

DYNAMIC MECHANICAL ANALYSIS OF EPOXY-MATRIX CROSS LINKING MEASURED IN-SITU USING AN ELASTOMER CONTAINER

Volker Trappe^a, Patrick Sachs^a

a: Bundesanstalt für Materialforschung und -prüfung (BAM) – volker.trappe@bam.de

Abstract: A new patented [1] dynamic mechanical analysis (DMA) is presented, where the tensile, bending- or torsional stiffness of a media can be characterized in-situ during the phase transition from liquid to solid. An epoxy system, e.g. Hexion L285/H287, is filled into an elastomer container, such as a silicone tube. This can be mounted into a conventional DMA and, based on a linear viscoelastic approach, the storage modulus (E' ; G'), the loss modulus (E'' ; G'') and the loss angle $\tan(\delta)$ can be measured at constant temperature as a function of time in order to investigate the liquid to sol-gel to solid transition. With this new method, the stiffness increase as a result of the cure process can be directly measured more precisely than with a rheometer in a shear plate set-up, because using an elastomer container gives a defined cross section for calculating the Young's modulus.

Keywords: dynamic mechanical analysis (DMA), thermoset polymers, cure process, cross linking

1. Introduction

Fiber reinforced plastics made with a thermoset molding technique are often used for high-performance applications including aircraft and wind turbine blades. To optimize the production process of these materials, the manufacturer must know the cure process for the cross-linking of the epoxy matrix system. A sufficient amount of stiffness of the composite structure has to be reached before the component can be removed from the mold and a subsequent post-cure outside of the mold can begin. The production rate of a component is ultimately dependent on the occupancy time in the mold.

Based on a linear viscoelastic approach [2,3], it is state of the art to measure the glass transition temperature (T_g) for polymer materials by measuring the storage modulus (E' ; G'), the loss modulus (E'' ; G'') and the loss angle $\tan(\delta)$ as a function of temperature (typically in the range of -150°C to 250°C , depending on the kind of polymer). For cross-linking thermoset polymers it is common to measure T_g at more or less perfectly cured specimens starting in the solid (glassy) state and moving in the entropy elastic “rubber” state at higher temperatures.

In this study, a patented [1] dynamic mechanical analysis (DMA) is used, where the Young's and shear modulus of a medium can be characterized in-situ during the phase transition from liquid to solid. In a first feasibility experiment, water was filled into an elastomer container, such as a silicone tube. This can be mounted into a conventional DMA and, by cooling down the temperature chamber from room temperature (RT) to -20°C , the phase transition from liquid to solid (ice) and vice versa can be investigated. The wall thickness and diameter of the tube was dimensioned with respect to the capability of the DMA, and the empty tube should have a stiffness of less than 1% of the total specimen stiffness in the solid state. Additionally, the glass transition temperature T_g of the elastomeric tube should be far below the investigated temperature range. In

this study, the T_g of the silicon tube was about -50°C . Based on the common linear viscoelastic approach [2,3], the storage modulus (E' ; G'), the loss modulus (E'' ; G'') and the loss angle $\tan(\delta)$ was measured at constant temperature as a function of time in order to investigate the liquid to sol-gel to solid transition of an epoxy resin.

2. Experimental

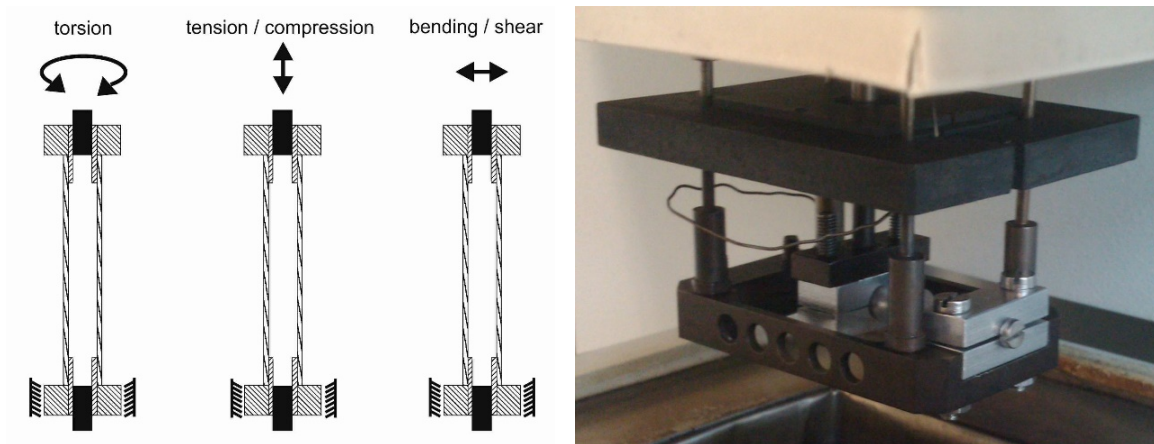


Figure 1. Left – measuring the cure conversion in a DMA in three possible set-ups according to [1]. Right – realized cantilever beam set-up in a Netzsch DMA 242D (bending / shear)

First a 3 mm inner diameter silicone tube, filled with the epoxy resin system Hexion L285/H287 was mounted in a Netzsch DMA type 242 D in a cantilever beam set-up (s. Figure 1). For a proof of concept, the modulus E' was measured at different constant temperatures. A torsional loaded tube with the same dimensions was mounted in a Myrenne DMA ATM3, and a second possible set up was checked successfully. Finally, the tension / compression loading set up should be checked. However, the capability of the Netzsch DMA was not high enough for cyclic loading of the cured epoxy resin. Hence, a polyvinylchloride (PVC) tube of 12 mm inner diameter was mounted in a 10 kN servo-hydraulic tensile testing machine with a temperature chamber. At different temperatures (RT, 40°C , 60°C , 80°C) every 15 minutes, the specimen was subjected to displacement-controlled cyclic loading with 0.01 Hz at a load ratio of $R=-1$, and hysteresis loops were measured. The dynamic stiffness was calculated according to [4,5]:

$$E_{dyn} = \frac{\sigma(\epsilon_{max}) - \sigma(\epsilon_{min})}{\epsilon_{max} - \epsilon_{min}} \quad (1)$$

and the dissipated energy according to:

$$W_{diss} = \oint \sigma d\epsilon \quad (2)$$

was calculated by numerical integration of the hysteresis loops. This procedure enables a deeper understanding, where the phase transition of the Hexion LR285/LH287 epoxy resin system was investigated in the time domain (s. Figure 2) [4,5]. In displacement-controlled mode, hysteresis loops were measured every 15 minutes and the specimen stiffness was calculated from the force

at the minimum and maximum displacement values (corresponding to Eq. 1). Additionally, the energy dissipation was calculated by numerical integration of the hysteresis loops (corresponding to Eq. 2). Furthermore, the specimen was loaded with rectangular and triangular displacement functions to analyze the constitutive material law beside a linear viscoelastic approach in the different material states of the epoxy system [4,5]. The specimen was held in a temperature chamber to investigate the cross-linking at different temperature-time runs from room temperature up to 80°C, with the possibility of testing up to 150°C.

Figure 1 displays the cure conversion of LR285/LH287 by means of the specimen stiffness increase (kN/mm) corresponding to the storage modulus E' and the slope of the dissipated energy (kN*mm) corresponding to the loss modulus E'' at room temperature [2]. Three hysteresis loops are exemplary displayed after 5 (a), 16 (b) and 80 (c) hours cure time. By moving the average calculation, the first derivative of the stiffness-time slope was derived, and the inflection point occurred at the same time as the maximum of the energy dissipation curve at approximately 16 hours.

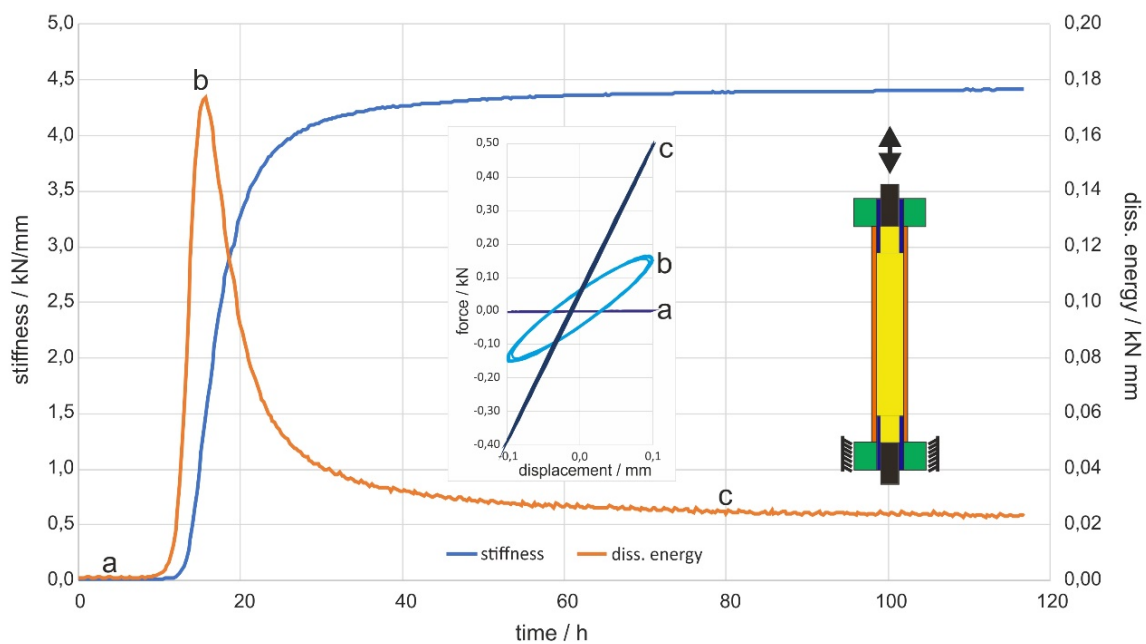


Figure 2: Liquid epoxy resin (LR285/LH287) was filled in an elastomer container, which was mounted into a servo-hydraulic tensile testing machine. Every 15 minutes, a force over displacement hysteresis loop was measured to monitor the cross-linking over time by calculating the dynamic stiffness and energy dissipation. Three hysteresis loops are exemplary displayed at 5 (a), 16 (b) and 80 (c) hours cure time.

In the next step, the epoxy resin was cured in addition to RT at 40°C, 60°C and 80°C and the force and displacement were normalized to stress and strain. The results are depicted in Figure 3. By increasing the cure temperature, the crosslinking is accelerated by means of a faster increase of the Young's modulus over time. However, the asymptotic reached maximum values of stiffness decrease systematically with shortened cure time at higher cure temperatures. Finally, it is well known that the Young's modulus of a polymer decreases with temperature even in the glassy

state. Hence, the effective Young's modulus reached with different cure processes are comparative measured at room temperature after each in-situ cure experiment. The results are listed in Table 1. The effect of a lower Young's modulus at higher cure temperature and accelerated cross linking remained quantitatively the same, but the effective stiffnesses are significantly higher than monitored in the in-situ experiment.

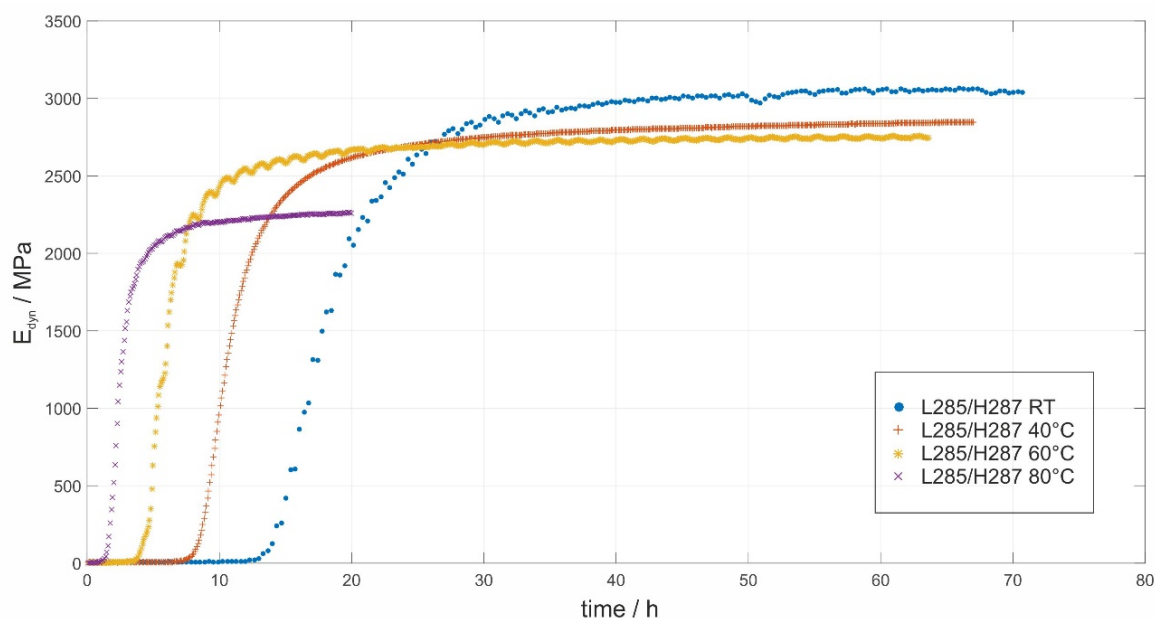


Figure 3: Increase of dynamic Young's Modulus over time at different cure temperatures for LR285/LH287 epoxy resin measured in-situ cure process

Table 1: Cure temperature and dynamic Young's Modulus, measured at RT.

Cure temp. [°C]	E_{dyn} at RT [MPa]
RT	3040
40	2990
60	2940
80	2700

Finally, the in-situ cure conversion monitoring using an elastomer container mounted in a DMA or tensile testing machine should be compared to the capability of a rheometer. Measurements with the same epoxy system were done with a Haake-Mars-III rheometer at room temperature with a plate-plate setup in rotating and cyclic loading. The results are comparatively depicted in Figure 4. Qualitatively, the in-situ measured shear G' - and loss modulus G'' correspond very well to the in-situ measured Young's modulus (in MPa) and energy dissipation (in J/m³) slope over the cure time. However, the capability of the rheometer is not high enough to measure into the fully crosslinked state. Additionally, the plate-plate setup is not capable of giving precise shear modulus values.

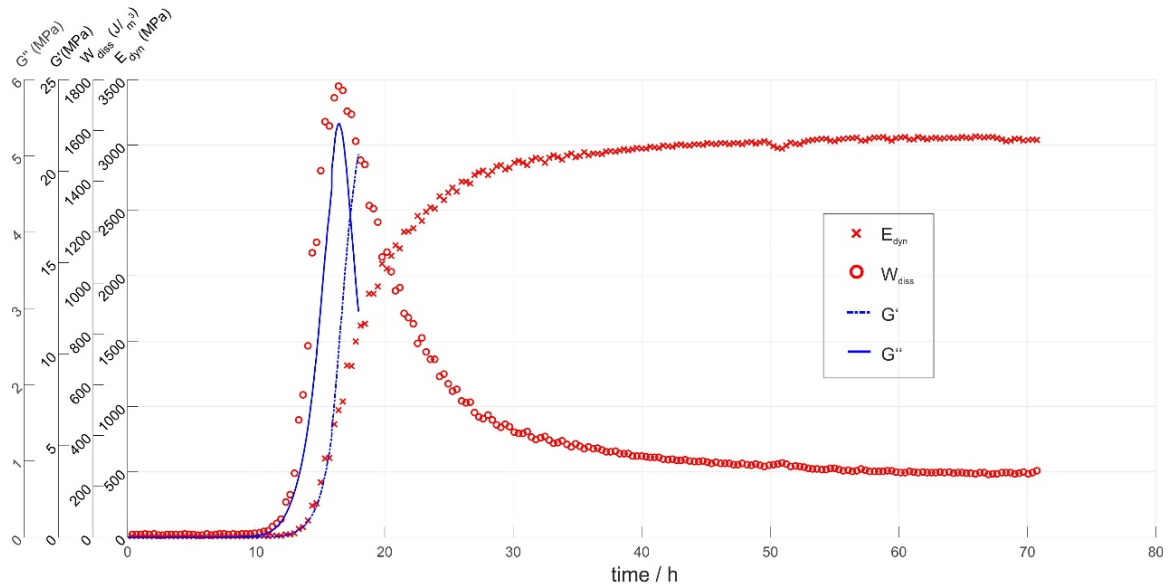


Figure 4: Cure conversion of LH285/LR287 at room temperature monitored comparatively with elastomer container technology and a Haake-Mars-III rheometer in a plate-plate setup.

3. Discussion / Conclusion

With the new described method of filling a epoxy system in a elastomer container and mounting into a DMA or tensile testing machine, the stiffness / Young's modulus increase as a result of the cure process can be directly measured. Using the temperature-time slope, as used in the component production process, a manufacturing optimization can be done. Using an elastomer container gives a defined cross section, and hence the Young's modulus can be calculated more precisely than e.g. with torsional braid analysis [6].

Compared to the viscosity measurement with a conventional rheometer, the resolution of the rheometer is much better at lower degrees of cure conversion in defining the effective pot life for the impregnation process. However, to monitor the Young's or shear modulus at higher degrees of cure conversion, the presented elastomer container technique is superior.

A decreasing Young's modulus at increased cure temperature and an accelerated cross linking was also reported by Ellis [7] and observed in [8]. A higher Young's modulus does not necessarily mean a higher degree of a cross linking density, and this has an impact on the fatigue or crack propagation rate in a cured epoxy polymer [8].

In future work, this method should be compared in greater depth to the outcomes of cure conversion in-situ monitoring using infrared spectroscopy [9] and ultrasound [10]. Preliminary results showed a good accordance with these techniques.

4. Acknowledgements

This investigation was supported by Hexion by providing epoxy resins and hardeners. The authors would also like to acknowledge Stefan Hickmann and Nicolai Schmidt for their support in specimen production, test setup and testing.

5. References

1. Patent DE102014108690A1; Sample holder for dynamic mechanical analysis (DMA) in the field of liquid-solid phase transition and its use for polymer materials, submitted 2014-06-20, granted / published 2017-08-03
2. Plastics - Determination of dynamic mechanical properties - Part 1: General principles (ISO 6721-1:2001)
3. Plastics – Determination of dynamic mechanical properties – Part 2: Torsion-pendulum method (ISO 6721-2:2008)
4. Trappe, V., Harbich, K-W. Intralaminar fatigue behaviour of carbon fibre reinforced plastics. *International Journal of Fatigue* 28(2006)1187-1196
5. Trappe V. Beschreibung des intralaminaren Ermüdungsverhaltens von CFK mit Hilfe innerer Zustandsvariablen. Reihe 5, Nr. 646, VDI-Verlag: Düsseldorf; 2002.
6. Gillham, J.K. Characterization of thermosetting materials by torsional braid analysis. *Polymer Engineering and Science*, 1976. **16**(5): p. 353-356.
7. Ellis, B. et al. *Chemistry and technology of epoxy resins*. Springer, 1993.
8. Trappe, V. Günzel, S., Jaunich, M. Correlation between crack propagation rate and cure process of epoxy resins. *Polymer Testing*, 31(5):654 – 659, 2012.
9. Erdmann, M., Trappe, V., Sturm, H., Braun, U., Duemichen, E. Cure conversion of structural epoxies by cure state analysis and in situ cure kinetics using nondestructive NIR spectroscopy. *Thermochimica Acta* 650 (2017) 8–17
10. Mc Hugh, J. Ultrasound Technique for the Dynamic Mechanical Analysis (DMA) of Polymers. Berlin 2008, BAM Dissertationsreihe (31), urn:nbn:de:kobv:b43-1278