Time- and Temperature-Dependent Dielectric Measurements of Thermosetting Resins

Dhidik Prastiyanto[1,4], Guido Link[1], Ulrich Arnold[3], Manfred Thumm[1,2], and John Jelonnek[1,2]

[1]Institute for Pulsed Power and Microwave Technology (IHM), [2]Institut für Hochfrequenztechnik und Elektronik (IHE), [3]Institute for Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, Karlsruhe, Germany
[4] Department of Electrical Engineering, State University of Semarang, Semarang, Indonesia

Abstract – The curing of fiber-reinforced thermosets using high-power microwave technology gains growing industrial interest. For successful system and process development, dielectric properties need to be investigated during the curing process. In this work a test set for dielectric measurements based on the waveguide transmission-reflection method at 2.45 GHz has been developed. It provides fully automatic temperature control and data acquisition. The dielectric properties are reconstructed from the captured *S*-parameters by full-wave electromagnetic modeling and by use of a neural network approach. Time- and temperature-dependent dielectric properties were measured to investigate the curing behavior of various resin compositions. Corresponding results obtained with epoxy resins based on bisphenol A diglycidyl ether monomer mixed with polyetheramine hardener are presented. The results show that both dielectric constant and loss factor increase in line with temperature increase, and start to decrease when polymerization begins.

Introduction

Microwave curing of fiber reinforced thermosets offers advantages of volumetric and selective heating compared to conventional processing that result in fast and energy efficient processing [1]. For accurate modelling and optimization of microwave-assisted curing processes, the dielectric properties of the materials during curing need to be investigated. Therefore in this work, a dielectric measurement system based on the transmission-reflection method has been developed for time- and temperature-dependent dielectric characterization of resins at 2.45 GHz.

In [2] dielectric properties have been measured at low frequencies (< 10 kHz) during the curing process. The system used is based on dielectric analysis of capacitance probe measurements. A waveguide-based approach for dielectric property measurement of solid material in the *S*-band has been developed and described in [3-4], where the waveguide cross-section is fully and partially covered by a solid sample. Analytical models and optimization methods were developed for the reconstruction of the dielectric properties from the measured *S*-parameters. In order to monitor the changing of dielectric properties during the curing process, a fast algorithm is needed. The reconstruction of dielectric properties based on FDTD simulation has also been developed [5]. The concept makes use of a radial basis function (RBF) neural network. Some liquids were measured and tested at 915 MHz. The results show good performance so that a neural network approach might be used for real-time monitoring of dielectric properties. Thus the development and implementation of a neural network for monitoring the dielectric properties during curing of thermosetting resins has been initiated. Many practical aspects need to be considered based on the experimental results.

Experimental Set-up

A special test-set design for in-situ dielectric measurements of thermosetting resin during curing has been developed. The measurement setup is shown in Fig. 1.

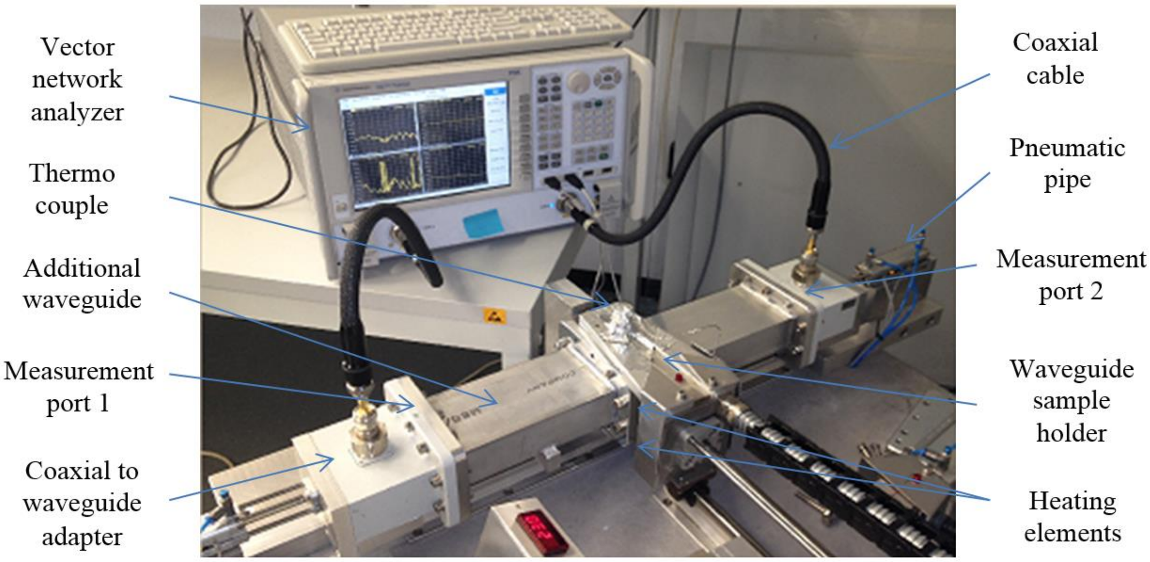


Fig 1. Measurement setup for temperature dependent dielectric properties at 2.45 GHz

The vector network analyzer (VNA-Agilent PNA 5224A) is connected to the waveguide transmission line by use of waveguide to coaxial adapters at the input and output port, respectively. The waveguide sample holder is installed between two additional waveguides with an adequate length of 20 cm to ensure sufficient suppression of higher order modes at the measurement ports. The waveguide sample holder, 53.7 mm in length, is equipped with a thermocouple to measure the temperature of the material. Four resistive heating elements are installed in the waveguide sample holder to achieve a uniform heating of the material under test. Those heating elements are PID-controlled to get the desired temperature in the waveguide sample holder. Therefore the difference between measured and preset temperature is used as feedback signal of the PID controller. The waveguide sample holder as well as the waveguide ports are equipped with computer-controlled pneumatic push rods. These enable remote-controlled shift of the sample holder to allow for insertion of the test sample. The use of those push rods to move the waveguide ports away from the sample holder before heating allows reduction of heat loss to the waveguide adapters. Any heating of the waveguides may influence the system calibration and therefore the measurement accuracy. Position sensors are installed to get feedback about the waveguide position (open or closed). The use of a multifunctional input/output device connected to a computer enables a remotely controlled measurement procedure. A fully automatic temperature control along any preset temperature profile and data acquisition allows the system to be used for monitoring dielectric properties of thermosetting resin during the curing process. The reconstruction of dielectric properties is performed continuously during the measurement procedure. Therefore the development of the measurement results can be easily displayed on a graphical user interface, indicating the progress of curing.

The dielectric properties are calculated online during the measurement process employing a trained multilayer perceptron (MLP) artificial neural network (ANN) (see Fig. 2). The MLP ANN with two hidden layers is trained using datasets from finite integral time domain (FITD) electromagnetic simulation utilizing CST Microwave Studio. The real and imaginary parts of permittivity ε' and ε'' are simulated in the range of 1 to 10 and 0.001 to 10, respectively, with 1000 normal distributed random data. One thousand pairs of simulated dielectric data and *S*-parameters are selected to train the network. The network is trained and tested with datasets from simulations of measurements.

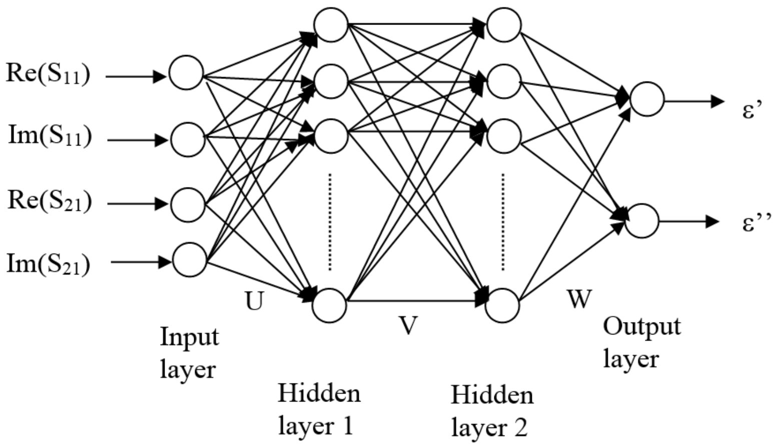


Fig 2. MLP ANN for reconstruction of dielectric properties.

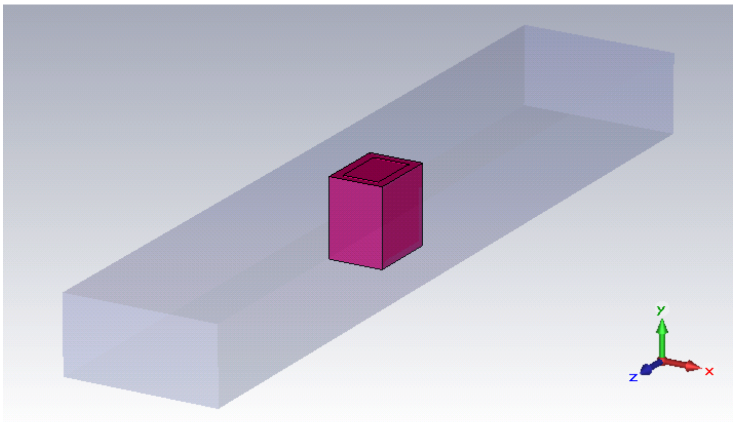


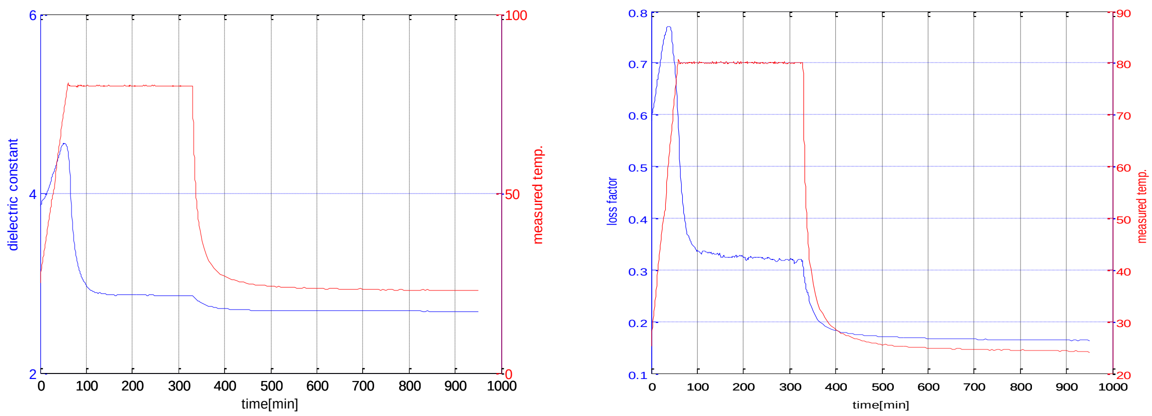
Fig 3. Model of the rectangular waveguide measurement setup in CST Microwave Studio.

For the reconstruction of the dielectric properties and for generating an appropriate dataset used to train the ANN a simulation model as shown in Fig. 3 has been used. It includes the waveguide sample holder, additional waveguides for suppression of higher order modes as well as an appropriate crucible filled with resin. The crucible is made from a 43.18 mm long segment of a rectangular Teflon tube with outer dimension 30x40mm and inner dimension 20x30 mm. The Teflon tube is closed on both sides using an aluminum tape so that the liquid sample can be contained. The aluminum tapes have direct contact with the top and the bottom of the heated waveguide sample holder so that better heat transfer can be achieved into the thermosetting resin.

Experimental Results and Discussion

Measurement of epoxy resin bisphenol A diglycidyl ether (DGEBA) mixed with a Polytheramin (PEA) hardener has been performed. The measurements were performed along a preset temperature profile with a constant heating rate of 1°C/minute to 80°C and a subsequent isothermal curing at constant temperature for around four hours. To allow for at sufficient heat transfer and temperature homogeneity within the resin sample, the heating rate has been limited to 1°C/minute.

At the end of the temperature profile the heating of the sample holder is switched off but the dielectric monitoring is continued during the cooling process for another 10 hours.



(a) (b)

Fig. 4. Dielectric constant (a) and the loss factor (b) DGEBA and PEA during the curing process.

This reveals the temperature dependence of dielectric properties of the cured thermoset. The results show that both real and imaginary parts of permittivity increase in line with increasing temperature and start to decrease when polymerization begins (see Fig. 4). In the cooling process, the dielectric properties decrease in line with decreasing temperature, and then become constant according to constant temperature.

The results demonstrate that the developed test set is a versatile tool for time- and temperature-dependent investigations of dielectric properties of resins and for monitoring the curing process. The results on isothermal curing allow for systematic investigation of the effect of temperature on the curing kinetics as is shown in Fig. 5 for temperatures in the range from 60°C to 80°C. The slope in dielectric loss factor is significantly higher at 80°C as compared to 60°C indicating an enhanced curing rate. Furthermore, the time until the measured data converges to constant values is significantly longer at 60 °C as compared to 80°C and the final loss data is somewhat larger at 60°C and 70°C indicating that the resin is still not completely cured.

Conclusions

A dielectric measurement system for investigations of curing processes of thermosetting resins has been developed. The system enables a fully automated and computer controlled measurement of dielectric properties during the curing process. It is a versatile tool for systematic investigations of temperature and time dependence of the curing kinetics. The results show that dielectric properties decrease during the curing process, that means during the phase transformation from liquid phase of the monomers into the solid phase of the thermosetting polymer. Higher temperatures promote the curing process which is indicated by steeper slopes of the time dependent dielectric properties and by a faster convergence to the final permittivity.

References

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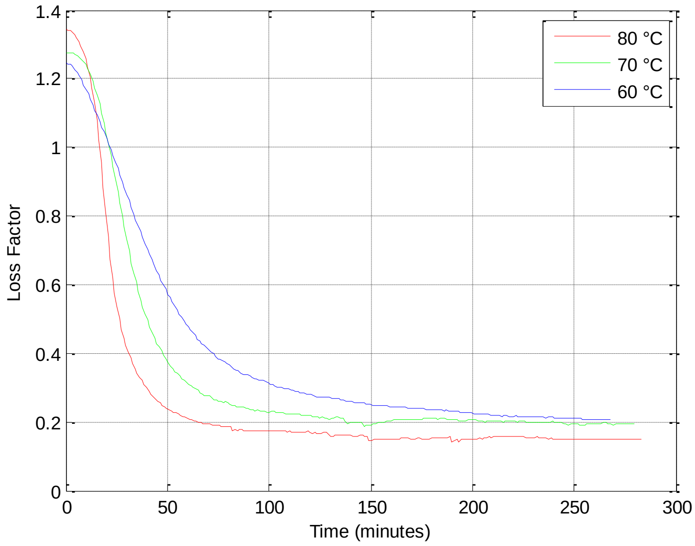

Fig. 5. Time and temperature dependence of loss factor of DGEBA and PEA during the curing process.

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