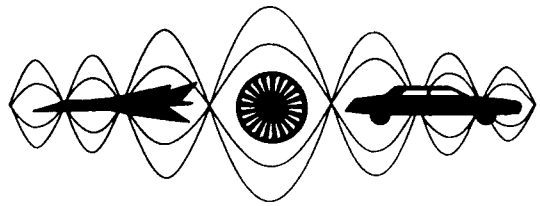

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CURE MONITORING OF THIN ADHESIVE LAYERS

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ABSTRACT

The quality of adhesive joints is usually determined in a destructive way by measuring the achieved strength. However, this paper describes an approach where we perform measurements on the curing adhesive (epoxy resin with hardener) and use these data to predict the final strength after correlations have been established. This method for nondestructive characterisation of adhesive layers is based on mechanical spectroscopy of resonant metal bars. The basic idea is that the resonance behaviour of two equal bars which are bonded displays a development from initially two independent bars to one single bar with a different spectrum. The transition from the initial liquid state of the adhesive to its final solid state is characterised by spectral changes of the resonance which are evaluated.
Besides this mechanical spectroscopy we also investigated whether dielectric properties measured simultaneously are also suited as indicators.

INTRODUCTION

Joining of metal parts can be performed in various ways. The use of adhesives seems to be very attractive since it can provide a homogeneous stress distribution with less manpower. The reason why adhesives have not yet replaced all other techniques is the lack of predictability and reliability: It is not obvious whether the intended strength has been achieved or not.
Various authors [1-5] described how the properties of cured adhesives can be characterised non-destructively, e.g. by measuring the speed of sound. As the final state of curing depends on temperature history it is obvious that results obtained on the large volumina of thick layers and the corresponding high temperatures of the exothermal reaction [6] cannot be transfered to the very thin layers of adhesive between flat metal surfaces. Therefore the curing function of thin layers where temperature is kept constant (due to the heat flow into the adjacent metal) deserves special attention. From the observed curing one tries to predict the final result at early stages. The mixture ratio of epoxy resin and hardener has a strong influence on the quality of

the final result. Therefore we investigated how the curing behaviour and the final strength depend on this ratio.

EXPERIMENTAL ARRANGEMENT

The samples that we used were cylindrical bars of ground stainless steel with polished flat surfaces. A thin layer of adhesive (with a variable amount of hardener) with typically 90μm thickness was applied to join two cylindrical bars of equal size (length 100 mm, diameter 15 mm) to one bar of twice the initial size. Fig. 1 shows the setup where an ultrasonic transmitter was attached to one side while the continuous transmitted elastic wave was detected on the other side.

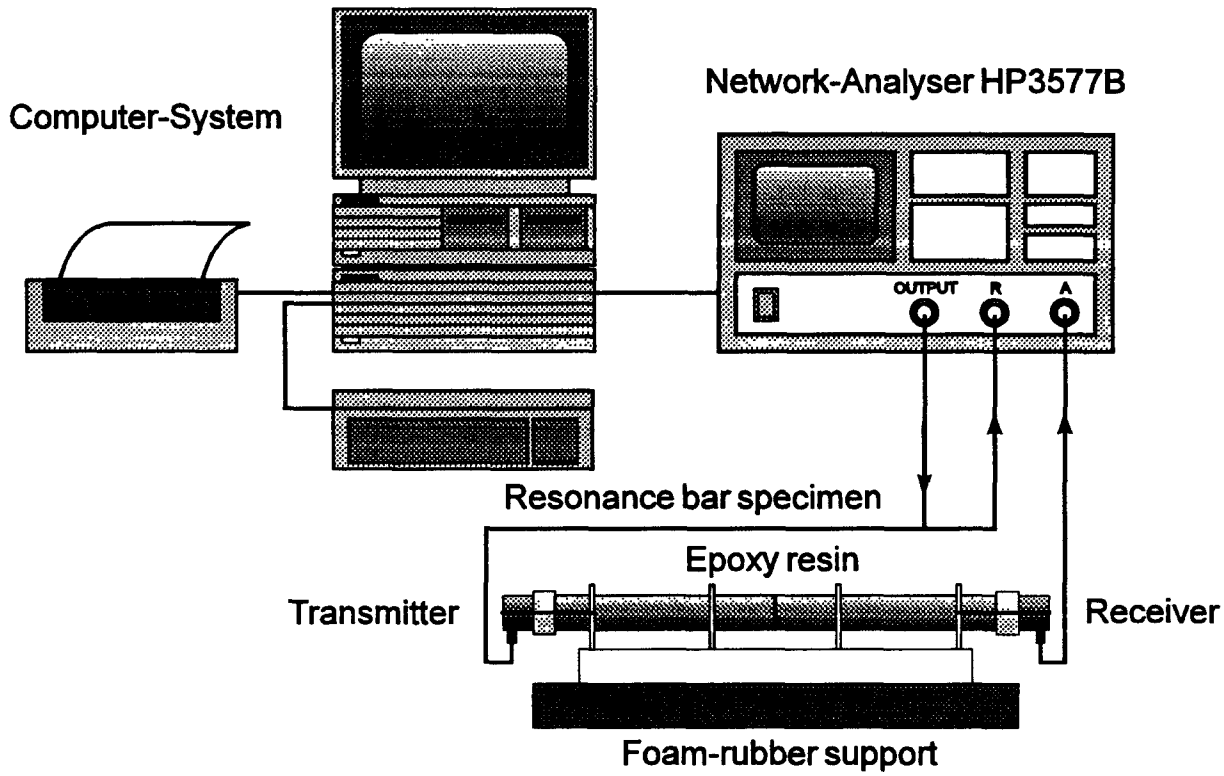

Fig. 1: *Experimental arrangement*

A network analyser (HP 3577 B) measured the transfer function which contains the eigenfrequencies of the system whose properties were modified by the curing adhesive.
The measurement starts with two separate short cylindrical metal bars, coupled face to face with the liquid adhesive. The coupling is weak, therefore the eigenfrequencies are similar to those of the uncoupled bars. As the geometry of the two bars is the same, they have the same spectra. So the resonances of the system are degenerate. At the end of the process there is only one cylinder with twice the initial length and hence half the distance between the eigenfrequencies. As the number of degrees of freedom is constant, it is obvious that the original degeneracy of eigenfrequencies is removed during the curing process in such a way that one frequency is unchanged while the other one (an odd mode) emerges and shifts towards the center between two initial eigenfrequencies. This curing induced change of the transfer function (Fig. 2) is used to characterise the transition from the initial liquid state to the final solid state of the adhesive.

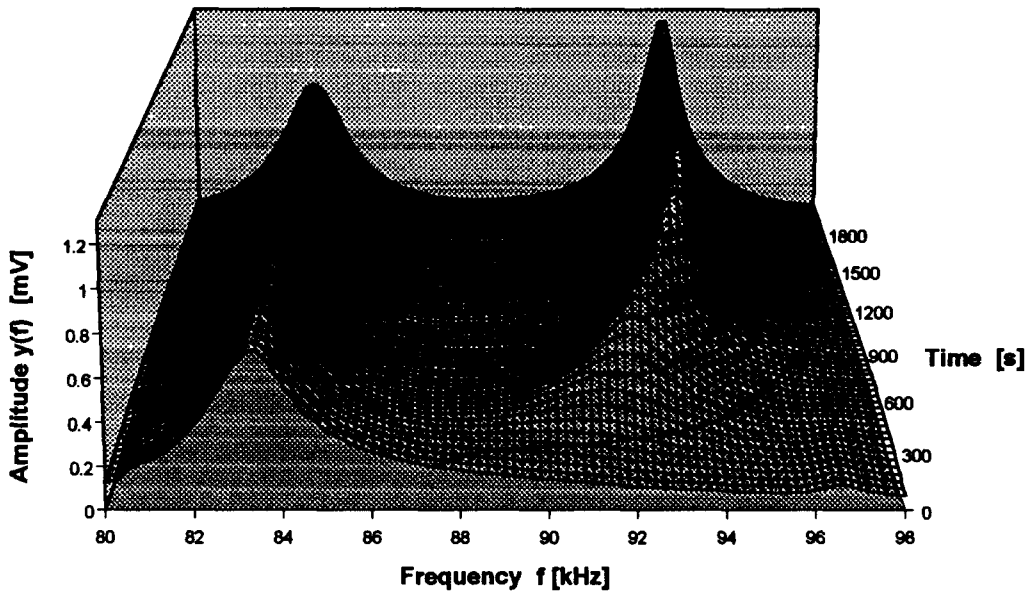

Fig. 2: *Spectra with even and odd mode*

The basic idea is that the odd modes depend on the existence of a molecular network which can transmit tensile stresses along the cylinder axis. A different way of description is that for elastic waves the transmission coefficient of the thin polymer layer changes when the adhesive cures.

THEORETICAL BACKGROUND

While the even modes of the system are not much affected by the liquid/solid transition of the adhesive, the eigenfrequencies of the odd modes are used as indicators. As each mode corresponds to one harmonic oscillator, the observed spectrum (Fig. 2) is a superposition of odd and even modes. As the analytical form is known [7] with the amplitude

$$y(\omega) = \frac{y_0}{m \cdot \sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(\frac{2}{\tau}\omega\right)^2}} \qquad (1)$$

and phase

$$\varphi(\omega) = \arctan\left(\frac{\Delta\omega \cdot \omega}{\left(\omega_0^2 - \omega^2\right)}\right) \qquad (2)$$

where ω denotes the angular frequency and $\Delta\omega$ the total width at 3 db height, one can isolate the odd mode by substracting the complex amplitude of the even mode from the observed spectrum. It is of interest how height and frequency of the shifting odd mode depend on time.

RESULTS AND EVALUATION

Fig. 2 is the primary result y(f) obtained for one kind of adhesive in the curing process. Different amounts of hardener give different curves y (f) and a different dependence in time,

and the problem is how to derive from these sets of data those parameters that are suited to characterise the curing process and its correlation to final strength.
As the modulus of the adhesive layer depends on geometry [8] and because even simple plates may have a very complicated spectrum [9], we tried to use the spectral energy defined by

$$E_S = k \cdot \int_{f_u}^{f_o} y(f)^2 f \cdot df \qquad (3)$$

where f_u = 80 kHz and f_o = 98 kHz and are lower and upper frequency, respectively, while k contains all non-variable quantities as a parameter to be derived from each frequency-dependent curve. This value characterises the energy put into the mode between f_o and f_u. The time dependence of E_s therefore displays how energy transfer by a certain mode is achieved. If this is applied to the odd mode, the odd mode energy (OME) is an indicator for the capability of the adhesive layer to transport stress gradients, therefore its dependence on time indicates the development of the molecular network. Such a curve is shown in Fig. 3.

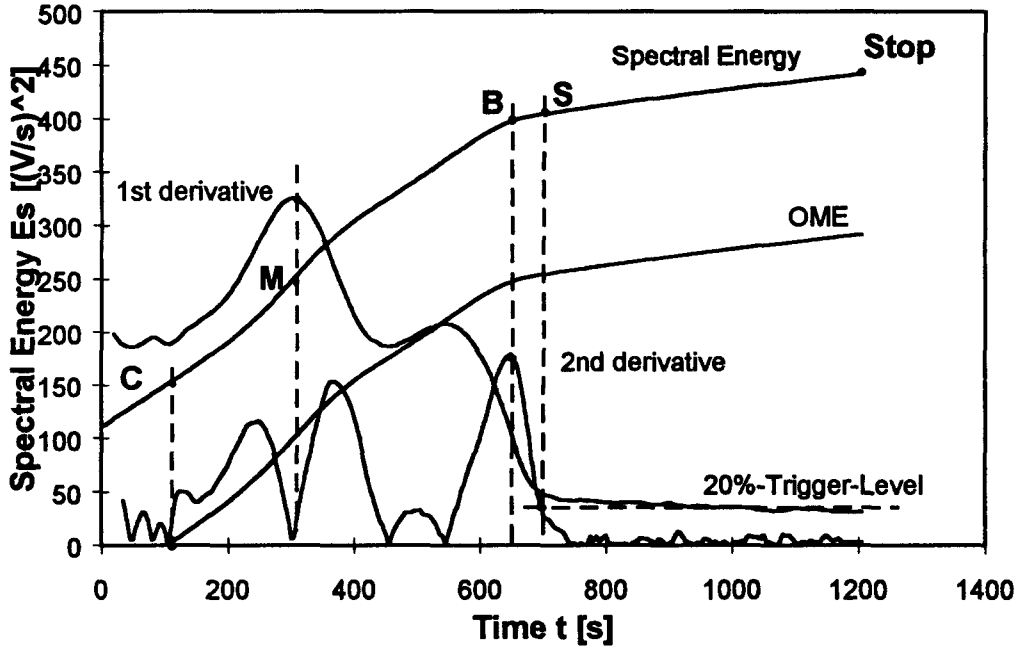

Fig. 3: *Spectral energy during hardening*

For convenience the OME curve was normalised to zero for the time before the odd mode appears. We found that the general shape of the OME-curves does not depend strongly on the mixture ratio of the adhesive. However, specific points of these curves obtained by the first and second derivative seem to be more useful. The points C, M, B, and S have the following meaning:

C: Frequency and 3 db-width can be determined for the first time. Spectral energy of odd mode (OME) starts to differ from zero at this point (100 sec, see Fig. 3).

M: Maximum of first derivative indicates highest speed of OME-increase.

B: Bending point of OME (maximum in the magnitude of 2nd derivative).

S: Straight line starts at this time: Point is arbitrarily defined by the moment where 2nd derivative decreases to 20 % of its value at B. First derivative becomes approximately constant.

In Fig. 4 it is shown how the times indicated by these points depend on the amount M of hardener.

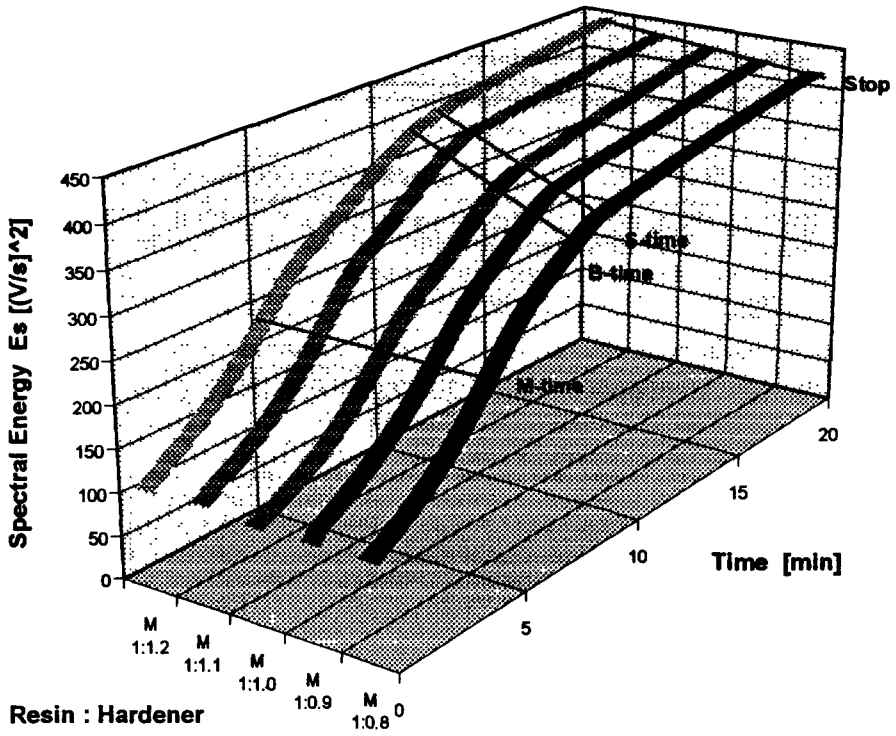

Fig. 4: *Spectral energy at several amounts of hardener*

After the dependence on frequency has been eliminated by introducing the spectral energy, one can derive data from the E_s-curves that are characteristic for curing.
By evaluating possible correlations for many sets of data we found that the integral of the E_s-curve taken between times M and B and normalised to its asymptotic value for $t \rightarrow \infty$ has the strongest correlation with the hardener content and the achieved strength. This value NQ

$$NQ = \frac{1}{E_S(t \rightarrow \infty)} \cdot \frac{1}{(t_B - t_M)} \cdot \int_{t_M}^{t_B} (E_S(t) - E_M) \cdot dt \qquad (4)$$

is shown in Fig. 5 together with the breaking strength F for the hardener contents of Fig. 3. The result is that from a non-destructively determined value NQ one can predict the strength F with an accuracy better than +/- 300 N.

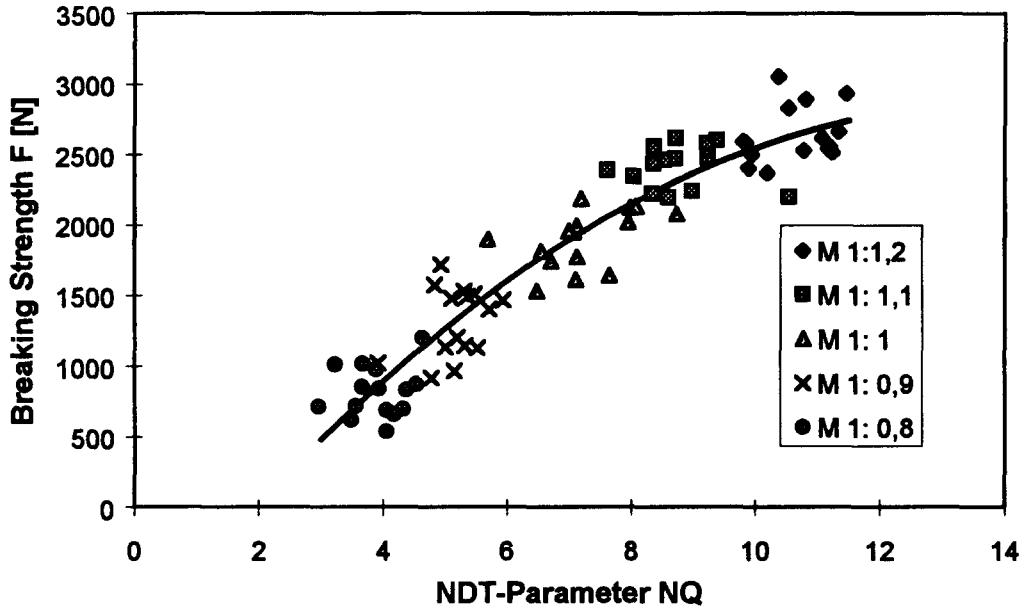

Fig. 5: *Correlation of breaking strength with NDT-Parameter NQ*

Besides these results obtained with mechanical spectroscopy we also performed simultaneously dielectric measurements. Here we use the metal bars as capacitor plates to measure the capacity. We used a frequency of 100 kHz in order to compare mechanical and dielectric data at the same frequency. The result (Fig. 6) obtained at various hardener contents indicates most of all the influence of different adhesive thicknesses.

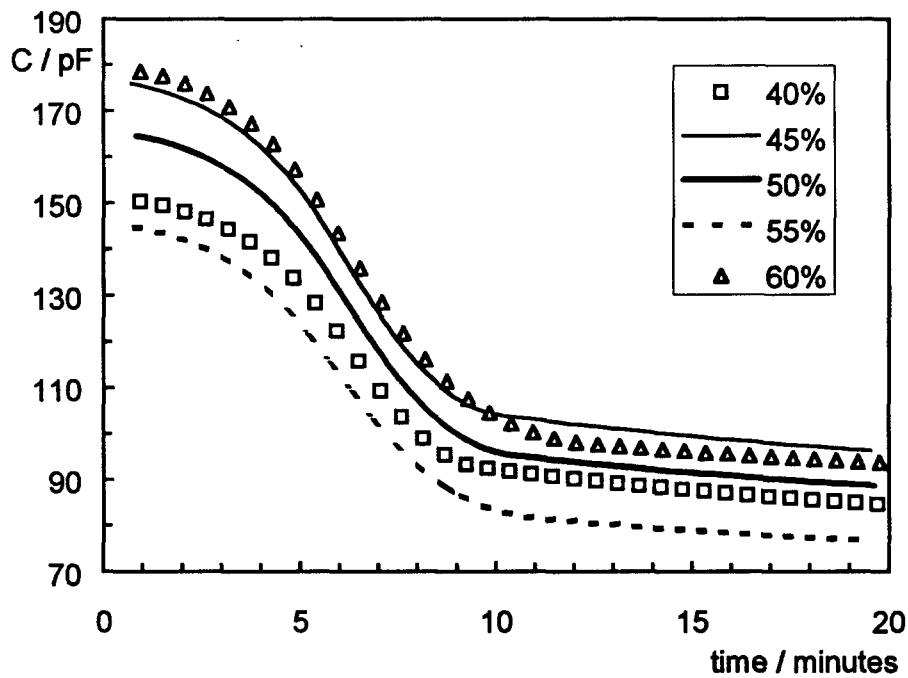

Fig. 6: *Sample capacity during the measurement*

However, the time where the strongest slope is observed (6 minutes) corresponds to the location of the M-point in Fig. 3, also the transition to the slow change occuring after 10 minutes agrees well to the location of the B-point in Fig. 3. The relative heights of the steps

after the first 10 minutes increase from 0.36 to 0.45 as the hardener content increases from 40 % to 60 %. So there is evidence that both mechanical and dielectric measurement are suited to characterise the decreasing network mobility in the curing process as well as the hardener content and the final strength resulting from it.

DISCUSSION

The method of resonance splitting provides a sensitive indicator to monitor non-destructively the changes of mechanical properties in the curing process of a thin glueline between metal components. The method should find applications in the quality control of adhesive joints to optimise the curing conditions and to predict the final strength under the aspect of basic research. Also it provides a means to monitor the development of molecular networks in the polymerisation process. Dielectric measurements - if they are simultaneously applicable - should improve both the understanding and the accuracy of strength prediction.

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