

ADHESIVE CURE MONITORING WITH ACOUSTIC METHOD

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Abstract: Conditions of adhesive cure process play a very important role in the quality of adhesive joints. It is known that the cure stage of adhesives correlates with the glass transition temperature and strength of adhesion. The objective of our present work was to quantitatively characterize cure of the adhesives with acoustic method. Pulse-echo mode was used for the study. Changes in acoustic parameters during cure time were simultaneously monitored. These changes are discussed with respect to the phases of the adhesive cure process. Dependence of the prepolymer/curing agent ratio on acoustic parameters and dynamics of cure are also investigated. Microstructure of the adhesives was investigated with acoustic microscopy at different times of curing. Changes in the adhesive's microstructure during curing time were observed. Acoustic techniques can be useful in industrial applications for non-destructive testing of the adhesive cure conditions.

Introduction: Adhesive joining is widely used in many manufacturing industries. Requirement of both high productivity and quality means the increasing need to improve quality control. Currently, no proper non-destructive in-field technique exists for adhesive bond joint evaluation.

The author's interest in ultrasonic studies of the adhesive cure process results from the necessity to evaluate the cure state of the material in adhesive metal joints where ultrasound is used for non-destructive evaluation of joint quality [1]. Improper setting of cure parameters during production could lead to joint failure or significantly decreased adhesion strength.

Network formation of the epoxy resin due to crosslinking is a complex process. During the cure reaction epoxy undergoes changes from low molecular liquid or paste to a highly crosslinked network.

Behavior of the adhesive during the cure process can be monitored by different methods: nuclear magnetic resonance, calorimetry, infra-red or Raman spectroscopy, dielectric measurements, dynamic mechanical analysis (DMA), and ultrasonic technique [2-5]. Acoustic technique has been used by many authors for studying adhesive. However, the previous ultrasonic studies [4-7] on epoxy curing process monitored only changes in the wave parameters and do not show changes in the microstructure of the adhesive during the cure process.

Because of the nature of the acoustic wave's propagation, acoustic technique directly measures the relation between acoustic wave behavior and material characteristics on microscopic scale. Ultrasonic images reflect these changes in mechanical properties of the material during the cure process and correspondingly in the physical state of the material. This technique is able to detect curing defects caused by improper cure conditions or inhomogeneous mixing of resin and hardener. In this study we apply ultrasonic technique for non-destructive characterization of the epoxy adhesive cure process and high-resolution acoustic imaging of the adhesive microstructure.

Results and discussion: Commercial low-temperature curing adhesive was used for monitoring the adhesive properties' changes during hardening. The ultrasonic setup consists of spherically focused 15 MHz immersion transducer, coupled with the adhesive sample in a specially designed test cell (Fig.1.). A water-glycerin mixture was used as a coupling medium to reduce reflection from the coupling medium-epoxy interface. The reaction chamber is 20 mm in diameter and 3 mm thick. PET film is thin enough so its presence does not create an additional reflected pulse at the coupling-epoxy interface. Flexibility of the PET film allows us to measure variation of the sample's thickness during curing and thus to monitor the material's density changes. The transducer was driven by the Utex 340 pulser-receiver, operating in pulse-echo mode. Output signal was registered by the Textronix TDS 5052 digital oscilloscope for further processing.

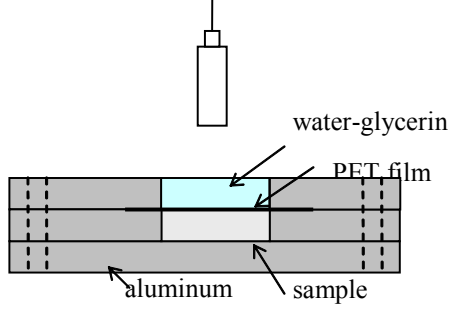


Fig.1. Test cell design for adhesive curing monitoring.

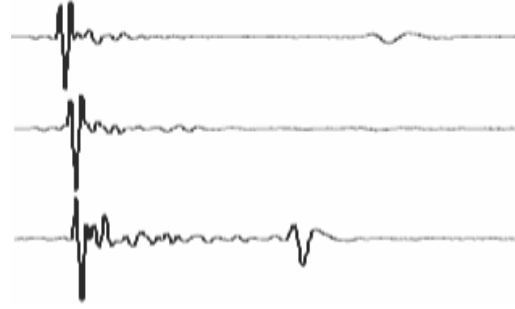


Fig.2. Pulse-echo waveforms for uncured epoxy (a), at gelation time(b) and cured (c) epoxy.

Polymerization of the epoxy resin occurs in two stages: 1) gelation -formation of elastic network structure and 2) postgel stage where gel fraction and crosslinking density increase up to full conversion. Acoustic technique is able to monitor all these changes in elastic properties of the epoxy. Typical pulse-echo waveforms are shown on Fig.2, where pulse t_1 is the reflection from the PET film; pulse t_2 represents the reflection from adhesive- metal interface. During the reaction, both signals moved towards each other (Fig.2.). Change of the signal t_1 position occurs due to epoxy shrinkage during the reaction. Current sample's thickness was calculated as follows:

$$h = h_s + \frac{c_{Lw}(t_{1i} - t_1)}{2}$$

where h_s is the final thickness of the sample, t_{1i} is time delay of the signal reflected from the film at the beginning of curing, t_1 is time delay of the signal reflected from the film at current moment and c_{Lw} is longitudinal sound velocity in water.

Both position and amplitude of the t_2 signal undergo significant changes. Because hardware setup is fixed, all these changes are due to alteration of the epoxy's elastic properties during the reaction. Almost full disappearance of the signal t_2 was observed after polymerization starts, approximately at the point where sound velocity's curvature changes. This phenomenon is related to gelation, when the polymer's network is formed in the crosslinking reaction [5].

Sound velocity c_L of the material can then be calculated as

$$c_L = \frac{2h}{t_2 - t_1}$$

Extension of the reaction is assumed to correlate with the sound velocity. Elastic modulus E was calculated as

$$E = \rho c_L^2$$

Adhesive cure reaction was monitored until amplitudes of the signals reached a plateau. Fig.3. shows that ultrasonic longitudinal velocity of the adhesive increases irreversibly during cure reaction. The velocity curve has a sigmoidal shape. Changes in ultrasonic properties result from modifications in the material's elastic parameters and show transformation from low-molecular viscous liquid to the cross-linked polymer's network as reaction occurs. Ratio of the epoxy resin/curing agent was varied and changes of the longitudinal sound velocity in the material are different with time of the reaction. Both excess and deficiency of the curing agent have sufficient effect on acoustic behavior of the material. Excess of the hardener leads to earlier gelation time and curing but final sound velocity is lower than for control ratio 1/1. Deficiency of the curing agent slows down the reaction and also brings lower final acoustic parameters of the material. Thus, the curing curve becomes more mildly sloping. Since correlation exists between acoustical parameters and adhesion strength, improper ratio of prepolymer/curing agent results in insufficient adhesion strength, which can be effectively detected with acoustic technique. Table 1. contains final acoustic parameters of cured material.

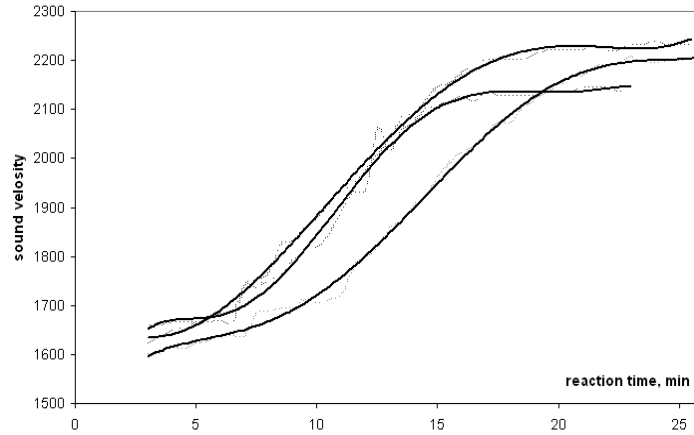


Fig.3. Longitudinal sound velocity in the epoxy adhesive with different epoxy resin/curing agent ratio measured during the curing. Epoxy/hardener ratio is: a- 1/1; b- 1/2; c- 1/0.5

Summary of measured parameters.

Table. 1.

Epoxy/hardener ratio	Cure duration, min.	Final velocity, m/s	Gelation point, min.	Elastic modulus,
1/1	20	2230	12	5470190
1/2	17	2165	10	5155947
1/0.5	25	2205	16	5348227

For non-destructive acoustic imaging of the adhesive structure, metal-thermoset adhesive-metal samples with different cure time were prepared. Sound velocity in the adhesive was calculated from thickness of the adhesive layer and time of flight difference between reflection pulses from metal/adhesive and adhesive /metal

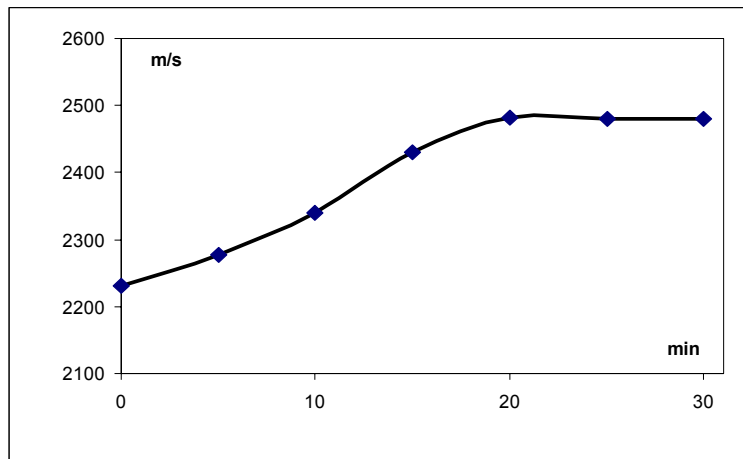


Fig.4. Dependence of the longitudinal velocity of the adhesive on curing time.

interfaces. Fig. 4. shows that sound velocity measured in the samples exposed different times at the standard cure temperature 180°C depends on duration of the reaction and reaches its maximum at 22 min. during curing. This

dependence of the acoustical parameters on cure degree can be used for the quantitative evaluation of the adhesive's cure state during the polymerization process.

Not only does sound velocity undergo significant changes during curing, but other parameters do as well. Ultrasonic attenuation is very sensitive to the viscous properties of the material. Though excessive attenuation in some materials (like epoxy) may lead to the limitations of the ultrasound penetration depth, this acoustic parameter can be very useful for the detection of the material's conditions and properties. Fig.5. represents images of the cured and uncured areas of the adhesive made in transmission mode. Ultrasound passes through the material; both amplitude and position of the received signal are monitored. Amplitude of the acoustic wave passed through the sample is mapped on Fig.5.1 and shows spatial distribution of the attenuation coefficient. The image has a good contrast (30%), clearly indicating areas with cured and uncured material. Darker color on the image represents higher ultrasound attenuation in uncured epoxy (b). This result gives a reliable practical method for the inspection of the curing conditions of the adhesive.

Signal's time of flight distribution (Fig. 5.2.) also shows some differences in cured and uncured areas but this image is much less sensitive and informative. In addition, thickness of the sample variations affects time of flight value.

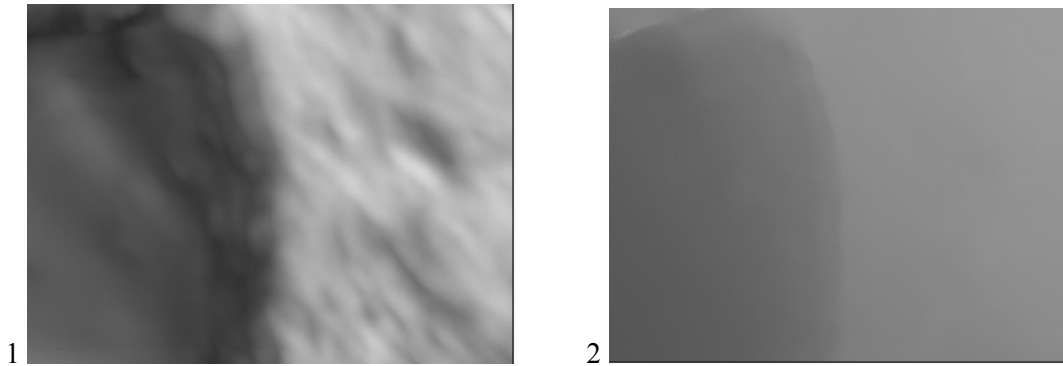


Fig.5. Detection of the cured (a) and uncured (b) areas of the adhesive in transmission mode.
1-signal's amplitude monitoring, 2-signal's time of flight monitoring.

Differences in the material's properties can also be visualized in the acoustical images. Fig. 6. demonstrates development of the microstructure in the epoxy adhesive – metal interface during cure at 180⁰C.

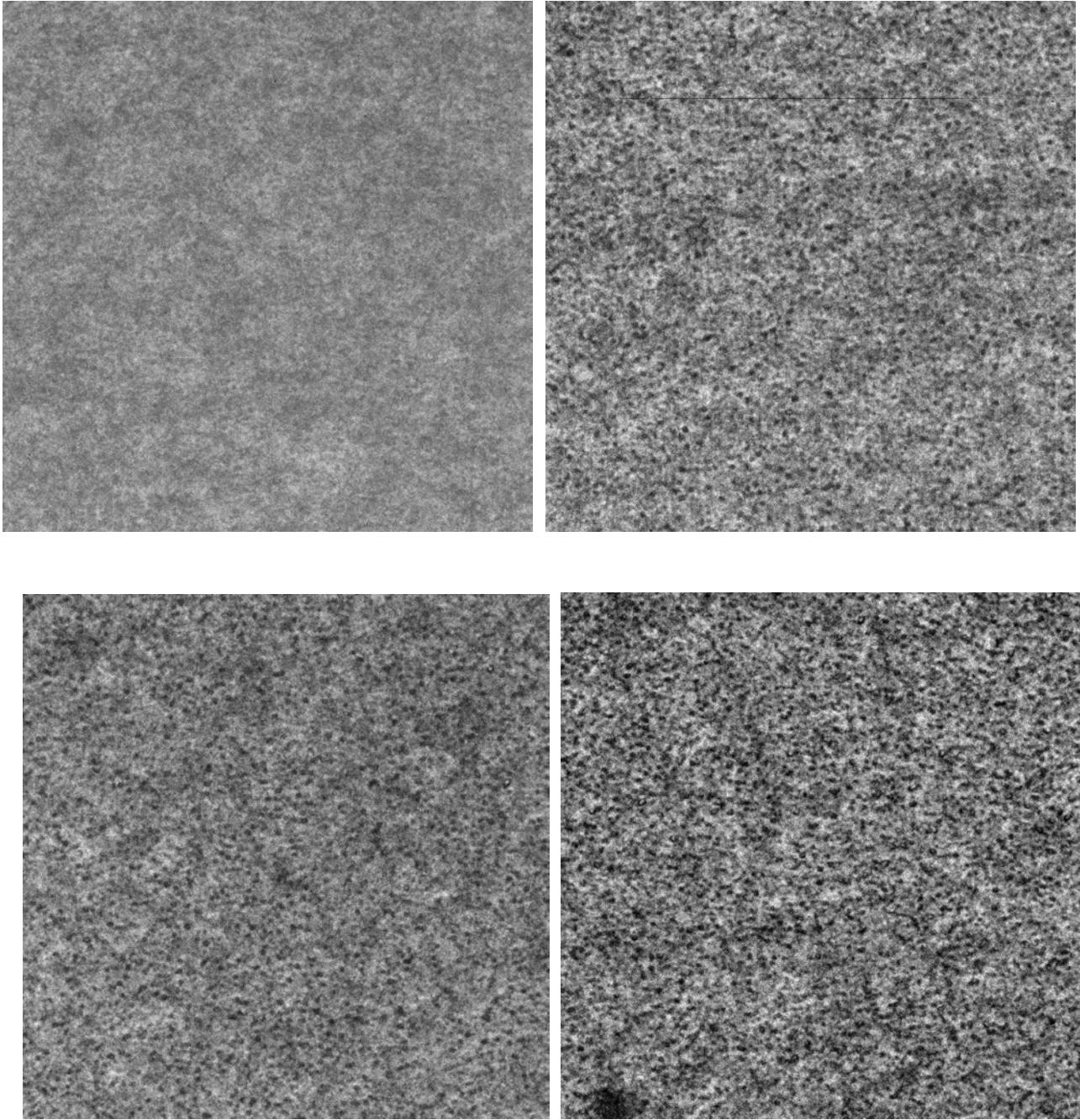


Fig.6. Microstructure of the metal/adhesive interface for uncured adhesive(a), cured during 5 (b) and 30 (c) min. at 180°C and overcured adhesive (d). 10x10 mm scanning area.

Microstructure of the uncured material does not have a clearly expressed structure. After the material has been exposed to curing conditions, interface image becomes more clear and contrast, granular structure of the interface appears after 5 min. and becomes completely developed by the end of the curing process (30 min.). Overcured material which was exposed to the higher temperature (200°C) becomes more brittle and adhesion strength decreases. Acoustical image of the overcured adhesive's interface becomes more fragmentary and starts to

reveal regions with higher amplitude of the reflected signal. That usually corresponds to physical changes in the material's properties and/or appearance of microdefects at the interface and in bulk.

Conclusions: Ultrasonic technique was used to monitor epoxy adhesive cure reaction. Changes in longitudinal velocity of the adhesive, its elastic modulus and density were measured at the time of reaction. It was shown that acoustical properties of the adhesive and reaction rate are dependant on epoxy resin/ hardener ratio. All modifications in the adhesive's properties are able to be monitored and point of the gelation can be determined.

The microstructure's images of the adhesive interface confirm significant changes in the material's properties and allow us to visualize the cure process. Ultrasonic method can be used to evaluate cure states of the adhesive materials.

References:

1. E. Y. Maeva, I. A. Severina, F. M. Severin, B. O'Neill, R. Gr. BMaev. Review of Progress in Quantitative Nondestructive Evaluation. Proceeding of QNDE, Green Bay, Wisconsin, July 27- August 1, 2003, p.31
1. R. P. Cocker, D.L. Chadwick, D. J. Dare, R. I. Challis. Int. J. of Adhesion and Adhesives, 18 (1998), 319-331.
2. S. Swier, B. V. Mele Polymer, 44 (2003), 2689-2699.
3. M. Younes, s. Wartewig, D. Lellinger, Polymer, 35 (1994), 5269-5278.
4. S. White, P. Mather, M. Smith, Polymer Eng. and Sci., 42 (2002), 51-67.
5. R. Freemantle, R. Challis, Meas. Sci. Technol., 9 (1998), 1291-1302.
6. M. Matsukawa, I. Nagai, J. Acoust. Soc. Am., 99 (1996), 2110-2115.