

EXPERIMENTAL METHODS AND RESULTS FOR THE REDUCTION OF RESIN SHRINKAGE BY THE ADDITION OF NANOPARTICLES FOR INCREASED DIMENSIONAL ACCURACY OF CARBON FIBER REINFORCED PLASTICS

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Abstract

Process-induced distortions of carbon fiber reinforced plastics (CFRP) are a result of the resin chemical and thermal shrinkage. One approach to overcome this problem is the reduction of the resin shrinkage by the addition of nanofillers. To investigate the influence of nanoparticles on the shrinkage, reliable experimental results are required. The determination of the coefficient of thermal expansion (CTE) can be easily measured by thermal mechanical analysis (TMA), while analyzing the chemical shrinkage of nanocomposites is more difficult.

In this publication, the method of video-imaging is compared to results measured by a rheometer. The advantages and disadvantages of both methods are discussed. In addition, results of the CTE and the chemical shrinkage of nanocomposites consisting of epoxy resin and nanoscaled aluminum oxide are presented. The influence of different filler contents on the shrinkage is shown and discussed in comparison to other results from literature.

The reduction of the thermal and chemical shrinkage of the epoxy resin by the addition of nanoparticles is finally transferred to CFRP. Using this method, a decreasing spring-in angle of the CFRP through the addition of nanoparticles into the matrix is demonstrated.

1. Introduction

The application of high performance CFRP for aerospace applications requires not only superb material performance, but also high dimensional accuracy of the components. The second requirement is difficult to fulfil due to process-induced distortions in the composite. Especially for complex geometries deviations from the tool design can be observed. The deviation can be found as reduced angles in curved segments or as curvature in plane components. The distortions of all cfrp are driven by material property gradients and stress gradients due to part-tool interactions. In addition, in angled geometries the distortions are mainly caused by the anisotropic shrinkage in-plane and through the thickness of the CFRP. During manufacturing, the resin's chemical shrinkage and the high coefficient of thermal expansion result in a reduction of the component's thickness. In-plane, the strain is determined by the fibers, which hinder most of the resin's shrinkage. This anisotropic properties lead to the reduction of the angle and thus to the components dimensional inaccuracy [1].

Therefore, a good understanding, as well as the reduction of the thermal and chemical shrinkage of thermosets is required for the production of high-quality composite parts.

To analyze the thermal shrinkage of thermosets, thermal mechanical analyses (TMA) are frequently performed. The TMA offers a straightforward and reliable method for determining the CTE of the

cured resins. In contrast, measuring the chemical shrinkage is more difficult. In literature [2, 3], many different methods are presented, but most of them have some inaccuracies due to non-isothermal curing conditions or adhesion between the resin and the measuring device. Recent studies present an advanced method to measure the resin's chemical shrinkage by video-imaging [4] to overcome these problems. For this method, a drop of resin is placed on a substrate. During the cure, the drop's shape is continuously monitored with a camera. The resin's volume is calculated from the drop's contour recorded by the camera. From these results the drop volume during the whole curing process can be calculated.

Another option to determine the chemical shrinkage is the measurement with the rheometer [5]. The rheometer provides a good method to measure the chemical shrinkage after the gel point, which is the relevant part for of the curing cycle in which the CFRP distorts. For the measurement, the resin is cured between the two plates of the rheometer. Once the resin gelled, the volume contraction leads to a normal force, which is balanced by adapting the gap size of the plates. This way the linear chemical shrinkage of the resin can be extracted and analyzed.

For small process-induced deformations of CFRP components, resins with little thermal and chemical shrinkage are needed. One option to decrease the shrinkage of thermosets is the integration of nanoparticles. The fillers do not only introduce a second phase with no chemical and low thermal shrinkage, but also alter the network mobility of the polymer. Thus, the shrinkage properties of the nanocomposite depend on the polymer properties as well as on the filler material, size, shape, content and modification [6, 7, 8]. The influence of nanoparticles on the thermal and chemical shrinkage is analyzed for different material systems, but most of the times only for one of the two characteristic parameters. In addition, this method has not yet been transferred to CFRP components very often.

Therefore, this study presents a discussion of video-imaging and rheometer measurements as two methods for analyzing the chemical shrinkage of thermosets. In addition, with these two methods the chemical shrinkage of nanocomposites is determined and the influence of the filler content is discussed. Finally, the thermal shrinkage of the nanocomposites is also analyzed and the results are transferred to the analysis of the dimensional accuracy of an angled carbon fiber reinforced nanocomposite.

2. Materials and Methods

The material used in this study is the commercially available resin RTM6-2K (Hexcel), which is an epoxy resin cured with amines. The nanoparticles AEROXIDE AluC are provided by Evonik. These are pyrolyzed aluminum oxide particles with a primary particle size of 13 nm. The particles are chosen due to the high number of hydroxyl groups on their surface, which have the ability to form strong interphases with the matrix.

The particles are dispersed into the resin to assure homogeneous particle distribution. The master batch with 30 wt.-% of solid is processed by a calendar (80E, Exakt). Milling is carried out until no further particle size reduction is observed. The master batch is diluted with the according amount of resin and hardener to produce nanocomposites with aluminium oxid contents from 1 to 15 wt.-%. Before curing, the fluid resin is degassed under vacuum at 80°C. Then the nanocomposites are cured for 120 min at 180°C.

Video-imaging and rheometer measurements are performed to analyse the chemical shrinkage of the nanocomposites. For the video-imaging the contour analysis system OCA-20 by DataPhysics Instruments Ltd. is used. For this newly developed method [4], a drop of resin is placed on an aluminium substrate. The experimental set-up is illuminated by a LED-light from behind. During curing, a CCD-camera continuously monitors the resins contour from the front. From these pictures the resin's volume is calculated over the curing time. Finally the volumetric chemical shrinkage ($\epsilon_{V, \text{video-imaging}}$) is calculated by Eq. 1, where V_2 is the final resin volume and V_1 the initial one.

$$\epsilon_{V, \text{video-imaging}} = \left| \frac{V_2 - V_1}{V_1} \cdot 100 \right| \quad (1)$$

For the rheometer measurements a Gemini HR nano by Malvern is used. The rheometer has a plate-plate setup, where the bottom plate is fixed, while the upper plate is free to move and is connected to a strain-gauge. The decrease in the resins volume applies to a force on the plate, which is compensated by adapting the gap size. From the change in gap size the chemical shrinkage ($\epsilon_{V, \text{Rheometer}}$) can be calculated using Eq. 2 [5], where h_0 is the initial gap size and h the final one.

$$\epsilon_{V, \text{Rheometer}} = \left[1 + \frac{1}{3} \left(\frac{h - h_0}{h_0} \right)^2 \right] - 1 \quad (2)$$

The thermal shrinkage is determined by the thermal contraction of the material. Thus, the CTE of the nanocomposite is analyzed by thermal mechanical analysis (TMA/SDTA 841e, Mettler Toledo). For analyzing, the samples are heated from 0 to 250 °C with a heating rate of 3 K/min. The cte is calculated as a mean value between 180 and 25 °C, which corresponds to the cooling from curing temperature to room temperature.

Finally L-shaped samples made of carbon fibre reinforced nanocomposites are manufactured by RTM-tooling using injection technology. Eight plies of carbon fibres (Style 797-1, ECC Cramer) are stacked to form a 2mm thick part with a (90, 0)_{2s} stacking sequence and a fibre volume fraction of 62 vol.-%. The CFRP is cured for two hours at 180°C. Afterwards the dimensional accuracy of the part is measured by a high precision 3D full-field ATOS measurement system. The spring-in angle is calculated by the difference of the tooling angle of 90° and the measured angle of the CFRP-angle.

All presented results in this paper are the mean value of at least three samples.

3. Results and discussion

3.1. Comparison of video-imaging and rheometer measurement

Chemical shrinkage occurs due to the conversion of van-der Waals linking to covalent bonding. Therefore the density of the resin increases during cure, while its volume decreases. During curing, the polymer chains successively increase their length until they grow into a network. At a specific degree of cure, a connected network develops for the first time. This is called the gel point. Before the gel point the resin still behaves like a liquid and can flow. Afterwards the resin starts to be able to transfer stresses. This means only chemical shrinkage after the gel point is relevant for process-induced deformations of CFRP components.

The rheometer provides a good method to measure the gel point and the chemical shrinkage in a single experiment. However, the resin and the rheometer plates have large bonded areas, which might hinder the free shrinkage of the resin. Systematic experiments are performed to analyze the influence of the plate diameter and of the gap size. The gap size is varied to be 0,5 mm, 1 mm or 3 mm, while the plate diameter is 8 mm, 25 mm or 40 mm. Fig. 1 presents the obtained results.

The results clearly show a strong dependence of the calculated volume shrinkage on the gap size (h) and on the plate diameter (d). In general, the shrinkage is reduces as the gap size and the plate diameter are reduced. Feilzer et al. [9] published a C-factor (3), which describes the relation between the bonded area (A_{bonded}) to the free area (A_{free}).

$$C - \text{Factor} = \frac{\Sigma A_{\text{bonded}}}{\Sigma A_{\text{free}}} = \frac{2\pi (1/2 d)^2}{2\pi 1/2 dh} \quad (3)$$

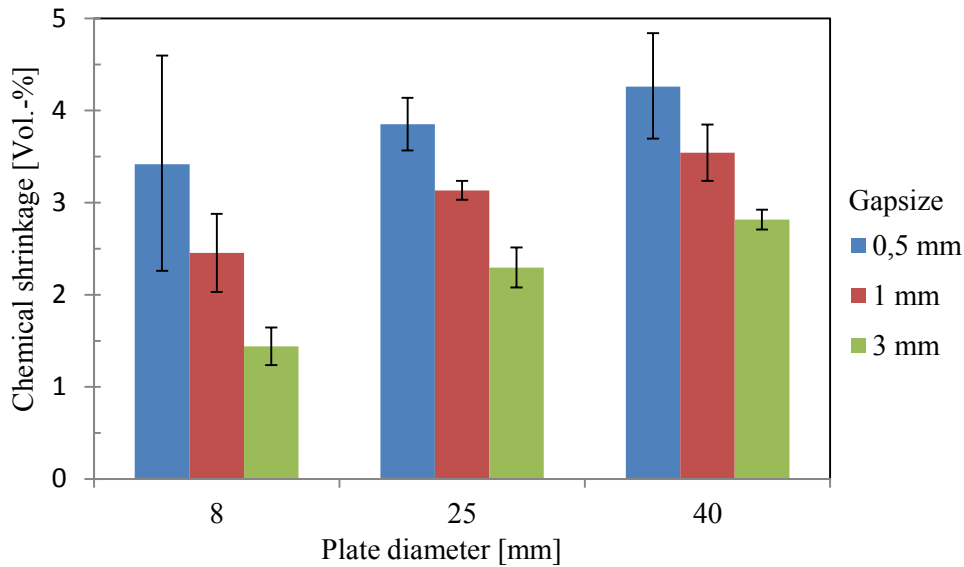


Figure 1. Chemical shrinkage of RTM6 measured with a rheometer at 180°C with different gap sizes and plate diameters

In fig. 2 the measured chemical shrinkage is depicted over the calculated C-factors. It can be clearly seen that the measured chemical shrinkage increases with increasing C-factor. Thus the more resin is bonded to the plates in relation to the free area, the higher the measured chemical shrinkage.

This is because the calculation of the chemical shrinkage from the rheometer data assumes that only the linear shrinkage perpendicular to the plates leads to adjusted gap sizes. The shrinkage in plane is assumed to be free and unhindered. The presented results indicate that this assumption is not true. In reality, the bonding between the resin and the plate hinders the shrinkage in plane and leads to in-plane stresses. These stresses will be partly released by lateral contraction. In addition, it might be possible that curing will not occur in an isotropic manner, which will lead to further contraction of the gap size.

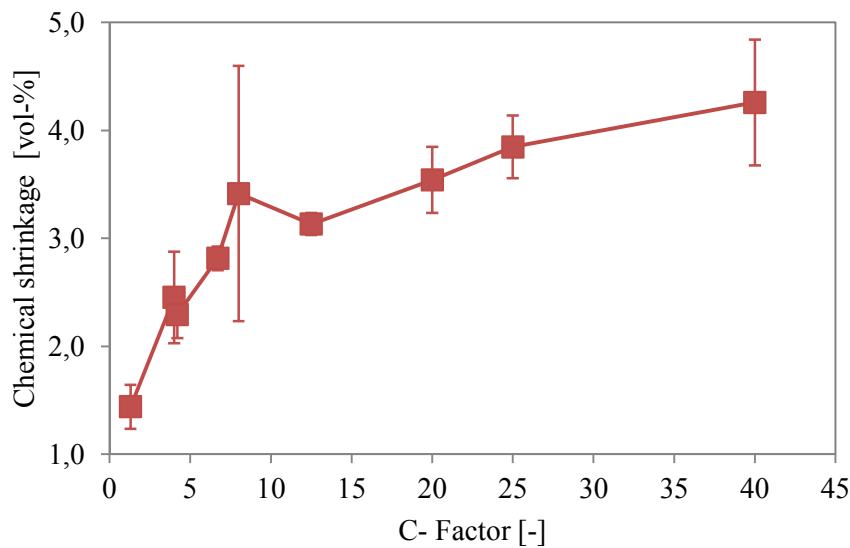


Figure 2. Chemical shrinkage of RTM6 measured with a rheometer at 180 °C according to the C-factor

In contrast, the video-imaging only has a small bonded area between the resin and the substrate. As reported in [4], the measured volume shrinkage of the polymer is independent of the experimental setup. However, with this method it is not possible to observe the gel point. The results represent the chemical shrinkage during the whole curing process. In the context of process-induced distortions, this is a disadvantage over the rheometer method. For this reason the chemical shrinkage of nanocomposites are measured with both methods.

3.2. Chemical shrinkage of nanocomposites

Video-imaging and rheometer measurements are used to analyze the chemical shrinkage of RTM6 with different filler contents of aluminum oxide nanoparticle. The filler content is varied from 0 to 15 wt.-%.

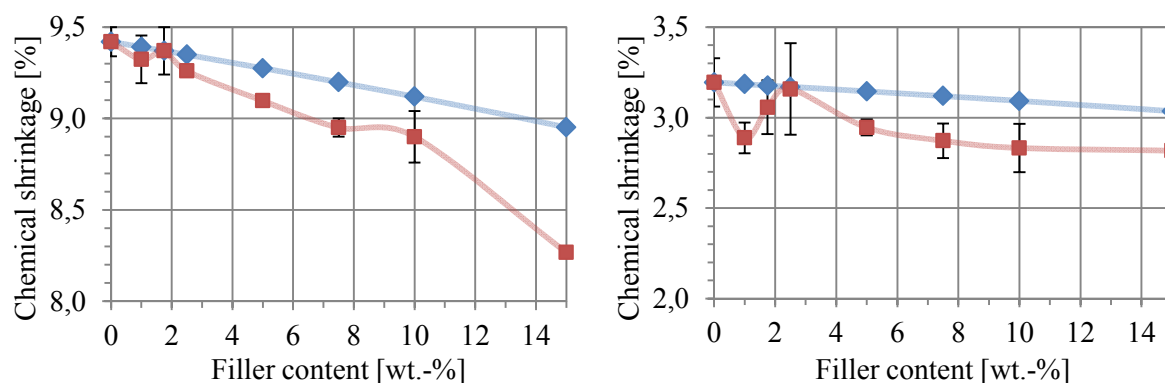


Figure 3. Chemical shrinkage of nanocomposites with different filler contents analyzed by video-imaging (left) and rheometer (right); blue: theoretical shrinkage; red: measured shrinkage.

In Fig. 3 the experimental results are depicted. The data clearly shows for both measurement methods a decreasing chemical shrinkage with increasing filler content. The shrinkage decreases in both cases by 12% from the pure resin to the nanocomposite filled with 15 wt.-% particles, even though the absolute values vary significantly. As already described, the video-imaging measures the chemical shrinkage of the nanocomposite over the whole curing period, while the rheometer only detects shrinkage after the gel point. Therefore the video-imaging results in chemical shrinkage of 9,4 vol.-% and the rheometer only gives approximately one third of this value (3,2 vol.-%).

For low filler contents the chemical shrinkage is particularly low. At the same time the standard deviation is very high. These two effects cannot be thoroughly explained at the moment but might be due to re-agglomeration or uneven particle distribution for these small filler contents.

In addition to the experimental results, the theoretical shrinkage is plotted in the figure. The theoretical shrinkage is understood as the shrinkage of the pure resin minus the volume content of the inert particles. This assumes that the particles have no chemical shrinkage, while the resin's shrinkage is unaffected by the filler. The calculation shows that this assumption is not correct. The experimental results show a larger reduction of the chemical shrinkage as calculated. A filler content of 15 wt.-% equates to only 5 vol.-%, while the shrinkage is reduced by 12 %. This difference can be explained by the altered polymer network around the particle. The crosslinking of the resin close to the particle surface is sterically hindered. Thus, the network density around the particles is decreased, which results in lower chemical shrinkage in the interphase.

3.3. Thermal shrinkage of nanocomposites

The thermal shrinkage is also determined for nanocomposites with 0 to 15 wt.-% filler content. Fig. 4 presents the results from TMA measurements. The CTE is a medium value between 25 and 180 °C. This temperature range correlates to the cooling range from curing to room temperature. Thus it is the temperature change which CFRP components experience after manufacturing.

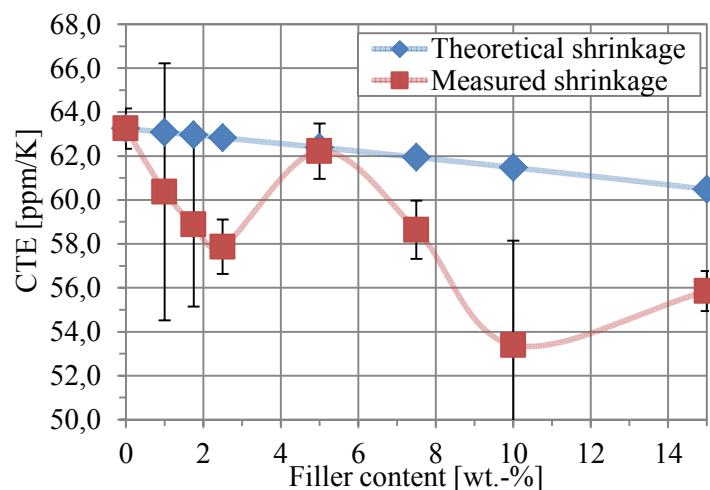


Figure 4. Coefficient of thermal expansion of nanocomposites with different filler contents measured by TMA.

The measured CTE of the nanocomposites show a decreasing thermal expansion with filler content. For low filler contents the CTE is particularly low, before the CTE raises again with increasing filler content. For these low filler contents, the same assumptions as for the chemical shrinkage are true and the reason might be re-agglomeration or uneven particle distribution.

As for the chemical shrinkage, the theoretical CTE is also calculated. For the theoretical value a simple mixing rule is applied: the sum of the CTE of the matrix and the CTE of filler weighted by their volume fractions. Again, the results show a larger reduction of the CTE as is expected from the theoretical calculation. This indicates a strong interface between the polymer and the particles, which hinders the thermal expansion while raising the temperature.

3.4. Process-induced deformations

Finally the chemical and thermal shrinkage results are transferred to L-shaped carbon fiber reinforced nanocomposites with different filler contents of aluminum oxide particles. Table 1 presents the results.

Table 1. Spring-In angle of carbon fiber reinforced nanocomposites with different filler contents

Filler content	Spring-In angle	Standard deviation
0 wt.-%	1,02°	0,03°
5 wt.-%	1,01°	0,06°
10 wt.-%	1,00°	0,01°
15 wt.-%	0,94°	0,06°

The results show a decreasing spring-in angle from 1,02° for the angle with pure resin to 0,94° for a

filler content of 15 wt.-%. This is an decrease of spring-in angle by nearly 9 %. Even though the improvement is lower as expected from the shrinkage results of the nanocomposites, these results show the ability of nanoparticles to increase the dimensional accuracy of CFRP.

4. Conclusions

This paper investigates the ability of aluminum oxide nanoparticles to increase the dimensional stability of angled CFRP components by reducing the chemical and thermal shrinkage of the polymer. Rheometer and video-imaging are discussed as methods to measure the chemical shrinkage of thermosets. The presented results show the ability of both methods for analyses, even though the results from the rheometer highly depend on the experimental setup, while the video-imaging does not show the gel point of the resin. For this reason both methods are used to analyze the influence of the filler content on the chemical shrinkage of an epoxy resin. Both results clearly show the decreasing chemical shrinkage with increased content of aluminum nanoparticles. The same result is obtained measuring the thermal shrinkage of the nanocomposites by TMA. The CTE of the nanocomposite is also clearly reduced by the filler.

Finally the results are transferred to L-shaped CFRP components. The measured angle shows a reduction of spring-in angle with raised nanoparticle content. Even though, this effect is not as clear as expected from the shrinkage results.

Acknowledgments

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