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Cure Monitoring using Single-Sided NMR

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Summary:

In industrial production, adhesives are often the preferred joining agent of choice. However, there is currently no standard method for non-destructive monitoring of the adhesive bond quality. In order to solve this issue, the use of single-sided NMR is suitable. This work demonstrates exemplarily for an adhesive that the NMR signal correlates very well with the curing. Thus, it is possible to create process models, which allow the monitoring of adhesive curing.

Keywords: Adhesives, curing, monitoring, NMR, prediction

Motivation

Driven by e-mobility and lightweight construction, adhesives have become increasingly important in recent years. In industrial production, they are often the preferred material of choice for joints due to their wide range of material types and properties. With the increasing use of adhesives, their quality assurance during the manufacturing process is also gaining in importance [1]. However, only destructive methods exist currently for testing adhesive joints. For this reason, there are various research approaches to enable non-destructive process control. Air-coupled ultrasound [2], terahertz [3] or single-sided nuclear magnetic resonance (NMR) [4] are suitable for this purpose. A recent research project focuses on the near-process monitoring of adhesive joints. First results are presented in the following.

Single-sided NMR for process monitoring

NMR measures nuclear spin relaxation times. These correlate very well with the molecular mobility of adhesive molecules. The decrease in relaxation times over time allows the non-destructive evaluation of the curing state of an adhesive. Beyond that, single-sided NMR offers a further advantage due to its special design. It enables cure monitoring of adhesive at different depth levels – even through the non-metallic joined components.

The single-sided NMR signal, which is evaluated e.g. by echo sums, can be used for the formation of process models due to its good correlation with various reference methods [4] and high reproducibility. This allows the definition of a process window for characteristic values such as viscosity or ion conductivity. In addition to process control, post-production testing is possible. Since single-sided NMR devices use rare earth permanent magnets, a constant magnet temperature is necessary due to their temperature sensitivity. In the case of hot samples, this is achieved by thermal decoupling or, in the case of adhesives, by small – and at the same time practice-related – layer thicknesses. When using thin adhesive films, only minimal temperature changes < 1 K are measured, which do not noticeably influence the magnet temperature.

NMR vs. rheological testing

As an example for the good correlation of single-sided NMR and rheological testing results of the two component epoxy adhesive DELO-DUOPOX AD840 are shown. The rheological reference tests in the plate/plate rheometer (Haake Mars, Thermo Fisher Scientific Inc.) were performed as double determination with a measuring frequency of 1 Hz, a gap distance of 1 mm and a temperature of 25 °C. For the measurements with the single-sided NMR (NMR-Mouse PM5, Magritek GmbH) a classical CPMG pulse sequence with 128 echoes and a measurement volume of 13 mm x 13 mm x 100 µm (L x W x H) was used as in previous work [4]. The samples consisted of two 1 mm thick cover glasses with an adhesive layer of (90 ± 10) µm thickness in between. The room temperature during the double determination of the adhesives was between 23 and 26 °C.

The signal curves of the echo sums as well as the viscosity during the adhesive curing together with the times of initial and functional strength according to the manufacturer's information are shown in Fig. 1.

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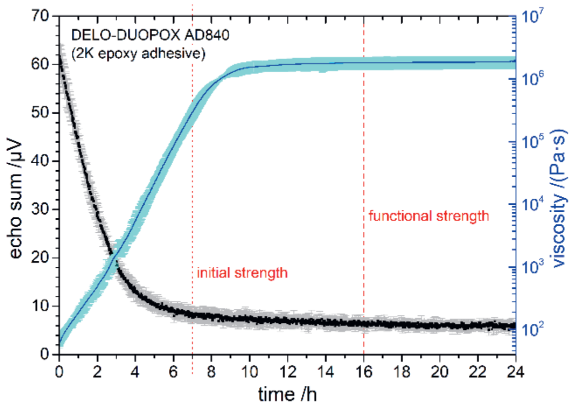

Fig. 1. Comparison of measurement curves of single-sided NMR and plate/plate rheometer.

The signal curves of the measurements in the rheometer show a relatively constant uncertainty range. For NMR measurements, the average relative error is about 11 %.The time uncertainty results mainly from the different starting times of curing after mixing and measurement. The variance of the echo sums results both from the different adhesive layer thicknesses and from potential inhomogeneities during mixing or network formation – the latter also applies to sample preparation in the plate/plate rheometer.

Process model for 2K epoxy adhesive

In the NMR experiments, the echo sums – as amplitude-weighted mean value of the relaxation times T_2 [5] – showed a bi-exponential course and can thus be fitted by equation (1):

$$A_{es} = A_{short} \cdot e^{-\frac{t}{T_{2m,short}}} + A_{long} \cdot e^{-\frac{t}{T_{2m,long}}} \quad (1)$$

Together with the rheometer measurement values, a process model can be generated which assigns a corresponding viscosity value to each echo sum at a certain point in time (see Fig. 2). This allows to monitor whether the viscosity values are still within the desired process window during the curing process.

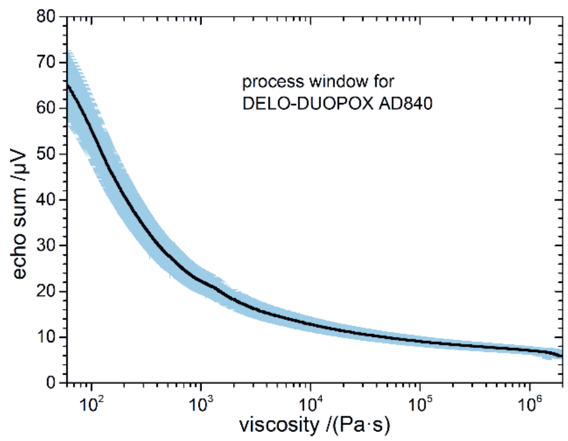

Fig. 2. Process model for DELO-DUOPOX AD840 linking echo sums with viscosity values.

The presented process model works well for characteristic times of curing. It can be assumed that a reduction of the uncertainty range of NMR measurements is possible by a more precise scheduling of the measurement start and by a more precise adjustment of comparable adhesive layer thicknesses.

The evaluation method demonstrated here can be applied in a similar way to other reference methods such as differential scanning calorimetry (DSC) and dielectric analysis (DEA). Furthermore, a transfer to characterize resins curing in composites is also possible.

Summary and Outlook

Single-sided NMR is well suited for non-destructive monitoring of adhesive curing in adhesive bonds. Thus, it is possible to create process models. In the further course of the project besides glass, also plastic substrates will be bonded. Furthermore, the research will be extended to one-component light-curable adhesives. In addition, the investigation of a possible correlation of the NMR values with the later bond strength – at the same pretreatment and adhesive layer thickness – is planned.

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