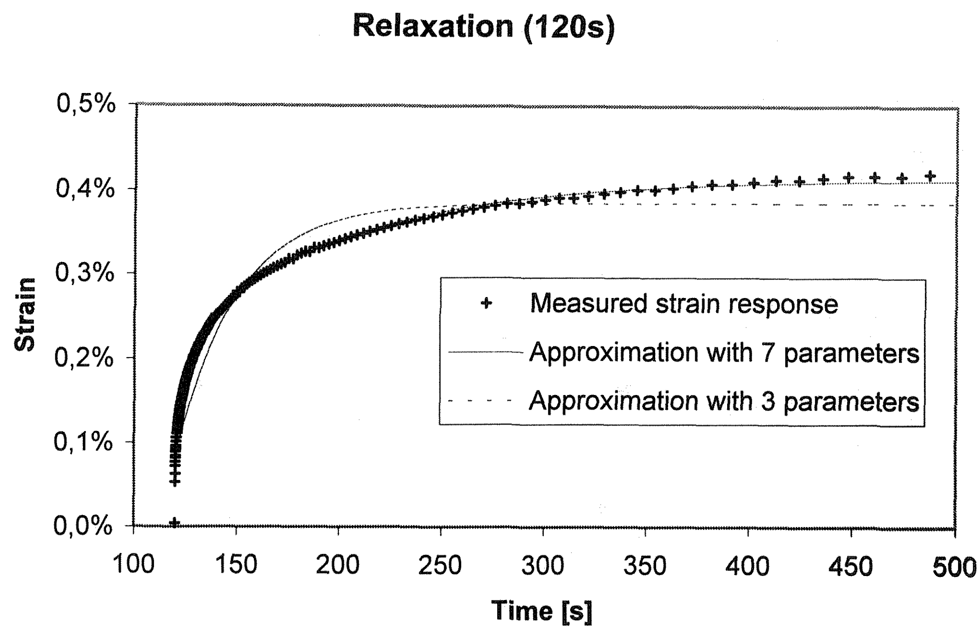

Figure 7: Fittings of the measured strain response (starting time 120s) with two material models (3 and 7 parameters)

The determination of the material parameters showed an other difference between the acrylates and the epoxies: The strain responses of the acrylates can be approximated very well using a three parameter model (E_1, E_2, η_2), to have a good approximation for the epoxy material a material model with seven parameteres (E_1, E_2, η_2, E_3, η_3, E_4, η_4) has to be used. This can be explained by the compound of the material of epoxy and acrylate material, but also by swelling effects. The part is cured within the vat, so substances of the liquid resin tend to diffuse into the network, this may be faster when the network is under stress. Either this material is involved in the reaction and causes additional shrinkage, or when the stress is released, the network tries to tighten, but this is retarded by the diffused material.

5 Simulation

To validate the material model the tests were simulated by the finite element method. Thus it is also possible to investigate the curing process not only of the whole layer but also of parts of the layer or the distribution of stress within the layer. Further observations on the influence of the uncured material, like the material flow of the liquid due to the volume shrinkage of the curing material, may be made (Figure 8).

The material law and the time dependent shrinkage of each element were implemented in the commercial FE solver MARC through the subroutine HYPELA. In the simulation the part is built as in the stereolithography process by single scan tracks. Based on the position of the laser the program calculates which elements begin to cure for each time step.

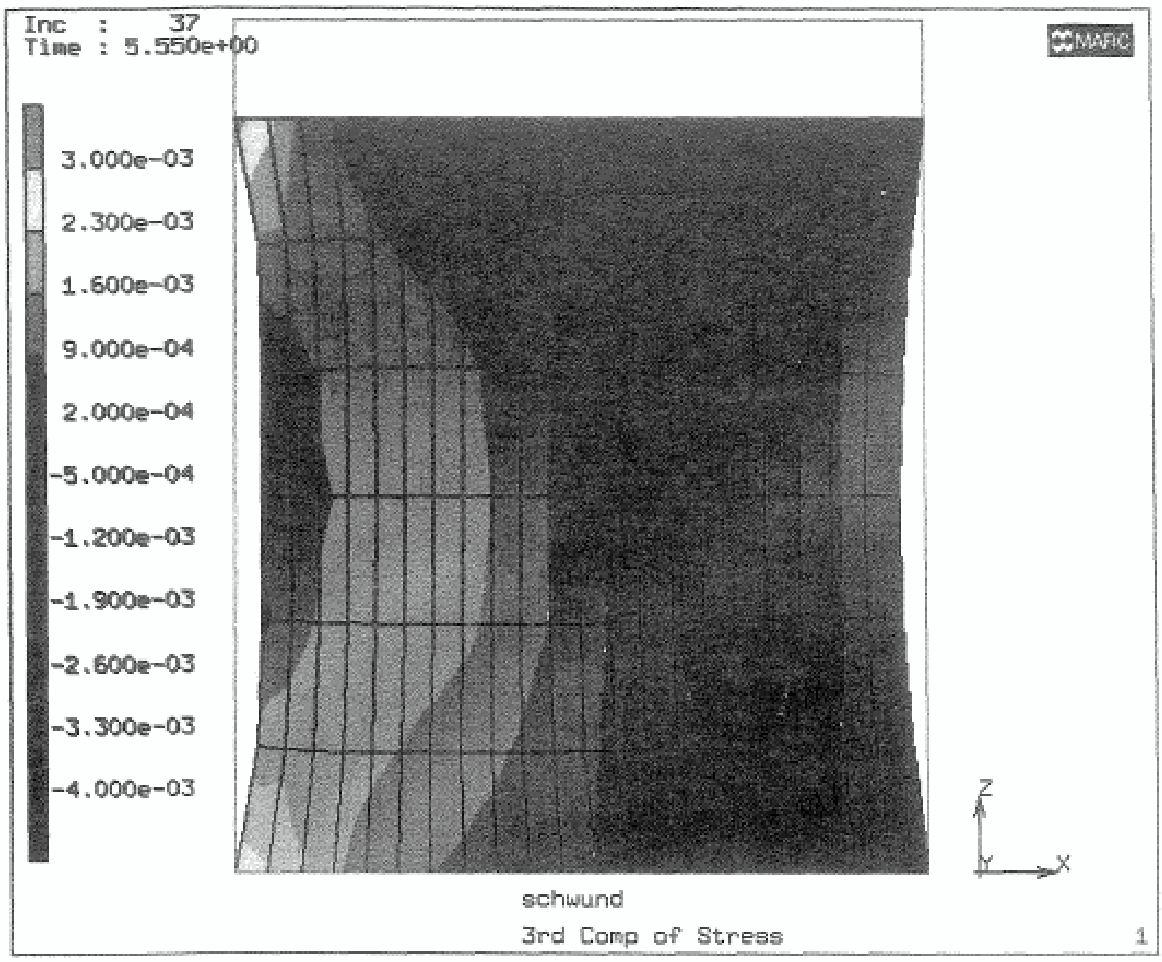

Figure 8: Simulation of free shrinkage (deformations scaled by 10, viewed from the top), colors show stress in length.

The comparison of measurements and simulations of several relaxation tests (different times, but same process parameters) shows good conformity (Figure 9). Of course, since in the simulation the Burger model with only 4 parameters was used, there is a deviation between simulation and experiments, this can be reduced when using a material model with more than 4 parameters (see above).
This model can be the basis to simulate the stress and distortion of complete parts. With the dramatic increase of computing power during the last few years, for small parts, this may already be achieved with work stations as they are used for CAD.

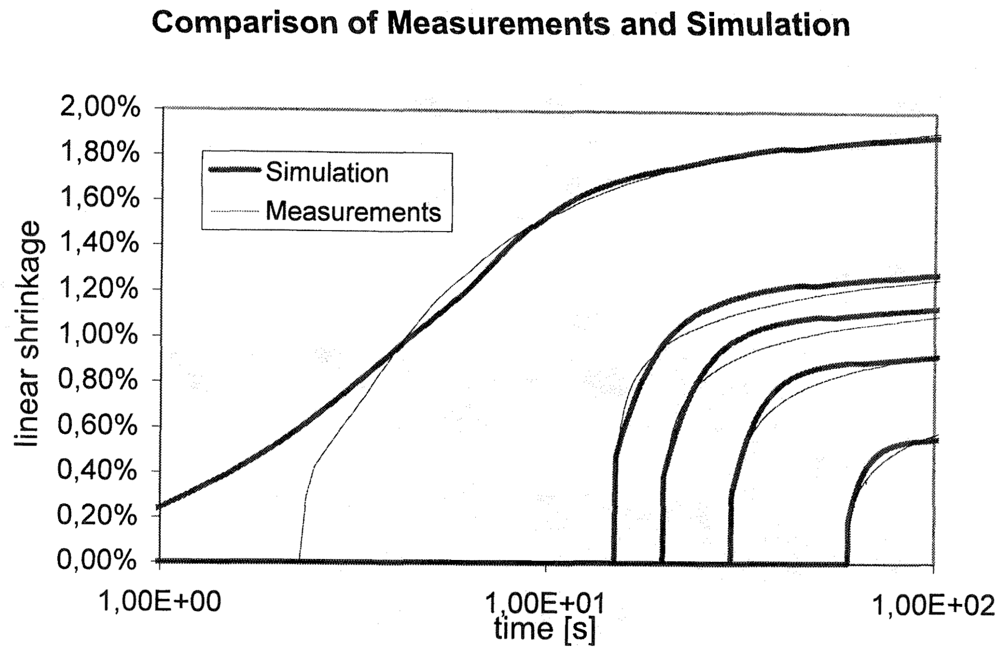

Figure 9: Comparison of simulation and experiments (Epoxy)

6 Conclusions

The differences between epoxy and acrylate resins become quite clear when investigating the material properties during the curing process. The epoxy resin show the same linear shrinkage, but because the cure slower, the stress due to the shrinkage is smaller. Together with the higher final stiffness this explains the better accuracy of parts.

References

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