DETERMINATION OF THE COEFFICIENT OF MOISTURE EXPANSION (CME)

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ABSTRACT

A test facility for the measurement of the length variation of polymer composites due to moisture evaporation is described. The measurement method is based on commercial laser interferometers with a resolution of 10nm and working under vacuum conditions yields a total accuracy of 0,1µm. The high sensitivity and resolution of the test facility is shown by CTE experiments with copper and Invar samples. The CTE results are in the expected range although the considered temperature regime is very small. CME measurements were performed on simple lay ups – unidirectional and bidirectional material- of carbon fibre reinforced polymers, which were preconditioned in water at a temperature of 50°C. Two methods for the determination of Δm

- determination of the initial and final sample weight (method 1)
- online-measurement of the sample weight during outgassing under vacuum condition (method 2)

are presented and a comparison of the CME results confirms the time effectiveness and reliability of the method 2. The CME values for the chosen material are in the range of 5E-6/% to 1E-2/%.

1 INTRODUCTION

A high degree of dimensional stability is often required for aircraft and spacecraft components. In order to evaluate polymeric composite materials for aerospace applications the coefficients of thermal expansion (CTE) and moisture expansion (CME) have to be determined.

The swelling/shrinkage of CFRPs due to moisture uptake/release is very small - CME values of CFRPs are in the range of <5E-5/wt%H_2O in the fibre direction and about 1E-3/wt% H_2O normal to the fibres.- and therefore length variation data can be obtained with high resolution /high accuracy measurement systems only. Conventional dilatometers cannot provide the required resolution and accuracy (typically ±1µm) and the commercial facilities cannot be operated in vacuum. Special inductive systems [2] and online external interferometric measurement systems [1] (moisture sorption or desorption and the according length variation in the same facility) are very sophisticated and the measurement times are far off economic needs. Therefore a methodology for the determination of CME from data which are available at acceptable cost and time consumption is of great industrial interest.

The presented methodology is based on laser micro interferometers operated inside the chamber leading

a) to a surpassing accuracy and hence to reduced measuring times, since all errors introduced by external interferometric systems (ambient temperature and pressure variations, external beam path deviations,..) can be eliminated – and
b) to a simultaneous multidirectional measurement due to the use of multiple miniaturised interferometers.

CME is defined by the ratio of the length variation to the mass variation [%] due to moisture evaporation or absorption:

$$CME = \frac{\Delta l}{l_0} \Big/ \left(\frac{\Delta m}{m_0}[\%] \right) \qquad (1)$$

l_0, m_0 ... initial length and mass respectively
Δl, Δm ... time dependent length/mass variation

Additionally to Δl values Δm data are needed. These data can be gained by directly weighing the sample before and after testing, but it will be shown, that online weighing during outgassing in vacuum yields more reliable results and reduce the measurement time considerably.

2 MEASUREMENT METHOD AND FACILITY

2.1 Interferometric methods

The principle of the Michelson interferometer can be used for the measurement of changes of distances. The reflected beams from the two mirrors show an interference pattern (constructive and destructive interference fringes) depending on the phase shift of the beams. If one of the mirrors is moving the distance can be determined by counting the passing interference

fringes. One passing fringe is caused by a mirror movement of half a wavelength. The wavelength of commonly used Lasers is in the visible light range of about 780nm. The resolution of interferometry can yield 10nm by using special detection and signal amplification methods. The difficulties and restriction of the achieved accuracies of the standard Michelson interferometers are:

- the alignment of the mirrors perpendicular to each other, while contacting one to the sample
- the refraction index of air (depends on the temperature/pressure and humidity) and of the mirrors (temperature dependence) cause measurement errors
- the operation under vacuum condition is difficult, because common lasers and detectors work only under ambient conditions, therefore the beam (initial and interfering) have to pass windows and distances in air, which rises additional errors.

The above mentioned difficulties can be prevented by commercial instruments (micro-laserinterferometers). They work very similar to the Michelson interferometer but the complete set up is integrated to one small instrument. The moving mirror, which can be mounted to the sample, is a sphere with the refraction index of about n=2 that reflects the laser beam parallel to the initial beam.
Tests of these instruments have been performed in a vacuum facility, which was adapted for the test. It was possible to stabilise the temperature of the instruments by fluid thermostats. The preferred operation temperature is about 22°C. Further a vacuum pressure of below 5*10E-6 could be reached in this facility. These tests are of great importance, because the instruments are not specially constructed for vacuum operation.

For the test the Micro-Laserinterferometers where mounted unto micro-positioners (moveable ±5mm by micrometer screw) for their adjustment to the mirrors in the two axes perpendicular to the beam. According to the proposed measurement principle one mirror was at the front and one at the rear the side of the „specimen“. The test set up consisted of one pair of lasers only , one for small distances (up to 100mm) and one for larger distances (up to 300mm). The complete set up was mounted a on a water cooled support plate and integrated in a vacuum chamber.

The experiences with the instruments indicate that the important properties of the measurement facility are:

- low CTE materials for the measurement system
- additional temperature stabilising for the instrument and support plate
- vibration damping
- adjustability of the micro-interferometers
- PC control and data acquisition for long term measurement

The measurement system is integrated in a vacuum chamber and is operated at a pressure of below 1E-3Pa. Special vibration isolation is required because the interferometers are very sensitive towards vibrations.
The facility which was designed and constructed in-house is shown in Fig.1.

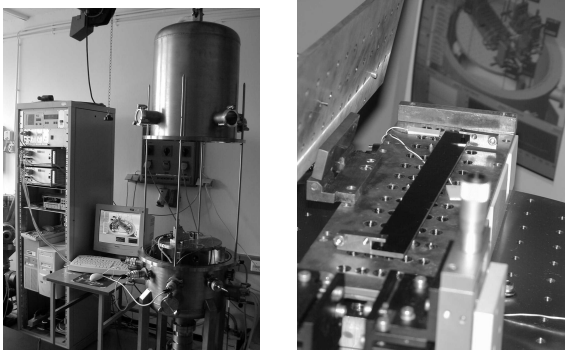
Table 1:Thermal expansion coefficient α (Δl calculated for l_0=100mm)

Material	α **[10^{-6}/K]**	Δ**l[µm] (ΔT=0,5K)**	Δ**l[µm] (ΔT=0,1K)**
Copper	16-18	0,8	0,16
Steel	13	0,65	0,13
Invar	1,8	0,09	0,018
Ceramics	0,1	0,005	0,001
Glass ceramics	<0,05	<0,0025	0,0005

For the support plate the material Invar (see Table 1 1) was selected. Ceramics and glass have lower thermal expansion coefficients but are difficult to machine.

Temperature variation may cause mechanical strain in the sensor, the cable and the plug. yields a drift (up to 0,1µm/h) of the laser. Furthermore the thermal radiation produced by the sample heating has to be carried off. The radiation temperature will be up to about 340K and affects the accuracy of the interferometer which is calibrated for ambient temperatures. Small temperature variations of the interferometers in the regime of about 20°C-25°C are corrected by an internal Peltier element. Therefore the interferometers must be temperature stabilised and fluid channels are integrated in the supporting plate.
A temperature change in the supporting plate is lower than ±0,1K (temperature stability of the fluid is about ±0,01K!).

Fig. 1: Vacuum chamber **Sample with mirrors**



2.2 Measurement principle

The length variation is determined by two laser interferometers, one focused to the front and one to the rear end of the sample. Special reflectors (spherical lenses gold plated at the rear side) are fixed to both ends of the sample and the laser sensors are adjusted to these mirrors.

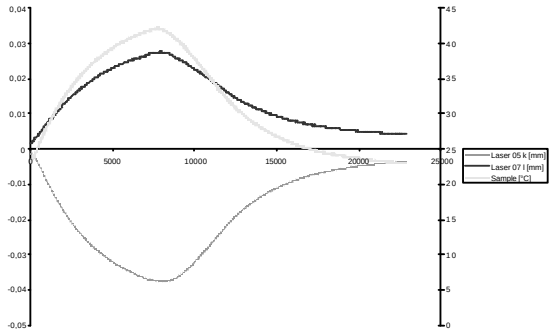
The sensors can be moved in the z- and x-axis (laser beam in y-axis) by special micrometer screws. Additionally the sensors are temperature stabilised by a fluid thermostat which is operated at about 22°C. Samples with the dimension of approximately 200mm x 40mm can be mounted. However, other than rectangular geometries (e.g. tubes) can be taken into consideration.

The temperature distribution within the vacuum chamber is measured by Pt100 thermoresistors in order to estimate the effective measurement errors. The interferometer signal is detected and the length is computed by PC. The wavelengths of the sensors are calibrated and for vacuum operation a correction of the air refraction index is not required.

2.3 Facility tests

In order to assess the functionality of the CME-facility and to gain experience on the operation conditions, mainly the temperature gradients and the time stability of the electronics and sensor, tests using copper and Invar samples were performed. To produce expansion and shrinkage the temperature in the copper plates was varied between 15 and 70°C and thus the samples temperature could be varied from 20 to 50 °C approximately. The figures show that Δl of a few microns can be detected easily and measurement times of days are no problem at all. From this measurements the coefficient of thermal expansion (α) was determined.

Fig. 2: Copper sample (Laser 5 is focused to the front end and Laser 7 to the rear end of the sample)



The estimated α at room temperature is 17,5 E-6 /K (literature values for copper: 16 to 18E-6).

From 3 different measurements like the above the coefficient of thermal expansion α (1/K) was estimated. An accurate determination is not possible if you consider the very small temperature range of 20 degrees centigrade only. Additionally with a sample length of 200mm it is difficult to yield an overall constant temperature during heating up. Nevertheless the values of α are in the expected order of magnitude and reproducible for different samples.

Fig. 3: Invar sample (Laser 6 is focused to the front end and Laser 7 to the rear end of the sample)

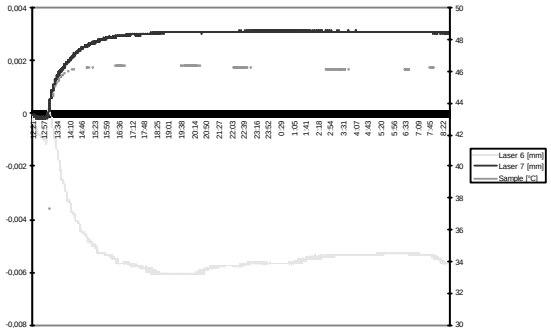


Table 2: Coefficient of thermal expansion (1/K) of Invar at room temperature

	a)	b)
invar-1	2,07E-06	1,28E-6
invar-2	2,04E-06	1,08E-6
invar-3	1,81E-06	1,34E-6

a) estimation from the above diagram (and two equal ones)
b) standard measurement by dilatometer (in-house measurement)
Literature values are in the range of 1-2E-6/K.

3 RESULTS

3.1 CFRP material

The resin systems selected for aerospace applications must endure high service temperature and exhibit high mechanical properties together with a high toughness to avoid matrix dominated failure. For service temperatures in the range of 200'C, resins based on aromatic monomers resembling or derived from the bisphenol-A component of conventional thermosets are required. Two different chemistries, commonly used for the radiation curing of coatings and inks, either

involve free radical or cationic propagation. Beyond obvious differences in monomer nature and in polymerization mechanisms, a number of other contrasting features may exert, in a direct or indirect manner, an adverse or a beneficial influence on the use properties of the materials.

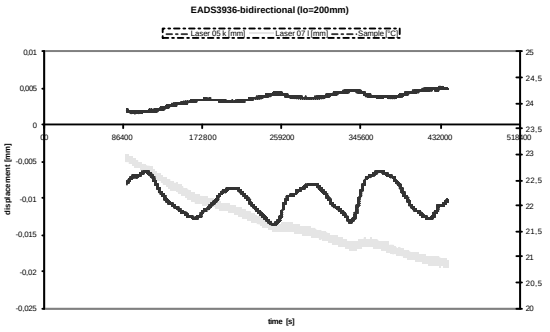
Table 3: CFRP samples (the fibres are IM 7)

Ref.No.	Description of the resin
3936 4444	EADS proprietary formulation, acrylate based resin polymerises via a free radical mechanism
3522	EADS proprietary formulation, epoxy based resin polymerises via a free cationic mechanism
3282	EADS proprietary formulation, acrylate based resin polymerises via a free radical mechanism

3.2 Method 1

During the measurement in vacuum moisture evaporates from the sample and the length of the sample decreases accordingly. Therefore the total length decrease Δl depends on the moisture content of the CFRP material. In order to increase Δl a preconditioning of the samples is necessary. It is also possible to investigate specimen as delivered (storage at ambient conditions), but the CME effect is expected to be very small then and might be beyond the Δl-resolution of the facility.

Fig. 4: CFRP bidirectional (sample length 200 mm)
(The Δl (left axes) values are in mm, temperature in °C (right axis), the time in seconds)



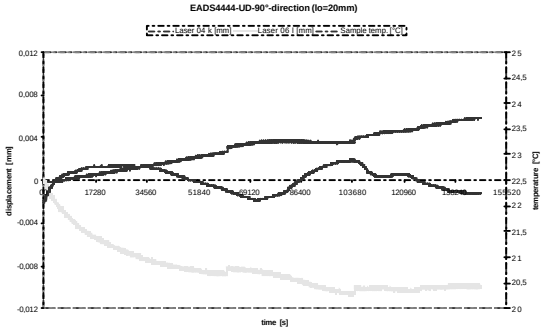
Result(approx.) after 4 days: Δl_{total}=-25µm , $\Delta l_{total}/l_o$=-1,25E-4

The diagrams Fig.4 -6 show the Δl measured by the two sensors versus time. These data show the original sensor signal -which is a counter number- multiplied by the calibrated laser wavelength of the according sensor. The diagrams prove the high sensitivity and resolution of the system and its long term stability.

The main problem is obviously the instability in the sample temperature, which is due to room temperature changes during the day although the sample temperature is stabilized by a thermostat system. The problem occurs because there is no good thermal contact between the sample and the cooling plates in vacuum. In order to improve the performance the facility shall be operated in an air conditioned laboratory and additionally the cooling system has to be improved.

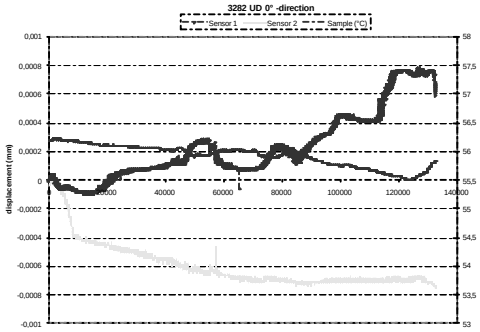
The weight loss due to moisture evaporation in vacuum was measured by weighing the sample before and after the test. From these data the values for CME can be calculated (see Table 4).

Fig. 5: Unidirectional material measured perpendicular to the fibre direction (sample width 20mm)



Result (approx.) after 1,5 days: Δltotal=-16µm , Δltotal/lo=-8E-4

Fig. 6: Unidirectional material measured in fibre direction (length 200mm)



Result (approx.) after 1,5 days: Δl_{total}=-1,5µm , $\Delta l_{total}/l_o$=-8E-6

The positive $\Delta l / l_0$ values are due to temperature increase during measurement. If there is thermal expansion of approx. the same magnitude of the moisture shrinkage the values for CME can only be roughly estimated because the CTE is not known for those materials and as shown in former reports it is very difficult to determine.

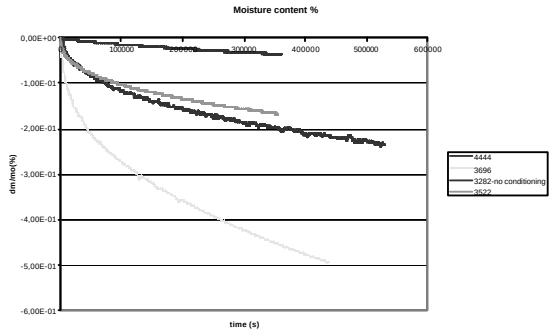
Table 4: CME results by weighing the samples

Sample	fiber direct	dl/lo (end of meas.)	dm/mo(%)	CME
3936	Bidirect (0/90°)	-1,30E-04	-4,20E-01	3,10E-04
4444	UD / 0°	-1,12E-06	-2,40E-01	4,66E-06
4444	UD/90°	-9,44E-04	-2,40E-01	3,93E-03
3282	UD/0°	-7,88E-06	-1,50E-01	5,25E-05
3282	UD/90°	-8,74E-05	-3,91E-02	2,23E-03
3522	UD/0°	1,32E-05	-1,60E-01	< 1e-6
3522	UD/90°	-1,02E-03	-1,60E-01	6,38E-03

3.3 Method 2

In order to produce more accurate and reliable CME values, another method for the determination of CME was chosen, the Δl measurement remains the same. The Δm_{total} was measured by an online method while the conditions for the samples (i.e room temperature and 5E-6 mbar) are comparable to the Δl-measurements. The Δm is determined by a high resolution balance operated in a vacuum chamber and recorded online. The sample size is approx. 20x50mm, which is comparable in the volume to surface ratio. This ratio affects the diffusion of moisture and therefore the Δm and Δl versus time. The Δm –measurements are also carried out in an in-house facility.

Fig. 7: Δm (t) for 4 CFRPs



The Δl_{total} (t)-curves can be compared to Δm_{total} (t)–curves and a CME (t)-curve can be calculated on this basis. As CME is expected to be a constant not depending on the initial moisture content of the sample the CME (t) –curves are expected to be parallel to the t-axis.

The diagrams Fig.8-11 prove this behaviour generally.

Fig. 8: Sample 3936 (compare Fig. 4)

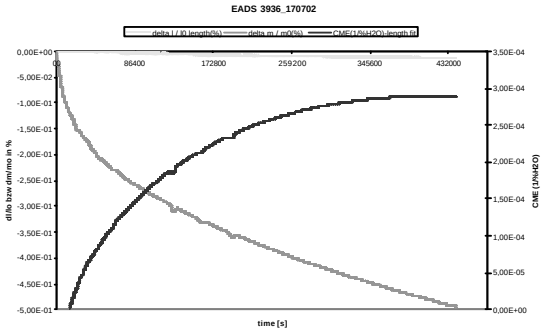


Fig. 9: Sample 4444 (compare Fig. 5)

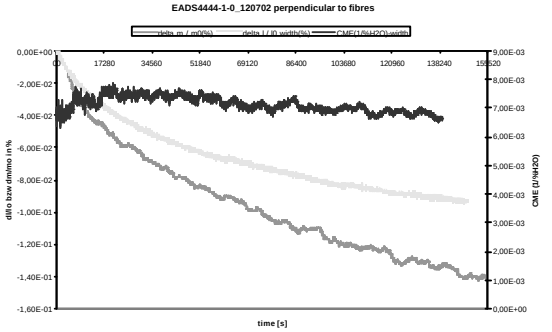
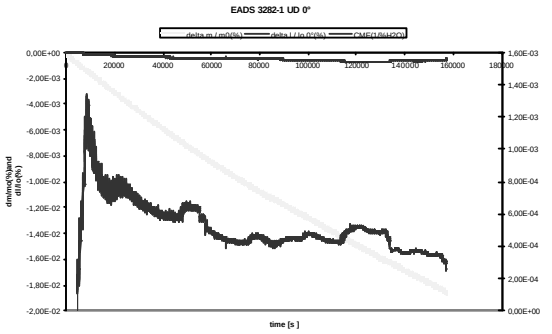
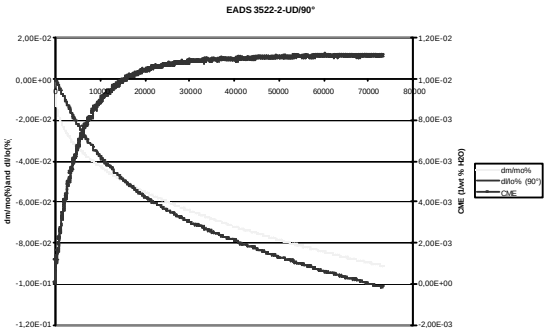


Fig. 10: Sample 3282 conditioned (compare Fig. 6)



The initial part of the curves is rising which is due to the standardization of the Δl_{total} / Δm_{total} –curves and partly due to the very small Δl_{total} which are beyond measurement resolution in the initial phase. The curves give also an indication, that in most cases a measurement time of approximately one /two days will yield reliable results. A conditioning of the samples in water or high humidity improves the measurement performance and accuracy, because of the increased Δl_{total}.

Fig. 11: Sample 3522 perpendicular to fibre direction



The CME values of method 2 are generally higher but if we look to the linear -parallel to x-axis- , behaviour of CME in the according diagrams the values are more reliable. In some cases CME has not yielded the parallel line which might be due to the short measurement time.

Table 5: Determination of CME (method 2)

Sample	fibre direction	dl/lo (end of meas.)	dm/mo (%)	CME
3936	Bidirect. (0/90°)	-1,30E-04	-4,94E-01	2,63E-04
4444	UD / 0°	-1,12E-06	-2,01E-01	5,57E-06
4444	UD/90°	-9,44E-04	-1,39E-01	6,77E-03
3282	UD/0°	-7,33E-06	-1,64E-02	4,47E-04
3282	UD/90°	-8,74E-05	-1,11E-02	7,88E-03
3522	UD/0°	1,32E-05	-9,13E-02	< 1e-6
3522	UD/90°	-1,02E-03	-9,13E-02	1,12E-02

It is obvious that the CME measurement in fibre direction is more difficult because the values are very small. Particularly the thermal expansion is of the same order of magnitude and a very temperature stable system is required. Even for the bidirectional sample 3936 (Fig. 8) it is difficult to reach the equilibrium in reasonable time, however the tendency can be observed and deliver the reasonable CME value.

4 CONCLUSIONS

- For space relevant materials it is of interest to measure at different temperatures (-200°C to 200°C) but the method presented herein is not easily adaptable for that extreme temperatures. Problems are the refraction index of the mirrors, which changes so much that the total reflection of the laser beam will no longer occur. Another problem is the thermostat system for the sample which operates by thermal radiation only and it will take a very long time to reach stable conditions. More research development and a new design of the thermostat is necessary. With this improved thermostat and the increased temperature range it could be possible to establish a system for the measurement of thermal expansion in high vacuum. This is of great interest for CFRPs used in space because with conventional methods like dilatometers CME and CTE are always mixed, in the vacuum system both coefficients can be considered independently.
- The method of just weighing the samples is not very accurate and pretends often lower CME values. The method of online measurement of Δm leads to the expected constant CME values and is therefore the more reliable one.

5 REFERENCES

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6 ACKNOWLEDGEMENT

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