# Monitoring Of Adhesive Cure Process and Following Evaluation of Adhesive Joint Structure by Acoustic Techniques

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**Abstract**. Structural adhesives become more popular in automotive production as a part of body assembling process. The development of new adhesive bonding technologies shows the necessity for effective non-destructive quality assessment of the joints. In the present work, curing reactions of the epoxy structural adhesive were investigated by acoustic methods in pulse-echo mode at 20 MHz at isothermal and non-isothermal conditions. The changes of acoustic properties at the reaction reflect all phenomenological changes, which occur in epoxy adhesive during cure. Method will help to determine optimal cure regime to achieve maximum conversion and develop high adhesion strength. A metal/adhesive interface of adhesive joints and bulk adhesive properties were then investigated by high resolution acoustic microscopy in frequency range of 25-250 MHz. Joints that have undergone thermal and hydrothermal degradation were also analyzed. Capability of acoustic microscopy to detect all major defects and damages, both in the interface and in bulk, was demonstrated. Results presented in this paper can be useful as a basis for development of NDT technique for monitoring adhesive joints quality in the automotive industry.

## Introduction

The wide utilization of adhesive bond joints in complex technological structures during recent years is caused by both development of new adhesives and broadening of the material selection used. Adhesive bonding becomes the primary or secondary means of joining, especially when essentially dissimilar materials are used to form an assembly. The importance of adhesives is demonstrated by their extensive use in the aerospace, automotive, and the marine industry as well as computers, telecommunications, and so on. Due to industry's increasing use of adhesive technology, non-destructive characterization of the adhesive joints has received attention in the past decades. Reliable quality control of such joints becomes a critical part of production.

Acoustic examination should be listed first due to its simplicity, sensitivity and safety. Direct correlation of the material's elastic properties with acoustic response provides a solid basis for estimation of the adhesive's condition. Evaluation of acoustic properties of the adhesive as it cures allows us to monitor changes that occur in the material and thus, estimate its cohesive properties.

It is known that the adhesive's microstructure substantially affects the mechanical properties of the joint. Ultrasound examination allows us to combine the microscopic inspection of the structure with total estimation of bond quality in one measurement. Both aspects are important for examination of changes in adhesive-adherent interface during the

cure process, as well as during its lifetime or due to often external influences (i.e. load, fatigue, chemical reactions and so on).

The pulse-echo scanning acoustical microscopy method is still the most reliable for such kind of examination, although transmission mode is also useful for some applications. Using frequencies 10 – 100 MHz gives us a resolution up to 20 μm with affordable depth of sound penetration in most materials. Visualization of the adhesive joint's microstructure in the form of B- and C-scans provides direct information about the nature, structure and spatial distribution of the defects.

## 1. Adhesive cure monitoring with acoustic pulse-echo method

### *1.1 Isothermal cure monitoring*

Commercial structural thermoset epoxy adhesive currently used in automotive industry was investigated. The ultrasonic setup consists of 20 MHz transducer, connected through a buffer rod with the adhesive sample placed in a specially designed test cell. Pulse-echo mode was used. Monitoring was performed at 100, 120, 140, 160 and 180$^0$C. At lower temperatures, the adhesive does not develop acceptable cohesive strength while higher temperatures cause material degradation. Longitudinal sound velocity and attenuation of the adhesive were monitored during cure reaction. Changes in sound velocity are shown in Figure 1. Sound velocity increases in sigmoidal manner as the reaction proceeds reaching a plateau at the end of the reaction. Different final sound velocities illustrate dependence of sound velocity on temperature. Slopes of the graphs increase with the cure temperature, which indicates higher cure reaction rate. There are lag-periods at the velocity curves for temperatures lower than 140$^0$C. Attenuation curves during cure reaction, represented in Figure 2, have developed maximums. As cure temperature increase, attenuation peak shifts to the earlier stages of cure reaction and become sharper. Highest maximum and final value of the attenuation is observed when the adhesive cures at 140$^0$C. This corresponds to the peak in attenuation for completely cured adhesive (not shown). Thus, curing regime (temperature and time of reaction) determine the kinetic and extent of the reaction.

To compare results obtained at different temperatures and evaluate cure state of the adhesive, sound velocity values were adjusted to their temperature dependence and cure reaction extent was calculated as

$$\alpha_{US} = \frac{V - V_0}{V_f - V_0} 100\%$$

where $V_f$ is longitudinal sound velocity for the completely cured adhesive, $V_0$ is the sound velocity value for the uncured adhesive. Data is shown in Figure 3. Adhesive cured at temperatures higher than 140$^0$C, reaches complete cure whereas epoxy cured at 120 and 100$^0$C reach only 96 and 85 % cure correspondingly. It is to be mentioned that $\alpha_{US}$ is based on the longitudinal sound velocity representing crosslinking rather than the degree of the reaction, or functional group [1]. Destructive tests performed afterwards show that cohesive strength of the joint correlates with acoustic parameters and acoustic reaction extent. Samples cured at 120$^0$C and higher show adhesive type of failure with shear strength 12-13 MPa. This indicates that acceptable joint strength is achieved at the reaction extent higher than 95%.

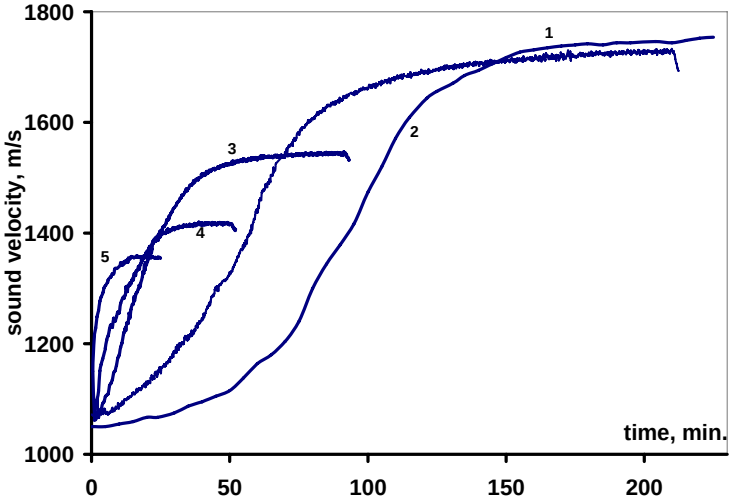


Figure 1. Changes in longitudinal sound velocity during epoxy adhesive cure at different temperatures. 1-100$^0$C, 2-120$^0$C, 3-140$^0$C, 4-160$^0$C, 5- 180$^0$C.

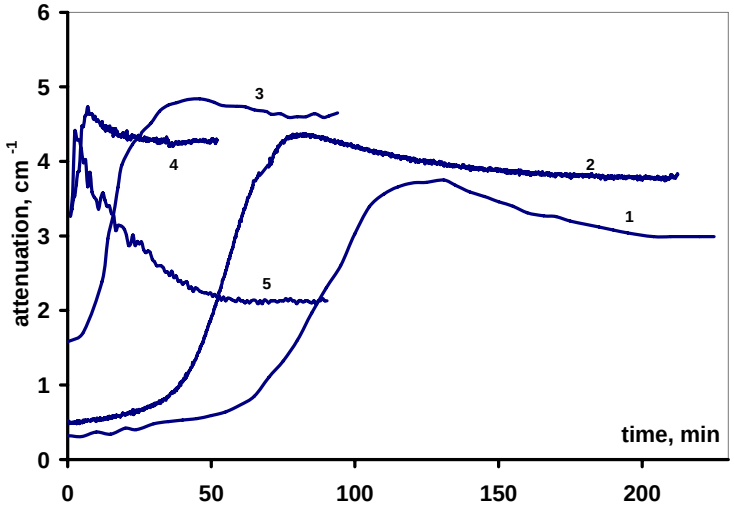


Figure 2. Changes in sound attenuation during adhesive cure at different temperatures. Notes are the same as in Fig. 1.

*1.2 Cure monitoring at continuous heating*

The acoustic parameters were monitored at continuous heating conditions. Temperature of the cure system increases slowly enough at a rate of 1$^0$C/min. Results of the acoustic velocity and attenuation changes are presented in Figure 4. Both sound velocity and attenuation show a change of slope 20 minutes after the experiment begins, which corresponds to the temperature of 58$^0$C. At this temperature, adhesive cure reaction starts. As the reaction proceeds, glass transition temperature *Tg* of the adhesive increases and, at some point, exceeds the cure temperature. Adhesive vitrifies at these conditions and mechanism of reaction changes to diffusion controlled [2]. Linear decrease of the acoustic properties corresponds to temperature dependence of these parameters. The reaction may restart again if the cure temperature becomes higher than Tg and molecular mobility of the partially cured adhesive increases. So-called residual cure is observed as the cure temperature reaches 135$^0$C. At this point, velocity sharply increases which indicates

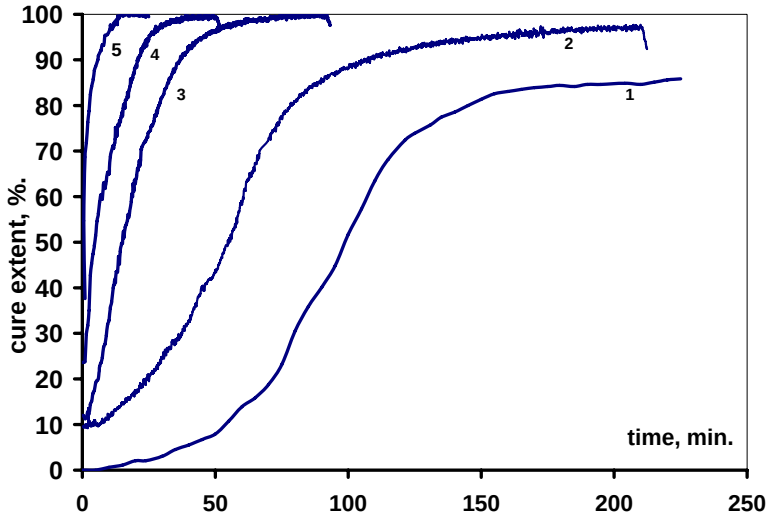


Figure 3. Acoustic extent of the cure reaction. Notes are the same as in Fig. 1.

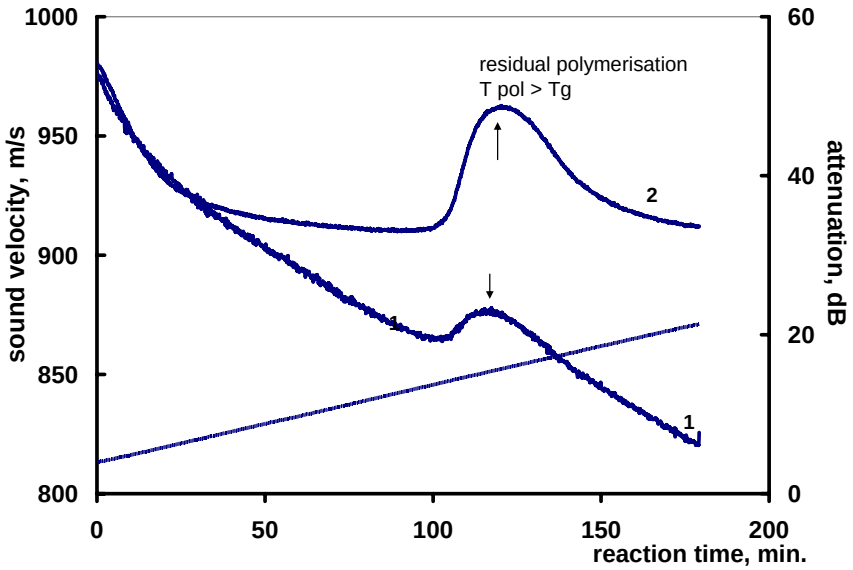


Figure 4. Changes of sound velocity (1) and attenuation (2) during non-isothermal cure. Straight line shows temperature profile. Heating rate is $1^0$C/min.

additional cross-linking reaction [3]. After cure is complete, sound velocity decreases again at the same rate. Attenuation curve shows more complex pattern as residual cure is overlapped with relaxation peak for cured adhesive, which is observed at $145^0$C. Figure 5 represents changes in storage L' and loss L" elastic moduli during non-isothermal cure. Both moduli shows similar behaviour as cure temperature reaches $145^0$C and exceed glass transition temperature Tg.

## 2. Visualization of the adhesive/substrate interface and evaluation of the joint quality

Evaluation of the adhesive bond joints using acoustic imaging method provides information about the adhesive's microstructure and the joint's defects, their size, location and classification. Some significant variations in the adhesive's properties (curing state, density, weight loss caused by hydrolysis) can also be detected but more efficiently in the transmission mode [4].

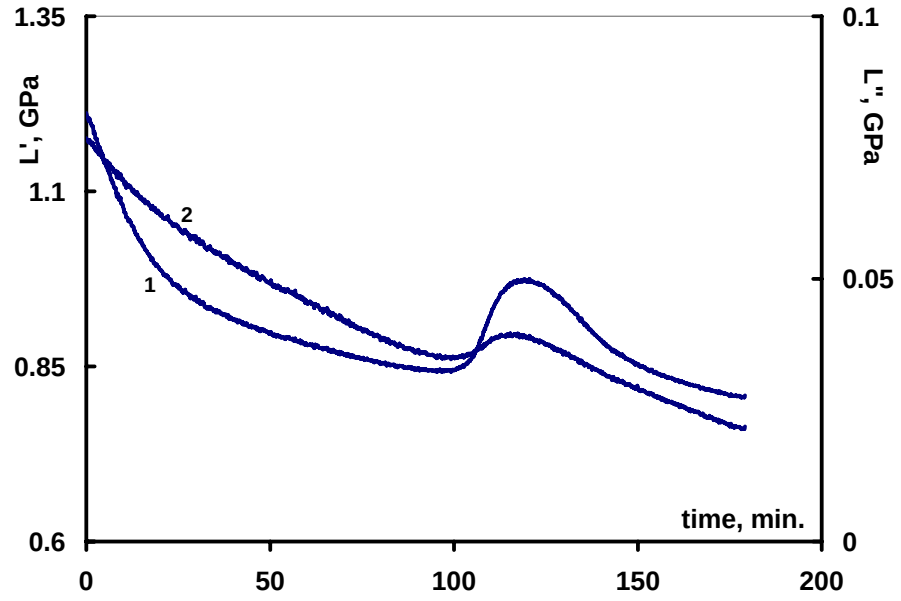


Figure 5. Changes in adhesive loss L" (1) and storage L' (2) moduli during non-isothermal cure. Heating rate is $1^0$C/min

There is no strong correlation between adhesion strength and the presence of some defects, both on the interface and in bulk adhesive. Presence of defects and their parameters are more likely to indicate insufficient joint manufacturing than possible joint failure [5]. However, many structural defects decrease the strength of the joint. There are three main types of adhesion defects: complete absence of the adhesive (voids, porosity), poor adhesion (absence of the interaction between adhesive and substrate) and poor cohesive strength, which means insufficient interaction between adhesive molecules. Absence of the adhesion is the easiest type to detect with the acoustic method and acoustic techniques are widely used to determine location of the voids and their size within the bond. There is considerable difference in the reflection coefficient for metal/air and metal/adhesion interfaces. Adhesion voids appear when adhesive is absent between two metal sheets (Fig. 6a). The main reason of adhesion absence is usually due to surface roughness, where air is trapped in the interface or there is an insufficient amount of adhesive material.

Adhesion problems (so-called zero-volume unbond) are usually caused by improper surface treatment and/or contaminant presence on the interface. This type of adhesive defect is characterized by complete contact, including acoustic, between adhesive and substrate without any bonding forming. Adhesion defects are the most complicated to detect. High resolution advanced acoustic microscopy is able to detect these defects with thorough specimen preparation. A Teflon layer is often used to model the adhesion problems on the interface; however, so far, this simulation is artificial. Oil or grease applied on the substrate approximates a more realistic situation. Figure 6b illustrates the ability of acoustic microscopy to visualize adhesion defects caused by oil being applied on the interface.

Poor cohesive strength is often a result of improper curing conditions (insufficient cure temperature or reaction duration, improper adhesive resin/hardener ratio). This defect is easier to detect in the transmission mode (Fig. 6c) when ultrasound propagates through the specimen. Elastic properties and, accordingly, sound velocity and especially attenuation essentially differ for cured and uncured adhesive. This results in different time of sound propagation and signal amplitude. Therefore, regions with uncured material are shown as darker areas.

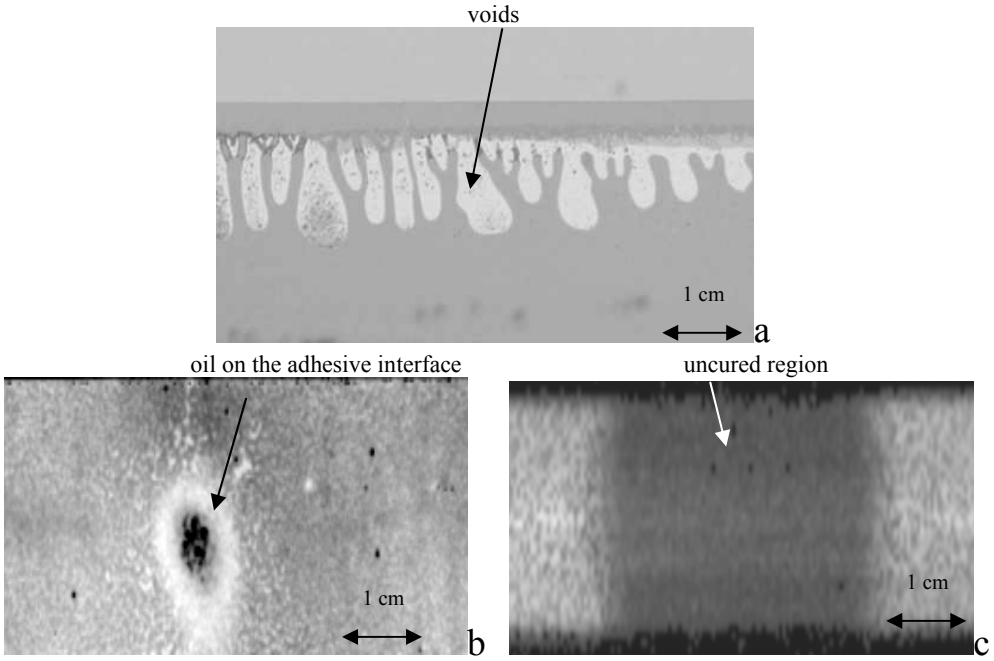


Figure 6. Acoustic C-scans illustrate the three types of adhesive joint defects. a-voids in the adhesive layer; b- adhesive problems on the metal/adhesive interface caused by oil presence; c-cohesion defects caused by improper cure. Images are obtained using 50 MHz spherical acoustic lens. Specimens consist of two steel sheets with a thickness of 0.8 mm, joined by a 0.3 mm layer of some industrial structural epoxy adhesive.

## 3. Adhesive joint degradation

Exposure of the thermoset adhesives to high temperature cause loss of strength due to microcracks formed in the adhesive. However, these conditions are not usually reached during normal lifetime of the adhesive. One of the greatest problems in environmental durability of the adhesive joints is its exposure to water [6]. Epoxies are rich in polar hydroxyl groups, which make them hydrophilic and sensitive to water exposure. Most thermosetting adhesives are hydrolytically stable in the presence of organic solvents and water at ambient conditions. However, these two factors combined exhibits potential danger. Even at slightly elevated temperatures (70-90$^0$C for epoxy), adhesives are more sensitive to water penetration than at the ambient conditions. Exposure to these conditions causes changes in mechanical properties and loss in cohesive strength of the joint. However, adhesive/substrate interfaces are the most sensitive to water. The standard gravimetric and mechanical analysis of the epoxy adhesive joints shows that the diffusion coefficient is higher on the bonded joints interface than in the bulk polymer [7]. This is due to so-called “wicking” effect. The result of aggressive media (temperature, humidity and, sometimes, electrolytes) exposure becomes apparent in an adhesive layer as some structure modification. Figure 7 illustrates adhesive joint interface degradation after exposure to the humid conditions at elevated temperatures. Microvoids form on the earlier stages of degradation in the interface; with time, they merge and form large delaminations in the interface (Fig. 7 a and c). This process is usually observed together with metal corrosion in the same areas. Later, small voids and cracks appear in bulk adhesive. These modifications in joint structure mean a loss of strength (both adhesive and cohesive) of the joint.

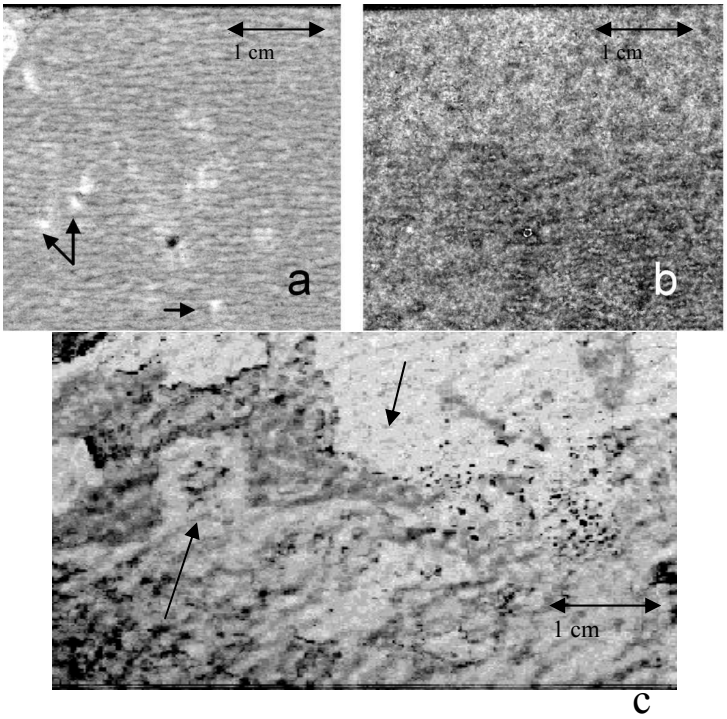


Figure 7. Acoustic C-scans images of the adhesive/metal interface (a and c) and bulk adhesive microstructure (b) obtained at a frequency of 50 MHz. Specimens were exposed to the high humidity and slightly elevated temperatures ($70^0$C).

## 3. Conclusions

Acoustic method allows monitor changes of the adhesive's properties during cure reaction. Curing regime (temperature and time of reaction) determine the kinetic and extent of the reaction. Acoustic properties of the adhesive allow approximate cohesive strength of the joint.

The range of the acoustic frequencies 20-100 MHz gives possibility for detecting and visualizing the different defects in the adhesive bond joints structures. These defects appear in a variety of processes during joint preparation and the utilization of the structures. The acoustic microscopy method provides a control for behaviour of an adhesive structure under environmental conditions influence.

## 4. Acknowledgments

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