

CORRELATION OF THE CURE DEGREE OF AN EPOXY RESIN WITH THE DIELECTRIC PROPERTIES

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ABSTRACT

To minimize the waste and the production time during the fabrication of fibre reinforced plastics, online quality control is gaining importance. In the resin transfer moulding production the curing is the most time and cost consuming step. Therefore the part should be taken out of the mould as soon as it is dimensionally stable, which is reached at a certain degree of cure. Dielectric analysis (DEA) is one method to monitor the curing of the resin system.

DEA measures the permittivity changes of the resin in a capacitor set-up while curing. After mixing the resin system consists of movable dipoles. During the curing process the molecules grow and form a network, what restricts the movement of the dipoles and changes the permittivity.

For the correlation first the curing behaviour of the resin system was analysed by DSC measurements, then the degree of cure was modelled as a function of time. By using the rheometer plates as a capacitor for the DEA, the dielectric properties were measured simultaneously with the viscosity in a rheometer. Finally, the dielectric properties were analysed, considering the feasibility and sensitivity to cure, and a correlation regarding the degree of cure was obtained.

1 INTRODUCTION

To increase the production efficiency and product quality for the fabrication of fibre reinforced plastics in series production, online quality control of the parts during the production is gaining more and more importance. In the RTM (resin transfer moulding) production chain the step, in which the reactive resin matrix is injected into the mould and the part is cured, is the most time and cost consuming step of the process. Therefore it is preferable that the part is taken out of the mould as soon as it is dimensionally stable, which is reached at a certain degree of cure. After this the part can be postcured without the mould, leaving it free for the next infiltration process to start. Thus online monitoring of the cure degree is a critical aspect to control and accelerate the process. Dielectric analysis (DEA) was investigated and pointed out to be feasible to monitor the curing of the resin system [1, 2].

The dielectric analysis uses the effect of the resin system that changes its permittivity during cure. Hereby the permittivity describes how a material responds to an electric field of alternating current. In polymeric materials this depends on two major mechanisms, polarisation due to charge migration and orientation of permanent dipoles [3]. Charge migration in polymeric material is present in the form of ionic conduction. Regarding the orientation of permanent dipoles they influence the measured permittivity in terms of the number of dipoles present and their ability to orient themselves in the electric field [4]. The time dependent orientation of dipoles is called dipole relaxation [3], which is described by characteristic relaxation times. All those phenomena described are frequency dependent. This dependency and the schematic progression of the complex permittivity (divided into real part

(storage permittivity ϵ') and imaginary part (loss permittivity ϵ'') during cure are shown in Figure 1 [3, 5].

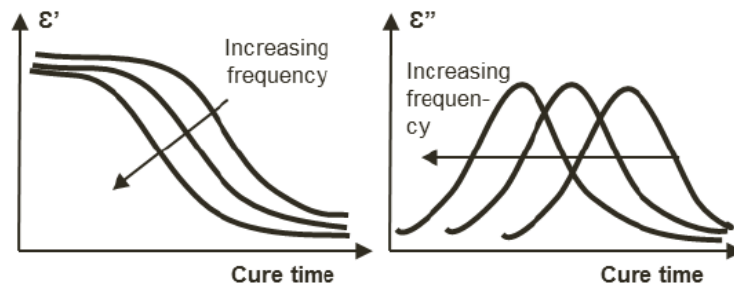


Figure 1: Schematic progression of the complex permittivity during cure [5].

The molecular changes during the cure of the resin system affect the dielectric properties in different ways. The increase of viscosity, due to crosslinking, results in a decrease of ionic conduction, which is proportional to the loss permittivity [3]. At lower frequencies this effect has a high sensitivity over several powers. Hence it is often used to monitor the curing process [4, 6, 7]. However, at higher frequencies this effect is no longer visible. During the cure of a thermoset resin system with polar reactants, the concentration of these reactants is decreasing while the concentration of the less polar product is increasing. This change in concentration of permanent dipoles results in a slight decrease of the storage permittivity at the beginning of the curing process. Due to the increasing molecule sizes during cure, the relaxation times of the dipoles increase as well, meaning the molecular motion to orient the dipoles cannot follow the measurement frequency anymore. This leads to a steep drop of the storage permittivity [3, 5]. Using higher frequencies this phenomenon will occur earlier in the curing process (Fig. 1). Regarding the loss permittivity, a peak can be monitored during cure. The loss permittivity increases with the increase of the relaxation times of the growing molecules. The peak of the curve is the point when the current relaxation time is reciprocal to the used frequency. Therefore the peak occurs earlier at higher frequencies [5].

The change of the complex permittivity during cure can be measured in a capacitor set-up. By using the rheometer plates at the same time as the capacitors for the dielectric analysis it is possible to measure the dielectric properties simultaneously to the complex viscosity in a rheometer. Thus the experiments can be done under controlled and reproducible process parameters and the cure can be monitored as well by the complex viscosity. At a certain frequency the permittivity ϵ^* is determined by the measured capacity C and the vacuum permittivity ϵ_0 , being dependent on the thickness of the sample d and the area of the sensor A (Eq. 1) [2].

$$\epsilon^* = (d C) / (A \epsilon_0) \quad (1)$$

Additionally the permittivity is dependent on changes of temperature and pressure.

To be able to correlate the dielectric properties with the degree of cure, first the curing behaviour of the resin system needs to be analysed by means of a differential scanning calorimetry (DSC). This is done by isothermal measurements, which follow the experimental parameters of the DEA set-up (see 2. Material and Methods). The degree of cure equals the current enthalpy of the experiment divided by the total enthalpy of the reaction. To model the degree of cure over time the widely used phenomenological equation of Kamal and Sourour can be used [8]. Taking into account, that as the reaction proceeds, the curing process becomes diffusion controlled, the model of Kamal and Sourour can be extended by a diffusion factor. Most common therefor is the diffusion factor of Fournier et al. [9]. Further literature on modelling of the cure kinetics can be found in [10-12].

By having the same time lapse for the preparation of the DSC and the DEA experiments, the degree of cure, obtained from the DSC measurements, can be correlated with the permittivity of the DEA measurements.

2 MATERIAL AND METHODS

The industrial epoxy resin RIMR 135 was manually mixed with the amine hardener RIMH 1366 (both distributed by HEXION, Esslingen, Germany) for 90 seconds, following the prescribed weight ratio of 100:30 using 10 g of resin and 3 g of hardener.

For the DSC measurements a TA Q-2000 DSC from TA Instruments was used. About 6-8 mg of the resin system were placed in a hermetic aluminium pan. Two kinds of measurements were carried out: firstly, a dynamic measurement with a heating rate of 10 °C/min from -80 °C up to 280 °C in order to determine the total curing enthalpy. Secondly, isothermal curing with a curing temperature of 60 °C. During the isothermal measurement the pan was first cooled down to -20 °C and then brought up quickly to the desired cure temperature of 60 °C. The resin sample was cured at this temperature until the heat flow remained constant for 3 minutes, meaning that at this point the reaction does not proceed significantly anymore. Subsequently the sample was quenched to 0 °C and the residual enthalpy was measured using a dynamic scan with 10 °C/min up to 280 °C.

For the DEA measurements an ARES G2 rheometer with a dielectric accessory (Agilent 4980A LCR meter) from TA Instruments was used. The measurement chamber was heated to 60 °C. Afterwards the resin system was placed between the rheometer plates (40 mm diameter, steel disposable), which were adjusted to a gap of 0.5 mm. The monitoring of the dielectric properties change was done isothermal at 60 °C for 4 hours. Considering the frequency dependency of the permittivity three different frequencies of 100 Hz, 10 kHz and 1 MHz were used.

3 RESULTS AND DISCUSSION

The results of the isothermal DSC measurement at 60 °C were transformed, so that the degree of cure could be plotted over time (Fig. 2).

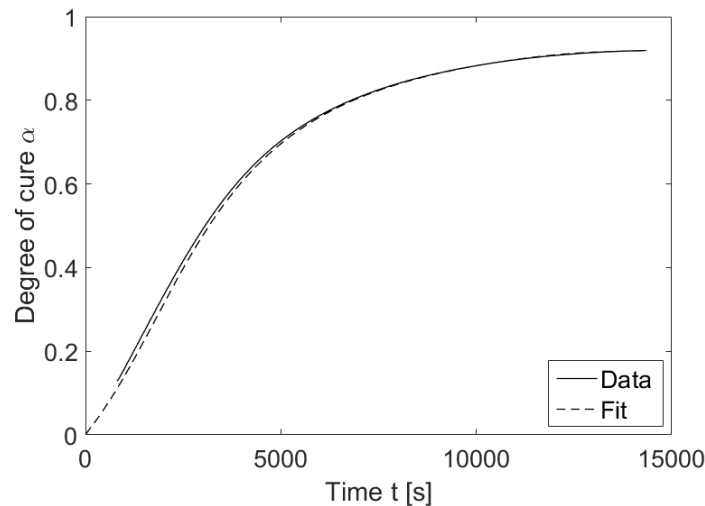


Figure 2: Degree of cure over time (original data from DSC and curing kinetics model fit)

It can be seen, that in the beginning the degree of cure rises in a steep slope, but flattens at a threshold value of about 0.92. Hence a total cure cannot be reached at the given isothermal temperature of 60 °C. This is due to the vitrification of the resin system at a critical glass transition temperature T_G : the T_G of the resin system increases together with the increase of cure degree. As soon as the T_G surpasses the curing temperature of 60 °C, the reactive system will be vitrified due to the glass transition. The curing process becomes diffusion controlled, which leads to a dramatic slow-down of the reaction.

In the DSC measurements it is inevitable that part of the curing already begins during the heat-up phase before the DSC is stabilised at the required isothermal curing temperature (in this case 60 °C), noticing the data starts at a degree of cure of over 0.1, as shown in Figure 2. With the model of Kamal

and Sourour and the diffusion factor of Fournier et al. the degree of cure can be fitted over time, taking in to account the initial reaction enthalpy before the isothermal measurement of the experiment. Figure 2 shows, that the model describes the progression of the data very well.

The change of both storage permittivity ϵ' and loss permittivity ϵ'' versus curing time are shown in Figure 3. The storage permittivity follows the description of the schematic progression (Fig. 3, left). Initially a slight decrease of the storage permittivity can be seen, which turns into a steep slope. Just as the degree of cure it ends at a threshold value. As mentioned above, the first slight decline is caused by the decrease of dipoles, whereas the second steep decline is caused by the increase of the molecule size, generating increasing relaxation times of the dipole orientation. Due to the frequency dependency the progression of the storage permittivity is shifted to shorter times and lower values with higher frequencies. At very low frequencies such as 100 Hz there is a steep drop at the beginning of the measurement before the curve follows the described run, which could not be explained yet.

The loss permittivity ϵ'' shows initially a steep decline, turning then into the described peak (Fig. 3, right), caused as well by the increasing relaxation times of the dipole orientation. The steep decline results from the decrease of ionic conduction. Comparing the frequencies, the decline is only visible until 10 kHz. At 1 MHz the change of ionic conduction cannot be observed anymore. However, even at the relatively high frequency of 10 kHz the sensitivity of the change of ionic conduction is not very high anymore, making the change of the ionic conduction not a viable process factor to monitor the resin cure over a broad range of frequencies. Additionally at the end of the steep drop caused by ionic conduction the hardening reaction is not finished especially at higher frequencies, making it not a point in the curve to verify the end of this reaction. The peak of the loss permittivity is shifted to shorter times due to the frequency dependency of the dipole polarisation.

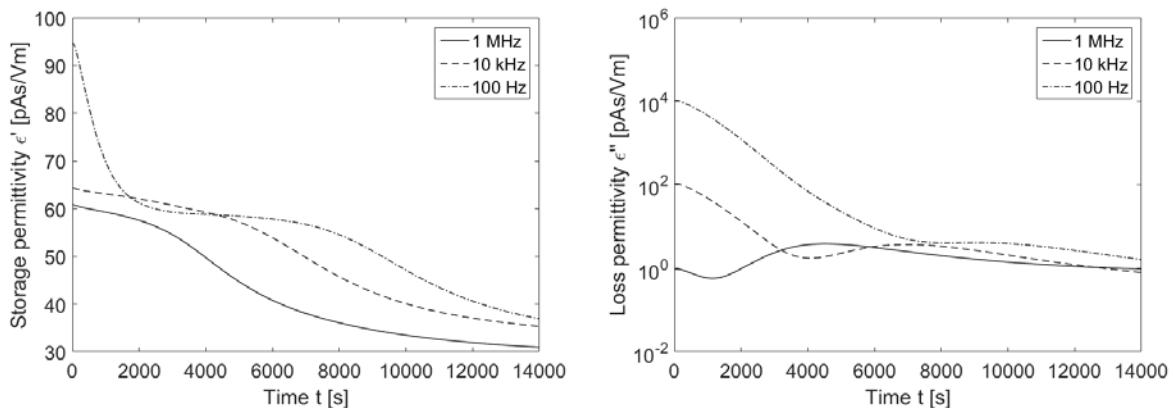


Figure 3: Storage permittivity (left) and loss permittivity (right) over time

The complex permittivity (Fig. 4, left) is the sum of the storage and loss permittivity. So the progression of the curve is dominated by the higher value of the two components. It can be seen that for 100 Hz and 10 kHz in the beginning it follows the progression of the loss permittivity for the steep slope and the progression of the storage permittivity. For the measurement of 1 MHz it follows completely the curve of the storage permittivity, because the values of the loss permittivity are very low. Hence the complex permittivity combines the characteristic features of both components, except the peak of the loss permittivity is too small to influence the progression of the complex permittivity.

To ensure a possible quantitative correlation the reproducibility of the DEA measurements needs to be taken into account. In Figure 4 on the right side three measurements of the storage permittivity over time are shown for the curing at 60 °C and 10 kHz. Considering the sensitivity of the process the reproducibility is very good. Small deviations do not result from the measuring method but from the prepared samples. The used rheometer plates have a barrier spring for overflow resin between the plates. The amount of resin in the barrier spring influences the measured value but not the progression of the curve. So if the dimensions of the sample are the same, the measurement will be exactly reproducible, given equation (1). All shown graphs are the mean value of three measurements.

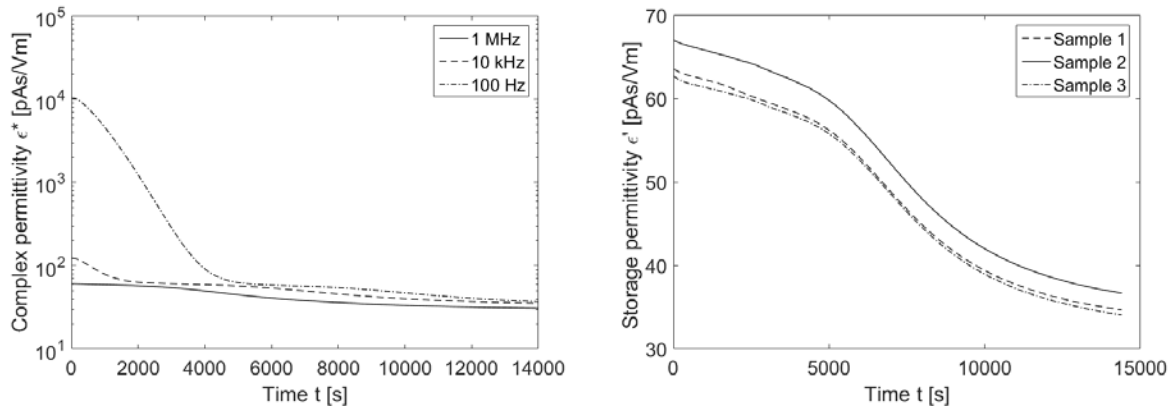


Figure 4: Complex permittivity over time (left) and reproducibility at the example of storage permittivity over time at 10 kHz (right)

In order to correlate the dielectric properties of the epoxy resin with the degree of cure, the storage permittivity is chosen to be a feasible characteristic. In contrast to the loss permittivity the storage permittivity shows a generally declining trend, enabling a clear correlation of the storage permittivity to the degree of cure. In case of the loss permittivity, due to the changing trend with the curing time, it is difficult to draw a general correlation as the same loss permittivity value could indicate multiple curing states without clearly differentiating the curing phase. Additionally the sensitivity of the storage permittivity stays in the same range over a broad field of frequencies, whereas the sensitivity of the loss permittivity and thus the complex permittivity decreases strongly with increasing frequency. Therefore the storage permittivity was selected as the representative dielectric property for the correlation with the degree of cure.

The progression of the storage permittivity was fitted with the rbf-tool from Matlab. By having the same time lapse of the DSC- and DEA measurements the fits of the storage permittivity were correlated with the model of the cure degree. The results can be seen in Figure 5. At 10 kHz and 1 MHz the storage permittivity has a slight decline until a certain degree of cure, where it begins to fall dramatically with a steep slope. This change is more apparent at a lower degree of cure with higher frequencies. This means that the storage permittivity is more sensitive for a farther band of the cure degree at the end of the reaction when the frequency is higher. At the frequency of 100 Hz the storage permittivity has a high sensitivity at low cure degrees until 0.2. For finding the right point to demould a part this band of cure degree is not feasible. Additionally the sensitivity at the end of the reaction is only for a very small band. In conclusion for the correlation of the degree of cure with the dielectric properties a high frequency is recommended.

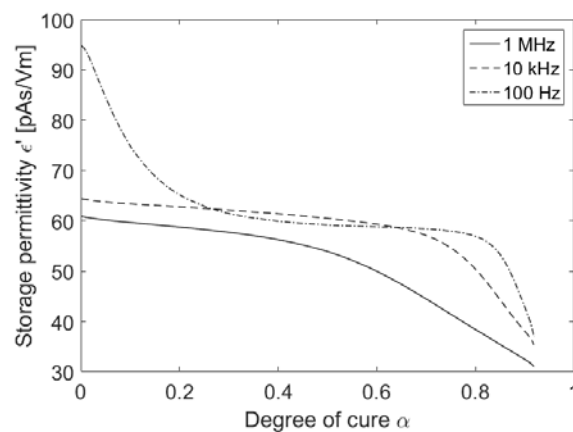


Figure 5: Storage permittivity over degree of cure

Figure 5 shows that a qualitative correlation of the dielectric properties with the degree of cure of a resin is possible. However, in order to evaluate, if a quantitative correlation is possible, certain factors need to be taken into account. As described before, the permittivity is dependent on the thickness of the sample and the area of the sensor. So for a quantitative approach these parameters need to be constant or normalised. During process control, the sensor would be positioned at fixed location in the mould, ensuring constant parameters for the measurements. The necessary reproducibility of the quantitative values of the measurement was shown in Figure 4 on the right side. Small deviations were caused by changes in the sample geometry, again showing the importance of keeping the parameters of equation (1) constant to ensure a correct quantitative correlation. This means that the given correlation is just valid for one scenario. As soon as the temperature profile, the measurement frequency, the dimensions of the tested area or the material changes a new correlation needs to be done. In conclusion the DEA is a good method for measuring the cure degree online for quality control.

4 CONCLUSIONS

In this paper, the degree of cure as well as the dielectric properties of an epoxy resin during an isothermal curing process were analysed. The curing kinetics were successfully modelled with the equation of Kamal and Sourour coupled with the diffusion factor of Fournier et al. The change of the complex, storage and loss permittivity during resin cure were measured and analysed. A successful qualitative and quantitative correlation of the storage permittivity with the degree of cure was shown, whereas a higher sensitivity for the in the production relevant band of cure degree can be reached at higher frequencies of the DEA measurement. A quantitative correlation is possible, if all parameters of the measurement are kept constant. During process control, the sensor would be positioned at fixed location in the mould, ensuring constant parameters for the measurements. So given a consistent temperature profile and a fixed measurement frequency, DEA is a good method for the online quality control of the cure degree for the shot-by-shot mass production.

The next steps of the work are to conduct further experiments both at different temperatures and higher frequencies to on the one hand correlate the cure degrees of different temperature profiles and on the other hand determine, if even higher frequencies like 10 MHz enable to have the same sensitivity of the storage permittivity over the full cure degree.

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