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DYNAMICAL MECHANICAL THERMOANALYSIS OF HIGH PERFORMANCE REINFORCED MATERIALS
Influences and problems

J. Wolfrum[1], *G. W. Ehrenstein*[1] *and M. A. Avondet*[2]

[1]Lehrstuhl für Kunststofftechnik, University Erlangen-Nuremberg, Am Weichselgarten 9 D-91058 Erlangen, Germany
[2]AC-Laboratorium, CH-3700 Spiez, Switzerland

Abstract

A sensitive method to characterize the thermomechanical behaviour of fiber reinforced composites is the dynamic mechanical thermoanalysis (DMTA) method. A Round-Robin-test with five different institutes was conducted to determine the role of the fiber orientation, processing conditions, test apparatus, the mode of loading, and the matrix materials on the determination of the glass transition temperature (T_g). The result shows that the DMTA is a suitable method to analyze T_g of long fiber composites. However, some major problems have to be taken into consideration:

- A direct comparison of results from different DMTA-systems is not possible
- The real temperatures in the specimens deviate from the temperatures displayed by the DMTA measuring system
- There is no clear and common evaluation method for the glass transition temperature.

Keywords: composites, DMTA, glass transition temperature, Round-Robin-test

Introduction

The glass transition temperature is an important material parameter for plastic materials. It is used as a method for quality control and inspection of new materials. It can be determined easily by several thermoanalytical methods, like Differential Scanning Calorimetry (DSC), Thermo Mechanical Analysis (TMA), and DMTA. The measurement results and test methods depend on many parameters that make the evaluation of test results very difficult to decifer. Moreover, even with one technique, for example the DMTA, there may exist large deviations in the measured values of the T_g. Several industrial standards try to minimize the amount of influencing parameters, but still there are no uniform guidelines in the determination of the glass transition temperature. It is evident that there is margin in how the exact value of the glass transition temperature (T_g) is chosen and for this reason, there are great uncertainties in how to evaluate material data sheets and T_g-values [1–4].

The term DMTA includes different measurement techniques: flexural, torsion, compression, or tensile mode with free or forced oscillation. The DMTA measure-

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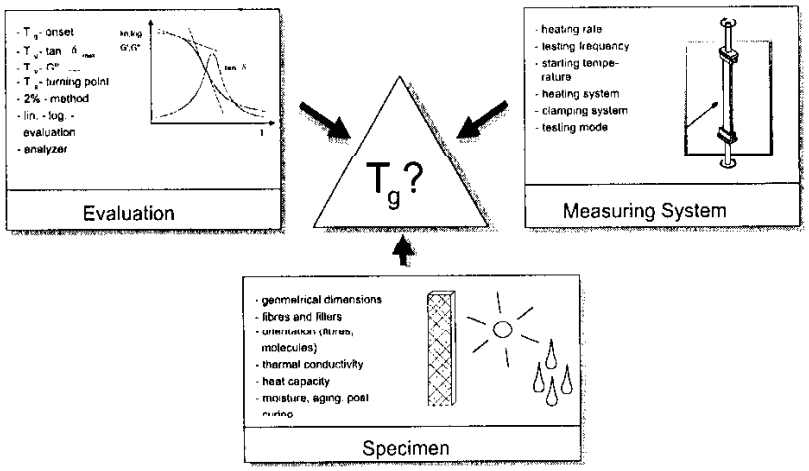

Fig. 1 Important parameters influencing the T_g of high performance composites measured via DMTA

ment provides the temperature dependent shear modulus, G', or the Young's modulus, E', as well as the loss moduli, G'' or E''. The material loss factor or loss tangent, tanδ, is the ratio of energy dissipated to energy stored per cycle of deformation. With the DMTA measurement, even difficult to monitor T_g values can be analyzed with high sensitivity. Compared to DSC experimentation, the accuracy of DMTA at relative low temperatures makes the DMTA a very powerful instrument in the determination of the T_g for materials with a high degree of cure and/or reinforced materials. Figure 1 illustrates some important factors that must be considered in the determination of the T_g of high performance composites.

Determination of the glass transition temperature by DMTA

Although there are several standards and recommendations for the evaluation of the glass transition temperature of fiber reinforced polymers by DMTA, uncertainties in the determination of the exact value of the T_g still exist. Due to these uncertainties, the glass transition temperature for the same material may vary by 60°C [1]. Since engineers have to make exact limitations to the maximum operating temperature, inconsistent data has made this a formidable task. For example, the highest operative temperature for high performance reinforced materials is often specified 28°C under T_g [5]. Thus, there exists a strong urgency for a more detailed investigation of this problem.

ASTM D 4065 declares that the maximum in the loss modulus is the appropriate standard value of T_g. ASTM D 4092 defines T_g as the approximate midpoint of the temperature range over which the glass transition takes place. DIN 65583 proposes a two-tangent method. The first tangent is drawn at the storage modulus curve at

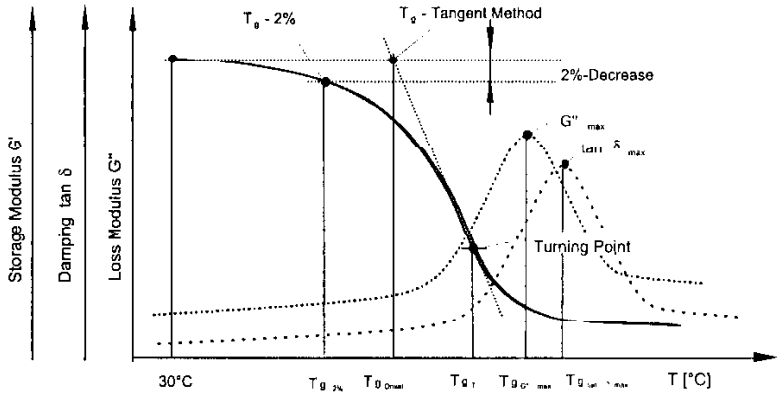

Fig. 2 Different methods to determine T_g by DMTA curves

30°C. A 'T_g 2%' is defined as the point of intersection of a parallel line 2% below the tangent of the storage modulus curve. The 'onset T_g' in DIN 65583 is the point of intersection between the first tangent with a second tangent drawn at the inflection point of the storage modulus. DIN 29971 defines a 'T_g 2%' similar to DIN 65583 with one difference, the first tangent is drawn at the storage modulus curve at 23°C. Figure 2 shows the ambiguity that persists in ASTM and DIN standards.

Examined materials and test program

The tests in this study were conducted using a commercially available 180°C cure Triazinphenolic-epoxy prepreg system, unidirectional (UD) carbon fiber (CF) STESATAPE EP 127 by the Stesalit AG Switzerland impregnated carbon fibers and neat Triazinphenolic Epoxy Resin-System, STESATAPE EP 127 also by Stesalit AG, Switzerland. The matrix material is a resin with a high heat distortion temperature, a low flammability, and good hot-wet properties. The neat resin plates were manufactured via the lamination of several resin layers together in an autoclave.

The prepreg was cured in 0.30×0.30 m panels in an autoclave using standard lay-up and vacuum bagging procedures at 4 bar pressure and subjected to the processing conditions of 180°C for 90 min. The carbon fiber panels were made of 16 UD-plys denoting a quasi-isotropic (QI) lay-up with $[0°/90°/+45°/-45°/+45°/-45°/0°/90°]_S$ fiber orientations and UD lay-up.

The DMA specimens were cut with a liquid cooled diamond wheel saw and dried in a vacuum oven for 30 min at ambient temperature. The specimens with the dimension of 60×10×4 mm were conditioned in two different environments: in a vacuum oven at 70°C over 1 week, and in a water bath at 98°C in a closed container for 48 h. After the exposure time, the samples were removed and sent to the different institutes in welded aluminum bags with a PTFE coating.

Table 1 Measuring systems used in Round-Robin-test

DMTA-system	Measurement mode	Frequency
TA-DMTA 982 system	bending	natural
TA-DMTA 983 system	bending	fixed
Myrenne Torsion Pendulum ATM 3	torsion	fixed
Rheometric scientific	3-point bending	fixed
Polymer laboratories DMTA	torsion	fixed

It is known from previous tests, that the experimental parameters have an influence on achieving a constant and reproducible determination of the glass transition temperature and the quality of data during a thermoanalytical experiment [1, 6]. In order to minimize instrumental factors that can affect the determination of the glass transition, some important test parameters were standardized: heating rate 3 K min^{-1}, frequency 1.0 Hz or natural frequency, temperature range –60 to +300°C. The determination of the influences of different load modes and instruments on the results the DMTA measurements were conducted with 5 different test systems. The DMTA measuring systems used in this Round-Robin-test can be classified in two categories: torsional and bending mode, natural and fixed frequency.

To separate the influences of the material, DMTA instrument and the evaluation on the determined glass transition temperature, a triple variance analyses was performed. The variance analysis allows a relatively easy statistical method to systematically separate the result from randomly occurring influences. For each of the three affecting factors, material, instrumentation, and evaluation, it is assumed by the null hypothesis that the three factors have no significant influence on the determination of T_g. If the test value T_g exceeds a critical value, depending on the significant level α (α=0.05 or 0.01), the null hypothesis must be rejected. A significant influence of the individual factor is proved. For every factor, the test value T_F is calculated by the division of the inter-class variance, as a measure for the difference of the single value, by the intra-class variance, as a measure for the random influences.

Results

Figure 3 illustrates the influence of the fiber orientation on the torsional stiffness and the mechanical damping for vacuum conditioned carbon fiber specimens. The laminate with quasi-isotropic lay-up exhibits the highest torsional stiffness, 8400 N mm^{-2}, at room temperature resulting from the torsional stiffness of the ±45 layers. The specimen with a fiber orientation of 0° has a torsion-modulus of 4400 N mm^{-2}. This is a slightly higher than for the specimen with a 90° fiber orientation.

The T_g-onset varies from 30 to 20°C for T_g–$\tan\delta_{max}$ due to variations in the fiber orientation. This variation in the T_g is due to the dependence of the specimen stiffness on the fiber orientation. Hence, the real transition temperature of the matrix can

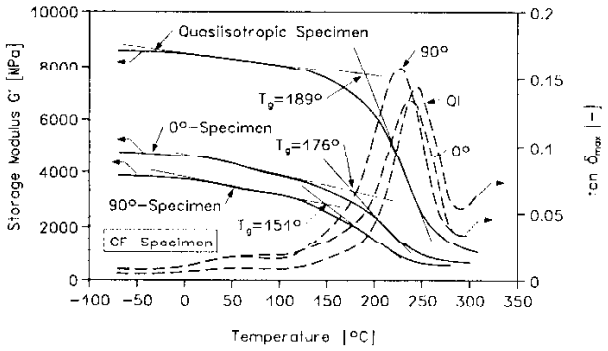

Fig. 3 Influence of the fiber orientation on the torsion-stiffness and the mechanical damping for dry conditioned carbon fiber test specimen tested in torsion mode

not be detected. It is obvious that the torsional modulus and the glass transition temperature are strongly dependent on the laminate structure even with the same matrix and fiber material.

Figure 4 shows the influence of the wet conditioning on the storage modulus and the damping curves for two quasi-isotropic carbon fiber reinforced test specimens. The absorption of moisture clearly shifts the glass transition temperature to lower temperatures. For temperatures up to 50°C, the moisturized specimens have a higher torsional stiffness than dry specimens. This effect can be explained by the increase of residual stresses and swelling effects of the resin due to the absorption of water. At about 70°C, the torsional modulus curves of moisturized specimens show a slight decrease in stiffness that can be explained by the desiccation of the trapped water. The maximum in the damping ratio of the moisturized specimens is shifting about 50°C to lower temperatures, while the absolute values of the $\tan\delta_{max}$ curve increase slightly.

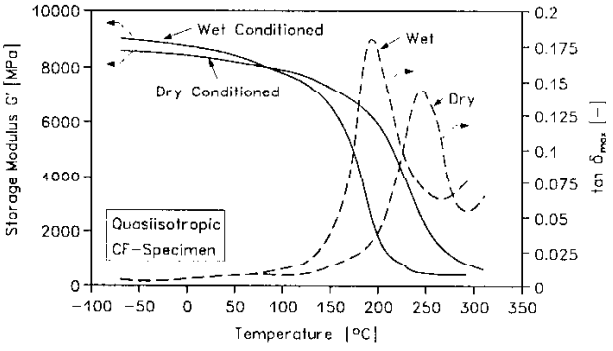

Fig. 4 Influence of conditioning in moisture for two quasi-isotropic carbon fiber reinforced test specimens

The evaluation the onset-T_g by the storage modulus curves is strongly dependent on the location of the tangents. To estimate the influence of the evaluation on variability of the results, every participant evaluated each curve. Figure 5 shows the onset glass transition temperatures determined for the dry conditioned carbon fiber samples (shown in Fig. 3). It can be seen that every participant of the Round-Robin-test identified a different glass transition temperature for identical curves. Thus, besides the before mentioned effects, the variability of the evaluation must also be taken into account. The ability to reproduce the onset-T_g for a single evaluator is relatively good. If a participant has to evaluate the same curve several times within a few days, the determined T_g shows only a variance of ±2.5°C.

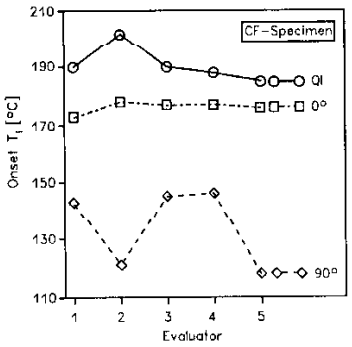

Fig. 5 Glass transition temperatures determined by five different evaluators, for the curves of the dry conditioned carbon fiber samples shown in Fig. 3

Besides the material, the influences of different measuring systems and evaluators on the determination of the glass transition temperature were investigated. The following diagrams show the different institutes and the corresponding determined glass transition temperature. A missing value means, that there was no, or no sensible evaluation possible. In order to give a correct representation for the variance of one measuring point, 5 to 6 specimens were observed. The measurement results for the carbon fiber laminates is shown in Fig. 6. The maximum in the standard deviations is approximately 4%. This shows the relative good reproducibility between one measurement system and one evaluator. Obviously, the highest values for the onset T_g are obtained with the quasi-isotropic specimens. This is probably due to the supporting effect by the fibers depending on their orientation, as discussed before. The influence of the conditioning on the determined glass transition temperatures is confirmed by the comparison of the different glass transition temperatures evaluated. The T_g values have consistently decreased 40°C due to the wet conditioning. It is interesting that institute 4 determines the lowest values for the glass transition temperature. A possible explanation for these extreme deviations can not be given. It is also interesting that the determined glass transition temperatures do not depend on the load mode of the DMTA system.

The results of the triple variance analyses show that influences of the material, DMTA instrumentation, and the evaluation on the determined glass transition tem-

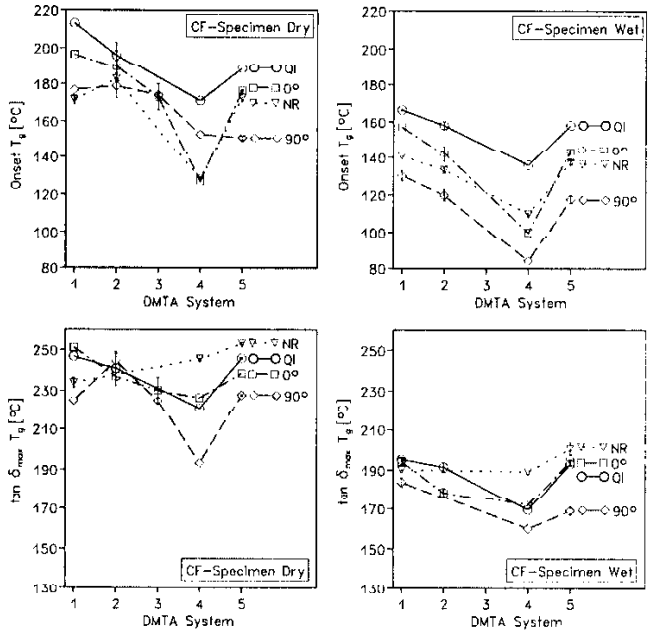

Fig. 6 Results of the Round-Robin-test. Determined onset and $\tan\delta_{max}$–T_g values of the dry and wet conditioned CF-specimen

perature can be separated be a significance level of 99%. This means that for every instrument and every evaluator with the same material, significantly different T_g values were determined. However, the test value, T_F, is different for every factor. As expected, the influence of the differences in the material on the T_g is significantly pronounced, such that differences in fiber orientations, different fiber materials, or the conditioning have a strong effect on the determined T_g. The weakest effect is determined to be the difference in the evaluators. Table 2 shows the results of the triple variance analysis.

Table 2 Results of the statistical test of differences [7]

Test of differences	T_F-value	Critical value		Remark
		α= 0.05	α=0.01	
Material	390	2.26	3.13	significant
DMTA-instrument	217	2.65	3.90	significant
Evaluation	4.3	2.06	2.75	significant

Conclusions

The investigation has shown that the DMTA is, in principle, a suitable method to determine the glass transition temperature of fiber reinforced composites. The influence of different specimen properties, such as the fiber orientation, fiber material, and the conditioning can be determined within one institute, with one instrument, and a reproducible evaluation. However, the Round-Robin-test reveals that for an identical material that the results are strongly dependent on the DMTA system used and the method of evaluation. Thus, no direct comparison of the glass transition temperature at different institutes is possible. This variance of the determined results can be attributed to two major reasons:

– There is no reliable and generally accepted method for evaluating the glass transition temperature by the curves determined in the DMTA test,

– The results are strongly dependent on the DMTA system.

These influences have been proved by the performed triple variance analysis.

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