ULTRASONIC PROCEDURES FOR
PREDICING ADHESIVE BOND STRENGTH

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As we heard earlier this morning, the use of composite materials is increasing tremendously and with this use has come a need for an adhesive bond that is reliable.

Now, the reliability of the adhesive bond can be related to the reliability of the nondestructive evaluation of that bond. If we can evaluate it properly, we can determine which bonds are good and which bonds are bad. The work that will be discussed in this talk which is related to this problem is currently underway at Drexel University under AFOSR contract number 73-2480A.

I am not talking about debonds here. This has been done already, a long time ago. I am talking about bonds that appear to be identical yet one will have a much higher strength than the other.

What are some of the variables that affect bond strength? Well, I could talk for three weeks on this. First there is the chemical composition of the adhesive itself and its age. Chemical differences in the adhesive could possibly affect its strength. Secondly, once you obtain the adhesive, you have to consider the effect of surface roughness of the substrates and its cleanliness upon the strength. Further, you have the curing cycle. These properties could possibly affect the strength of the bond. Thirdly, once you complete your bond, then you get into things like environmental degradation; heat cycling, load cycling, things of this nature. These can also affect the strength of the bond.

So, we have many, many parameters that all go together and you come out with a final bonded joint. It is going to have some ultimate strength. Now, what do we do?
Studies have been conducted to relate some of these pre-assembly parameters to the strength of the bond. People have measured the cleanliness of the surface. They have measured the surface roughness. They have measured all kinds of things before they put the bond together, and this is very good. The only problem is that this procedure assumes that these parameters remain constant from the time they are measured until the time the bond is completed. This assumption may not be true. Again, this procedure ignores altogether the possibility of a change in the bond after it is completed due to environmental degradation.

The goal of our work is to relate the overall strength of an adhesive bond to a nondestructive test parameter. Given an adhesive bond, can we examine it and say the strength of this bond is good; is it a strong bond or is it a weak bond?

We did some very preliminary work a while back in this area. We were working with, basically, step lap joints as shown in Fig. 1. We started out with a Scotchweld adhesive. As I said, this was basically a feasibility study. Scotchweld adhesive is a 3M Corporation product. We assembled several bond specimens using aluminum substrates. We used an immersion ultrasonic system to eliminate coupling problems, and a five megahertz transducer that produced a relatively long pulse. It was more like a CW burst. Using the pulse echo technique, we observed the reflection from the bond from both sides, although the pulse itself was long enough that we got superposition of the echoes from both interfaces of the bond.

A schematic of the inspection system is shown in Fig. 2. We used a basic pulser, oscilloscope, stepless gates, and spectrum analyzers for the signal analysis. We looked at the different specimens and found that the peak-to-peak amplitude, the overall amplitude, of the reflection from the bond varied from specimen to specimen. I would like to mention at this point that the specimens were examined for uniformity; that is, whatever the peak-to-peak amplitude of the reflection was, we made sure there was no variation over the bond surface. In some cases it did vary. These specimens were eliminated from the test sequence.
Fig. 1—Step-lap joint test specimen. (SI conversion: 1 in. = 25.4 mm)

Fig. 2—Block diagram showing ultrasonic test circuit.
So, we did find that there was a variation in the echo amplitude. A very preliminary hypothesis would be that the stronger bonds would permit more coupling from metal to metal and allow more energy to pass. The weaker bonds would allow poorer coupling and reflect more energy.

We decided to use as a parameter the ratio of the front wall echo to bond echo, the front wall echo being the amplitude of the reflected energy from the top surface of the upper substrate. This was used as a reference in case there were any variations in our ultrasonic equipment, and anybody who has used the ultrasonic equipment available today will probably admit that you can get very large variations in the same equipment.

We then broke these bonds, tested them to failure, at a very low strain rate, and we found that there was a correlation between the overall strength of the bond and the front wall echo-to-bond echo ratio, as shown in Fig. 3. This was encouraging. We then decided we would get into the details of bonding a little more deeply and see if we could determine a better description of what was happening.

We talked to some people, several people, who are experts in adhesive bonds. I would like to mention at this point these were all adhesive failures, that is, the failures all occurred at the adhesive interface. I will come back to that. Upon discussing the nature of bonding with some of the experts, we came to the question of, "What is it that causes a bond to fail; why does it fail; how does it fail; why are some stronger than others?" Nobody could really give us a satisfactory answer on that. They gave us some characteristics of the bonds when they failed. They said, "First of all, there is surface type failures, interface type failures, that occur because of poor surface preparation." They have observations on other failures, cohesive-type failures, that occur entirely with the adhesive. They have found that during the bonding process, it is possible that some of the chemicals making up the adhesive will migrate to the interface. That causes a chemical imbalance through the thickness of the bond and does cause a deterioration, a decrease in the strength of the bond, as a function of the thickness. Different areas of the bond have different strength. This is a possible explanation of the cohesive failures.
Fig. 3—Curve showing failure load versus FWE/BE for an aluminum-to-aluminum step-lap joint with 0.012 in. Scotch-Weld bondline thickness. (1 in. = 25.4 mm)
So, we talked about our preliminary work and mentioned that most of these failures had been adhesive, that is, interfacial in nature. We were then told that adhesive failures aren't really counted in statistical tests by these people. They said if they encountered an adhesive failure, they eliminate it from the test because somebody did something wrong. That is the point we are trying to make. We want to detect something that somebody did wrong before a wing falls off an airplane. We can't tell a pilot that if the wing falls off because it was an interface failure that it doesn't count.

We want to take these possible explanations of bond failures and model them to see how these explanations will affect the ultrasonic wave propagation through the bond.

We started out with something rather easy, a three-layer model (Fig. 4a). Let's assume that we have two aluminum substrates and an adhesive layer in the middle. Using a one-dimensional wave propagation model, we can say the wave will be propagating from the top aluminum layer into the adhesive, a portion will be reflected, and a portion will be transmitted. This will give us the reflection from an ideal bond, perfect coupling at the interface, uniform density in the adhesive, no flaws. This model is to be used as a reference, the reason being this type of analysis is not to discover flaws that are not supposed to be there. We are not looking for echoes that shouldn't be there, because at the interface of the bond you are going to get an echo. You are supposed to get one, but some bonds are going to be stronger; some bonds are going to be weaker. We are not looking for the presence of echoes but differences in them, and these differences may be rather small compared to their absolute size. We need a reference, and the three-layer model is going to be our reference.

The chemical migration phenomenon, we feel, could possibly be represented by some sort of density gradient through the thickness of the adhesive; we are going to represent this by assuming that the adhesive layer is made up of several sublayers to which we can assign various thicknesses and various densities (Fig. 4b). In this way, we can say a certain density
FIG. 4 - MODELS USED IN ADHESIVE BOND ANALYSIS

a.) three layer model

b.) N-Layer model

c.) double area discontinuity model
gradient will give us a certain type reflection. The surface treatment model, we are going to say, is really a problem where you have, say, oxides, dirt, and areas of inadequate cleaning, on the surface. Let's assume that these conditions result in uniformly distributed microscopic debonds--ones that are not gross in nature and ones that cannot readily be detected individually, but which will cause an overall decrease in the bond strength. Let's model these by a double area discontinuity at the interface between the adhesive and the substrate (Fig. 4c).

Now, the purpose of these models is to show us what kind of differences we could expect in the reflection of an ultrasonic signal to point out to us what type of equipment, what type of ultrasonic pulses, is going to be most sensitive to these anomalies. It is not as though you are trying to detect a crack. Again, as I said before, almost any pulse shape will give you a reflection from a crack, where there was none in a block that had no flaw. In adhesive bonds you are trying to detect anomalies in signal shapes that may be sensitive to one frequency or another. You want to know whether you should use continuous wave, pulse echo, broad band, narrow band, high amplitude, or low amplitude signals. This is the point we are trying to make. This is where we are trying to go.

We went back and started manufacturing new bonds using an American Cyanamid adhesive, a supported film. We split the group into two parts, one having the surface preparation as specified by the manufacturer, and the other in which the chromic acid etch was deleted. Other than that, substrates were cleaned in the usual manner and bonded in the same way as the "good specimen".

We found that there are definite differences in the ultrasonic reflection amplitudes of certain portions of the signal that can--that do indicate that the surface specimens have not had adequate surface preparation.

These models have been developed for stress waves propagating through the materials. What we see on the oscilloscope are electrical voltages applied to and received from the crystal. This is not necessarily the shape of the wave you get in your material, so what we have to do is work backwards to see if the observed differences do correspond to the, say, surface preparation problems in these models. We have not really gotten into the density gradient yet.
We have observed differences. We have had a few bonds that have failed cohesively in nature at lower loads than the rest, and we have observed differences in the spectral profiles of these echoes, but as I said, we are still in the process of doing this work.

Regarding the inspection technique used on these samples, we have taken all kinds of data. We have pulse echo. We also have taken thru transmission, oblique incidence, double thru transmission where we send a pulse completely through the bond, to a reflector, and back through the bond, so we have tremendous amounts of data that need to be analyzed yet.

This is something that Dennis Corbly mentioned, some of his equipment could be of fantastic use.

For those interested in acoustic emission, we do have some acoustic emission data on the bonds; however, we have not really studied it yet. As I said, we're still really in progress, but things do look very, very encouraging. They look very good for the surface preparation case.
DISCUSSION

DR. DON THOMPSON (Science Center, Rockwell International): Would you say a little more about your density gradient model? What is the physical background for assuming the variation in densities?

DR. PAUL MEYER (Drexel University): We talked to some people from the Materials Research Lab in Glenwood, Illinois, and they have observed that sometime during the bonding process for some reason that is not really known, certain chemicals making up the adhesive may migrate to the interface between the adhesive and the substrate. Now, this imbalance in chemicals will affect the strength of the bond. We are going to say that it will also affect the acoustic properties of the bond, that is, you may get a different acoustic impedance in one area than another. It is not really just a density gradient model; it is more of an acoustic impedance gradient model.

DR. BRUCE THOMPSON (Science Center, Rockwell International): Well, I can see in your three-layer model and your N-layer model, that you have infinite planes. You can solve this very nicely with plane wave analysis in your double area discontinuity model, at least as you drew the sketch--

DR. MEYER: That is just for sketching purposes. We are assuming the points are microscopic in nature and that is only a representation of it.

DR. THOMPSON: So you use this sort of a plane-wave analysis there?

DR. MEYER: Yes, plane-wave analysis.

PROF. HENRY BERTONI (Polytechnic Institute of New York): What sort of waves do you find will show up the differences the most, shear waves or longitudinal waves?

DR. MEYER: We have been using longitudinal waves. I haven't gotten around to analyzing the oblique incident data yet which uses shear waves. As I said, only portions of the signal seems to be affected, and this is probably due to the electromechanical conversions at the crystal, but there are differences in the shear wave, taking a very quick look at it. That is all we have done on that data, though.
MR. ROBERT CRANE (Air Force Materials Laboratory, WPAFB): You have assumed in your model that you get diffusion of some chemical substance away from or to the interface which will account for a change in bond strength, is that right?

DR. MEYER: Yes.

MR. CRANE: And that diffusion gives rise to density gradients which, therefore, gives rise to differences in the reflected spectrum? My question is the following: Have you made any calculations of the diffusion possible in your adhesive bond, given the temperature of the cure?

DR. MEYER: No.

MR. CRANE: And what kind of distances would you expect based upon those diffusion gradients? What kind of density differences then would you expect from that?

DR. MEYER: No. No, as I said, we haven't really gotten into the density gradient model yet. It is just a basic or first attempt to model that kind of anomaly.

MR. CRANE: Just as a first order of approximation, what kind of distances would you expect and what kind of changes in density would you expect?

DR. MEYER: Well, we were told that these chemicals can migrate all the way to the interface and, in fact, someone suggested that we combine these models because the migration of the chemical to the interface can actually cause degradation of the metal at the interface. As a first order of approximation, I would talk about acoustic impedance variations of maybe 10 per cent. That may be high; that may be low.

MR. CRANE: Do you have any idea what those chemicals might be?

DR. MEYER: I don't really know.
DR. DAVID KAELBLE (Science Center, Rockwell International): I can give at least some partial answers to both questions. The chemicals very often will be unreacted crosslinking agents in the cured epoxy network. Unrelated low-weight material which is completely incompatible with the cross-link network of the system will tend to migrate and concentrate at an interface or any other surface. The rate of migration will depend upon the self-diffusion coefficients in the network, and this of course, depends on its physical state. If you are 50 degrees or so above the glass transition temperature, which is a very common situation for the initiation of curing, that diffusion coefficient can be a thousand or more angstroms per second. If you are below the glass transition, you effectively freeze these small molecules into a fixed position because the diffusion coefficient goes down to ten to the minus four angstroms per second, so there is a tremendous change in diffusion rate with resin liquid-solid state and it depends upon the effective local viscosity in the system. If the resin is in a solid state, it displays a very high viscosity. If it is a fluid state, it is a very low effective viscosity.