

IN-SITU DETECTION OF PHASE TRANSITIONS OF SEMI-CRYSTALLINE CARBON FIBER REINFORCED THERMOPLASTICS USING DIELECTRIC ANALYSIS AND ITS CORRELATION TO DMA AND DSC

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Abstract

The mechanical performance of carbon fiber reinforced thermoplastics is strongly influenced by fiber volume fraction, fiber orientation, crystallization conditions, and in case of polyamides humidity. Commonly, the degree of crystallization is verified applying thermo-physical investigations after fabrication, which is often considered cumbersome and time-consuming, especially in a production site. Therefore, this work shows the potential of the in-situ detection of phase transitions such as glass-transition (T_g), melting and crystallization of polyamide-6 (PA6) reinforced by 45 vol.% of carbon fibers using dielectric analysis (DEA). Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to verify the observed phase changes measured by dielectric analysis. The glass transition temperature was determined using DEA, DSC and DMA during heating and cooling at a rate of 2 K/min. It can be seen that the glass transition temperature obtained from the analysis of the loss modulus E'' measured by DMA is in good agreement with the glass transition temperature determined from dielectric loss ϵ'' of the DEA. Consequently, the dielectric properties of carbon fiber reinforced semi-crystalline thermoplastics are strongly related to the molecular mobility changes at the glass transition temperature. This shows its potential as a high-sensitive inline measurement technique during the manufacturing of thermoplastic composites.

1. Introduction

Due to their combination of lightweight potential and high mechanical performance carbon fiber reinforced plastic (CFRP) are increasingly used for the manufacturing of automotive and aviation components. Because of their capability of short cycle times, their flexible processability and weldability compared to highly cross-linked thermoset materials, thermoplastic materials are receiving considerable attention for components and structural assemblies. The scope of use of thermoplastic composites strongly depends on the glass transition temperature. Whereas some polymers are used in their flexible condition above T_g , components, especially in automotive or aviation application require a dimensional and thermal stability, which is given below the glass transition temperature [1].

Usually, the glass transition temperature is determined in time-consuming process accompanying or post-process quality control. Here, the well-established dynamic mechanical analysis or differential scanning calorimetry are commonly applied. In many cases the glass transition temperature of carbon fiber reinforced polymers is not accurately detectable by DSC. In such cases 3-point bending by DMA is widely used to determine phase transitions (ISO 6721-11 / ASTM D7028-7). In previous work [2]

it has been reported that dielectric analysis is able to detect phase changes such as crystallization and melting in carbon fiber reinforced polyamide-6 using dielectric analysis as an inline-monitoring system.

This work shows the influence of different frequencies on the glass transition and the potential of dielectric analysis as an inline detection system during the manufacturing of neat and carbon fiber reinforced thermoplastics. Furthermore, the correlation to the frequency dependent T_g values determined by DMA is presented. In the use of DMA it is well known that the glass transition temperature depends on the penetrating frequency [3-5] that makes it more important to predefine the desired frequency. 1 Hz is often used as sinusoidal stress.

2. Experimental

2.1 Materials and sample preparation

For this study pure polyamide-6 and unidirectional carbon fiber reinforced polyamide-6 composites are used. Pure polyamide-6 was supplied by BASF SE in pellet form. For CFRP investigations an unidirectional polyamide-6 prepreg by Celanese GmbH having the commercial name PA6-CF60 was used.

Reinforced carbon fiber laminates (CFRP) for DMA investigations were fabricated using the FiberForge Relay®2000 automated tape laying machine and a subsequently consolidation step in a heated press at a pressure of about 20 bar. The CFRP laminates were prepared out of 32 unidirectional plies with an overall thickness of about 4 mm. Pure polyamide-6 plates were fabricated by melting the pelletized material and a subsequently cooling at atmospheric pressure. The samples had a total thickness of about 4.5 mm. Plates and laminates were cut into rectangular specimen of 50 x 10 mm. In case of reinforced polyamide-6 the fiber orientation was kept in the sample axis direction.

For dielectric measurements on carbon fiber laminates the raw prepreg material in stacks of six plies with dimensions of 30 x 15 mm and a total thickness of about 800 μm was used. Fixed onto the sensor the material was heated above the melting temperature at 260 °C and cooled down to ambient temperature in a laboratory furnace. This was done to guarantee a good contact between sensor and laminate. The same procedure was done with the pure polyamide-6 pellets.

For differential scanning calorimetric measurements the prepreg material was cut into round samples with a diameter of 6 mm. Stacks of six plies were placed in aluminum pans and closed with a pierced lid.

2.2 Setup and procedure

Dynamic mechanical analysis was conducted using a DMA242 by NETZSCH-Gerätebau. Samples were tested in 3-point bending with an effective span of 40 mm with varying frequencies of 1, 10 and 100 Hz. The force of 9.7 – 9.9 N at the sample was applied as a sinusoidal stress and resulted in an amplitude of 4 – 14 μm sample deformation. Two heating and cooling ramps under nitrogen atmosphere were performed at a rate of 2 K/min each in the temperature range between 25 to 260 °C. The glass transition temperature was determined using the peak of the loss modulus E'' . The same temperature program was used for DSC measurements with a NETZSCH DSC204.

Dielectric measurements were conducted using a NETZSCH DEA288 in combination with the appropriate laboratory furnace and disposable IDEX-FFC35 sensors having a line spacing of 115 μm and 21 electrode couples. The substrate of these sensors is polyimide that provides flexibility and temperature stability up to 275 °C. The DEA288 operates with a cable compensation 4-point measurement technique. This allows for high sensitivity and thus enables the investigation of weak

material response by preventing cable capacities. To be able to perform dielectric measurements on CFRP the disposable sensors were additionally covered with a 12.5 μm thick polyimide coating to avoid short circuits due to the contact between carbon fibers and the measuring electrodes.

A DEA measurement is prepared by placing a stack of six PA6-CF plies on the polyimide film, which covers the sensor and a pressure of about 1.5 bar was applied to ensure the contact between sensor and test material (see Figure 1). Similar to the DMA measurements two heating and cooling ramps from 25 to 260 $^{\circ}\text{C}$ with a rate of 2 K/min were conducted under nitrogen atmosphere. The frequencies used were in the range from 1 Hz to 100 kHz with a sampling rate of 8 per minute for each frequency. Analysis was conducted using the dielectric loss ϵ'' . Based on the results of [6] that describe the pressure dependency of T_g , the different manufacturing steps for DMA and DEA specimen at a pressure of 20 and 1.5 bar, respectively, is resulting in a maximum shift of 1 K.

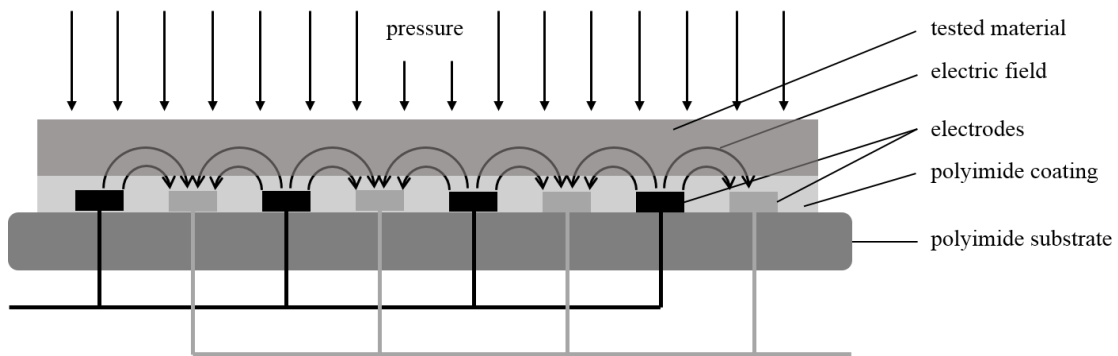


Figure 1: Dielectric measurement setup (according to [5]).

DMA and DEA have in common that a sinusoidal stress is applied to the sample resulting in a shift in strain. Thus the mathematical calculation of the mechanical E'' and dielectric ϵ'' are very similar. They are given by the following equations:

$$E'' = (\sigma_A / \epsilon_A) \sin \delta \quad (1)$$

$$\epsilon'' = (D_0 / E_0) \sin \delta \quad (2)$$

σ_A and ϵ_A are the stress and strain at the defined maximum amplitude, D_0 the electric displacement at maximum amplitude of the applied voltage, E_0 the electric field at the maximum voltage amplitude and δ the phase difference between input and output signal.

3. Results and discussion

3.1 Glass transition temperature of carbon fiber reinforced polyamide-6

The glass transition temperatures determined by DMA using the maximum in the peak of the loss modulus E'' according to ASTM D7028 [7] are listed at various frequencies during heating as the average of three measurements in Table 1. As described in literature [3-5] the calculated mean values of the glass transition temperature are increasing with increasing penetrating frequency.

Table 1: DMA glass transition temperatures at different frequencies.

| <i>DMA</i> | | |
|-------------------|-------------------|-------------------|
| <i>1 Hz</i> | <i>10 Hz</i> | <i>100 Hz</i> |
| T_g (°C) | T_g (°C) | T_g (°C) |
| 53.2 ± 3.1 | 58.0 ± 3.4 | 62.0 ± 4.6 |

Similarly, dielectric analysis reveals a frequency dependent glass transition, Table 2. Figure 2 shows the characteristic behavior of the dielectric loss ϵ'' as a function of temperature for different frequencies in the range from 1 kHz to 100 kHz. Below 1 kHz data evaluation is restricted due to polarization effects that become pronounced while using the electrode covered by the polyimide layer. The dielectric loss ϵ'' in Figure 2 shows distinct peaks in the range of 60 – 90 °C that are shifted to higher temperatures with increasing frequency. These can be attributed to an α -relaxation process, which occurs in the glass transition range of amorphous or semicrystalline polymers [8]. In the observed temperature range the polyamide-6 matrix is in the solid state. Thus, the dielectric loss is dominated by dipole relaxation effects and these peaks are associated with the relaxation of deflected dipoles. In contrast, at higher temperatures (shortly before melting temperature and above) dielectric loss is dominated by electrical conductivity effects. To determine the glass transition temperature the maximum values of ϵ'' for each frequency is used. The calculated values as the average of four measurements are listed in Table 2.

Table 2: Frequency dependent dielectric glass transition temperatures.

| <i>DEA</i> | | | | | | | | |
|--------------|--------------|--------------|--------------|---------------|---------------|---------------|---------------|----------------|
| <i>1 kHz</i> | <i>3 kHz</i> | <i>5 kHz</i> | <i>7 kHz</i> | <i>10 kHz</i> | <i>30 kHz</i> | <i>50 kHz</i> | <i>70 kHz</i> | <i>100 kHz</i> |
| T_g (°C) | T_g (°C) | T_g (°C) | T_g (°C) | T_g (°C) | T_g (°C) | T_g (°C) | T_g (°C) | T_g (°C) |
| 69.2 | 72.8 | 74.3 | 75.6 | 77.3 | 83.1 | 85.3 | 87.3 | 89.8 |
| ± 2.5 | ± 1.2 | ± 1.3 | ± 1.4 | ± 1.5 | ± 1.3 | ± 1.0 | ± 1.1 | ± 0.8 |

Comparing the standard deviation it is evident that the dielectric glass transition temperatures show less deviation compared to the values identified with DMA. This can partly be caused by the manufacturing conditions of the measured specimen. However, the major effect is caused by the measurement principle. The response of the sample used for dynamic mechanical investigations is strongly dependent on laminate quality over the entire test plate. Dielectric analysis is based on the motion of charge carriers and alignment of dipoles and, therefore, the glass transition temperature is much less influenced by the laminate quality. However, the intensity of the signal depends on the fluctuation in fiber volume content over the entire laminate.

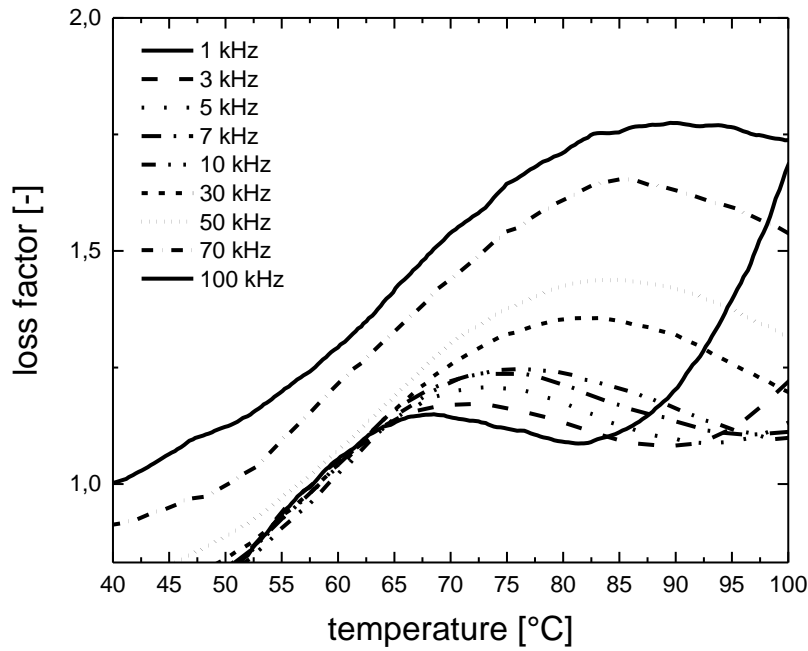


Figure 2: PA6-CF dielectric relaxation effects investigated by the loss ϵ'' .

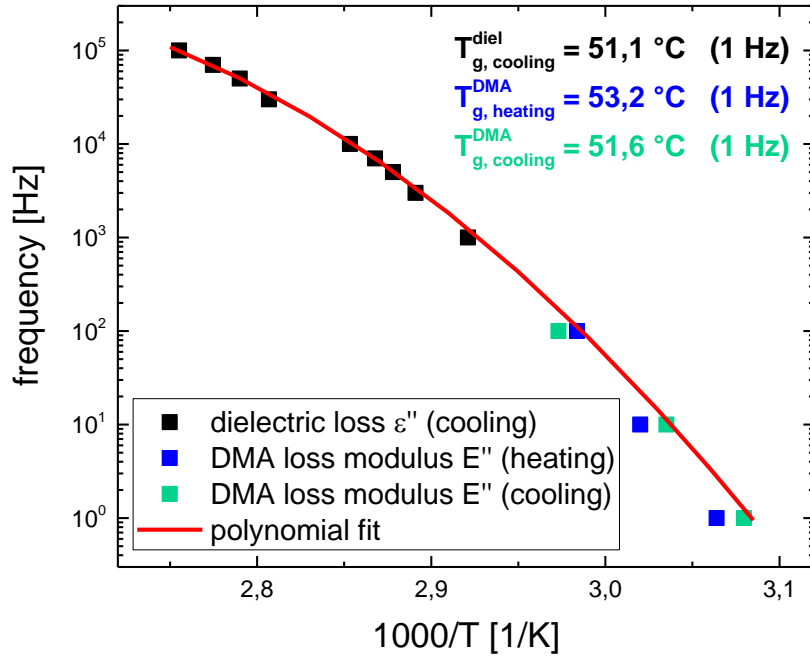


Figure 3: PA6-CF DMA and DEA glass transition temperatures for different frequencies.

Figure 3 represents the glass transition temperatures determined by DMA and DEA using E'' and ϵ'' , respectively, in the frequency range from 1 Hz to 100 kHz. Dielectric glass transition temperatures are included for the frequency range from 1 kHz to 100 kHz. DMA data are shown for the frequencies

1, 10 and 100 Hz. The polynomial regression line was calculated considering dielectric data only. It can be seen that the dynamic mechanical glass transition temperatures are very close to the extrapolated dielectric glass transition values.

3.2. Melting and crystallization of carbon fiber reinforced polyamide-6

While studying melting and crystallization of dipolar materials in dielectric spectra using the relative permittivity ϵ' is the consequential choice. This is due to the fact that ϵ' is a dimension for polarizability of the device under test. In case of phase transitions of dipolar materials from solid to liquid a significant increase can be expected. Figure 4 shows the melting and crystallization behavior of carbon fiber reinforced polyamide-6 comparing dielectric and calorimetric results.

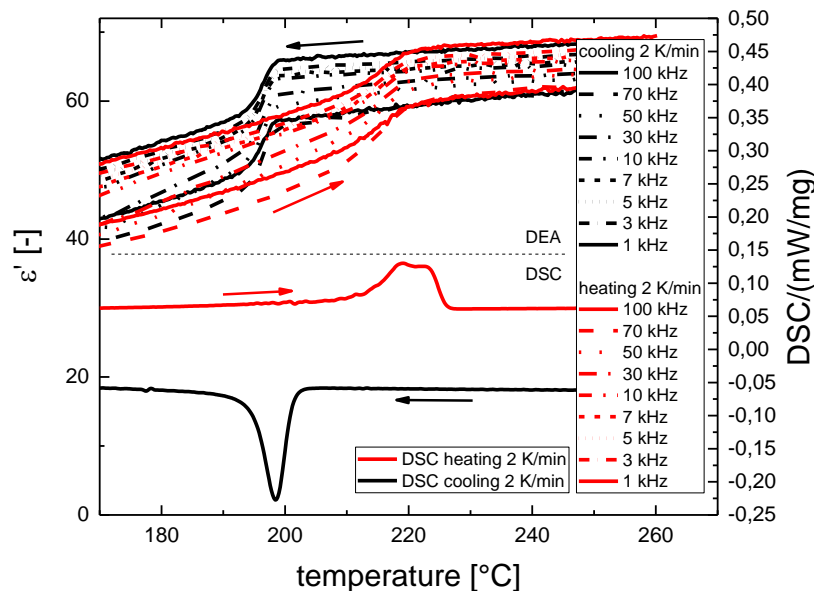


Figure 4: Dielectric and differential scanning calorimetric phase transition for carbon fiber reinforced polyamide-6 during heating and cooling at a rate of 2 K/min.

As expected relative permittivity ϵ' exhibits a significant step during melting and crystallization. Furthermore it is obvious that ϵ' , similar to the heat flow determined by DSC, reveals a hysteresis of about 20 K between melting and crystallization temperature at a rate of 2 K/min. This hysteresis is observable in the heat flow during calorimetric measurements, because the nucleation step preceding the crystal formation is not accompanied by an exothermal heat flow. Thus, the onset of the crystallization peak is often shifted significantly to lower temperatures compared to the melting temperature [9]. By comparing the hysteresis in the relative permittivity ϵ' it can be seen that nucleation causes a similar effect on a molecular level. The mobility of dipoles remains also unaffected. The step in ϵ' that occurs upon further cooling is related to the crystal formation and growth. The irregular molecular chains with large space of motion are folded into ordered lamellae. This leads to a reduction of free space and thus to a reduction of dipole deflection due to extinction of the quantity of local dipoles. It can further be seen that the temperature range of melting and crystallization in ϵ'' is independent of the applied frequency. The frequency dependency is commonly defined by the mechanical mobility of the molecules and their dipoles. This indicates that the dipoles of polyamide-6 below and above the melting point can move as easy as in the molten state. In contrast to this phenomena the motion of molecules and deflection or relaxation of dipoles below T_g exhibits a frequency dependent behavior as shown during the determination of the glass transition temperature.

4. Conclusions

The present work shows a strong relationship of dynamic mechanical and dielectric analysis for the determination of the frequency dependent glass transition temperature. The frequency dependency of the glass transition temperature between dielectric analysis during the cooling of a carbon fiber reinforced polyamide-6 laminate with a rate of 2 K/min is in agreement to the post-processing dynamic mechanical analysis during the first heating of the laminate with a rate of 2 K/min. In order to investigate melting and crystallization it is shown that relative permittivity determined by dielectric analysis is similar to the results of differential scanning calorimetry. These results show the huge potential of an inline glass transition determination using dielectric analysis instead of a process attendant or post-process quality control.

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