

Evolution of bond efficiency of aluminium-polyethylene adhesive joint

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Abstract

The main purpose of this article concerns the application of ultrasonic methods to predict the limits of adhesive joint efficiency. Ultrasonic data are related to metal-polymer adhesion phenomena by studying joints strength, fracture morphology and surface chemistry (ESCA).

Cohesive or adhesive joint failures are predictable by non-destructive inspection of metal-adhesive interface.

Riassunto

La giunzione mediante adesivi organici di parti metalliche tra loro e con parti non metalliche viene sempre più diffondendosi, soprattutto nelle industrie aeronautica ed automobilistica, perché, attraverso una più favorevole distribuzione delle tensioni (l'eliminazione delle concentrazioni di tensioni dovute ai cordoni di saldatura ed ai fori per i rivetti, nella chiodatura), permette un alleggerimento delle strutture, ed inoltre, la realizzazione di collegamenti privi (o quasi) di tensioni residue e di coppie galvaniche, e tendenzialmente impermeabili ai liquidi ed ai gas. A questo tipo di giunzioni è stato già applicato, da tempo, il metodo del controllo ad U.S., per la verifica della buona esecuzione, intesa come mancanza di difetti macroscopici, del singolo giunto.

Si è verificato, già in alcuni lavori precedenti, che a mezzo degli U.S., con tecniche particolari, si possono evidenziare anche i "limiti di efficienza" del tipo di giunzione, correlati alla difettosità micro e sub-microscopica, che, in relazione al tipo di giunto, può essere più o meno contenuta, ma non eliminata del tutto.

Queste tecniche di studio della efficienza del tipo di giunto, mediante l'impiego del rapporto (A_0/A_1) tra frazione trasmessa e frazione riflessa del fascio U.S., della mappatura ad U.S., e dello studio delle superfici per osservazione diretta (morfologia) e per esami con apparato ESCA (analisi chimica strumentale), sono state, in questo caso, applicate allo studio di un giunto particolarmente complesso, perché l'adesivo era formato da un materiale (il polietilene) che varia le sue caratteristiche di adesione in relazione alla addizione di un dispersoide (filler), apparentemente inerte (zeoliti), effettuata con granulometria costante (brevetto ENI-Ricerche).

Come aderendi sono state adoperate lamine di alluminio.

Le prove di trazione hanno evidenziato un massimo di resistenza meccanica per tenori in filler tra 1 e 5%.

Gli esami ESCA hanno evidenziato, in concordanza con l'osservazione frattografica superficiale, che si aveva, dopo rottura, un massimo di superficie dell'aderendo ancora coperta da adesivo (rottura "entro" l'adesivo) per gli stessi tenori percentuali in filler.

Appaiono chiaramente correlabili a questi gli esami per mappatura ad U.S., mentre l'esame del rapporto (A_0/A_1) delle frazioni, trasmessa e riflessa, del fascio U.S. ha evidenziato ancora un massimo nell'intervallo fra l'1 e il 5% di filler, dimostrando così la validità del metodo "Non Distruttivo" agli U.S. per la valutazione della "efficienza del tipo di giunto incollato".

Introduction

Among different techniques used to realize fixed joints between equal or chemically different materials, the use of adhesives is widespreading, in the recent years, for industrial applications. Diffusion of structural adhesives for joining metals is relevant in motor-car and aeronautical industries, besides conventional manufacturing industry.

The main advantage of adhesive joint technique results from a more favourable stress distribution; in principle it is possible to reach a more uniform distribution of applied loads over the entire joint area; localized tensions are avoided and consequently a better joint strength, both to static and dynamic loading, is expected.

Moreover adhesive joints do not need holes (riveted joint technique needs holes), in the neighbouring of which local weakness due to intense stress are often produced.

In addition to the above main advantages, other quite important factors have to be taken into account:

- 1) lack of residual stress and microstructure alteration due to thermal cycling;
- 2) good gas and liquid seal;
- 3) no galvanic corrosion, since the direct contact between different metals is overcome.

On the other hand, there are some difficulties to perform all joining steps in clean conditions to avoid any contamination (suitable clean-rooms are often required); owing to adhesive organic nature the life temperatures are necessarily quite low and a rapid weathering can occur; moreover joint efficiency cannot be easily controlled by adequate non-destructive testing procedures.

In a preceding work, the limits of efficiency of the metal-adhesive bond were examined by means of ultrasonic (US) technique (frequency spectra analysis) and fracture studies; afterwards, the results were correlated with mechanical tests data (1).

Part of the present work concerns an increase of the above-mentioned study, in particular it uses ultrasonic methods as a reliable tool to predict adhesive joint strength.

1. Test specimens preparation

1.1. The Adhesive

A new structural adhesive was used as bonding layer; adhesive constituents are thermoplastic polyethylene resins and crystalline active zeolites.

The resulting composite masses exhibit strong adhesion to metal substrate, in particular to aluminium (2).

This adhesive was studied and designed to get a convenient compromise between mechanical performance and low cost.

Three different contents of zeolites are considered in present work: 1%, 5% and 10% w/w respectively, in order to obtain a qualitative behaviour, from which we can argue the influence of the filler on joint mechanical strength.

Unfilled polyethylene (here referred to as 0% zeolite content, having poor adhesive properties) was used as reference for mechanical and physical-chemical properties of filled adhesive.

1.2. Joint dimension and joining method

A commercial Al type (99.5% purity, UNI 4507) was chosen as metallic substrate; this metal is currently used when brightness and mechanical strength are both required.

Samples were cut from aluminium sheets with dimensions of 120 mm × 25 mm; joints were obtained by overlapping couples of specimens and then laminating with an adhesive layer.

Since there are no limits due to standard dimension requirements, thickness of the two specimens were chosen as 5 mm and 3 mm for each joint. Different specimen thicknesses are required from ultrasonic method used in evaluation of adhesively bonded interfaces. When Al specimens of equal thickness are bonded, ultrasonic investigation becomes complicated for the interference with a second echo signal of reflected waves on the adhesive layer, which superimposes to the echo coming from the bottom layer of the sample. This is shown in Fig. 1. The length of overlapping portion was set at 20 mm, taking into account ultrasonic transducer size.

Metal specimens were degreased by organic solvent washing; then they were grinded by means of three abrasive papers (corundum abrasive particle size of

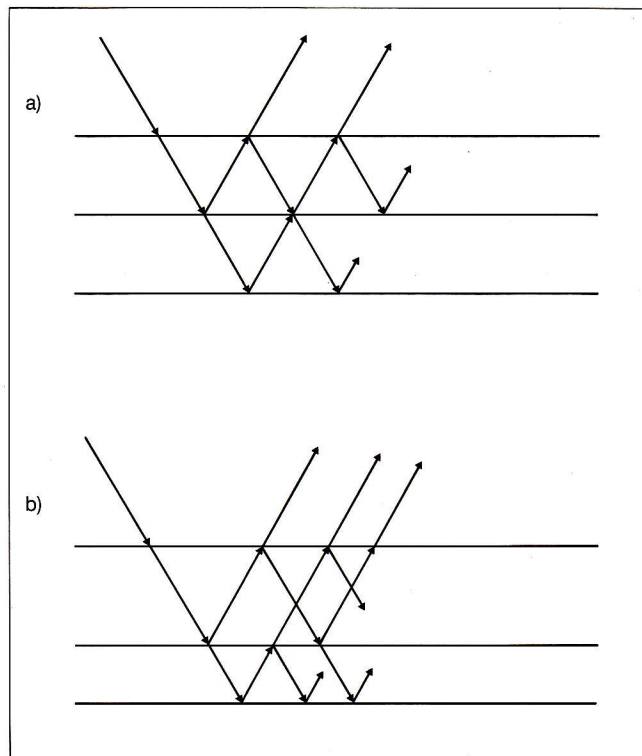


Fig. 1 - Reflecting waves at the adhesive layer for equal (a) and different (b) specimens thickness.

280, 320, 400 mesh) in order to obtain a mean surface roughness of $\pm 20 \mu\text{m}$ (absolute roughness value $[\lambda_g] = 40 \mu\text{m}$); thereafter the samples were cleaned again with solvent.

A uniformly applied pressure (1 Kg/cm² about) helps a tight interaction between adhesive-substrate surfaces, allowing homogeneous bonding.

However the pressure, due to low adhesive viscosity at the operating temperature (180° C), tends to shift the area joint, so that the overlapping geometry tends to modify itself. These difficulties were overcome by using a sample locking device, which allows the simultaneous fabrication of six samples. The device is a steel jig, on which couples of adherent metal specimens are placed, holding a parallelepiped hollow space (dimensions: 25 × 20 × 0.3 mm); the hollow is filled with an adhesive layer of the same thickness (0.3 mm). The steel jig block may be disassembled to draw the joined samples out.

2. Strength of adhesively bonded joints

Determination of mechanical strength of bonded structures was carried out by a 25 kN tensile tester Instron.

Specimens were stressed, according to a single lap-shear test (ASTM method D3163-73), by applying a tension load at a constant crosshead speed of 1 mm/min (correspondently $\dot{\epsilon} = 5$), until joint failure occurred. Thus the maximum tension load was registered and reported as τ_{mx} (specific maximum lap-shear stress) vs filler percentage, in a plot as it is shown in Fig. 2.

3. Chemical analysis of surfaces (ESCA analysis)

X-Ray photoelectron spectroscopy (XPS) gives detailed information, both in quality and in quantity, on atomic composition of outer surface layers of solid materials. From this point of view XPS-technique is also cited as ESCA (electron spectroscopy for surface chemical analysis).

Since ESCA measures the energy of photoemitted electrons, the sampling depth depends on the electron free path. Concerning polymeric materials the average sampling depth is approximately 50 Å and 20 Å for metals.

The apparatus used for this work is an A.E.I. (Kratos) spectrometer ES-100 model, a block diagram of which is given in Fig. 3. The spectrometer uses $Al/K\alpha_{1,2}$ radiation line, as X-Ray source ($h\nu = 1486.7$ eV). According to basic principles of this analytical technique (3), samples undergo the impinging of an X-Ray beam.

Fig. 2 - Specific maximum lap-shear stress as a function of the filler percentage.

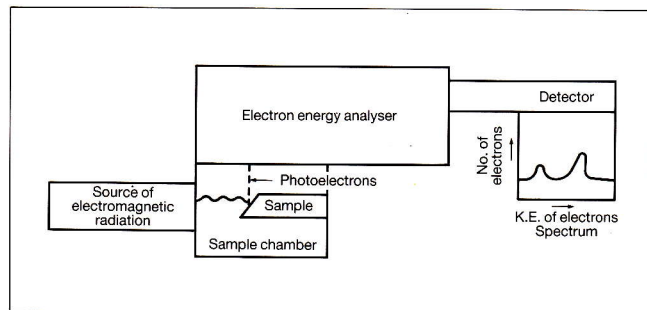
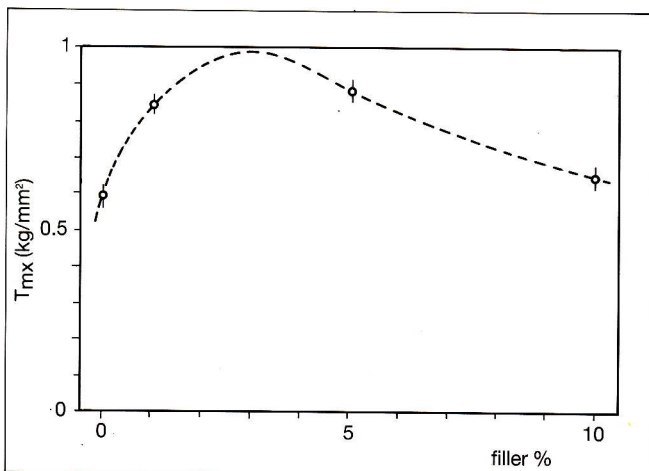


Fig. 3 - Block diagram of the XPS apparatus A.E.I. (Kratos) ES-100 model.

The absorbing atoms emit photoelectrons from inner core levels. Due to the mean free path, in a solid sample, the escaping photoelectrons are those coming from a few atomic surface layers; these electrons enter the spectrometer analyzer practically without loss of their original emission energy.

Thus kinetic energy distribution characterizes each atomic species and ESCA-spectra exhibit set of sharp lines; the lines often exhibit a fine structure due to chemical shift effects.

Kinetic energy of ESCA-photoelectrons can be expressed by:

$$E_k = h\nu - E_b$$

where ($h\nu$) is the photon energy of X-Ray beam and (E_b) is the electron binding energy.

The quantity E_k is expressed in eV and in our case ranges from 0 eV to 1486.7 eV.

The surfaces of our interest are Al-surfaces resulting from joint fracture in lap-shear tests.

The most meaningful ESCA spectra are reported in Figs. 4 a, b, c where binding energy is in abscissa and the ordinate is proportional to atomic species amount. Exactly, peak areas are proportional to atomic species amount, according to a set of atomic sensitivity factors and to corrective factors depending on line energy (i.e. sampling depth).

In our case, each spectrum shows evidence of intense carbon and oxygen lines, while the presence of filler signals (Si, Al and Na relative abundance 1:1:1) was never detected.

Carbon line intensity (I_c) is attributable to residual organic adhesive and oxygen line (I_o) is due exclusively to Al-oxide surface layer of adhesive free substrate regions. Thus we assumed (I_c) proportional to specimen portion which is still covered with residual organic adhesive (cohesive failure); (I_o) is proportional to adhesive free Al-area (adhesive failure).

Carbon and oxygen line intensities should verify the

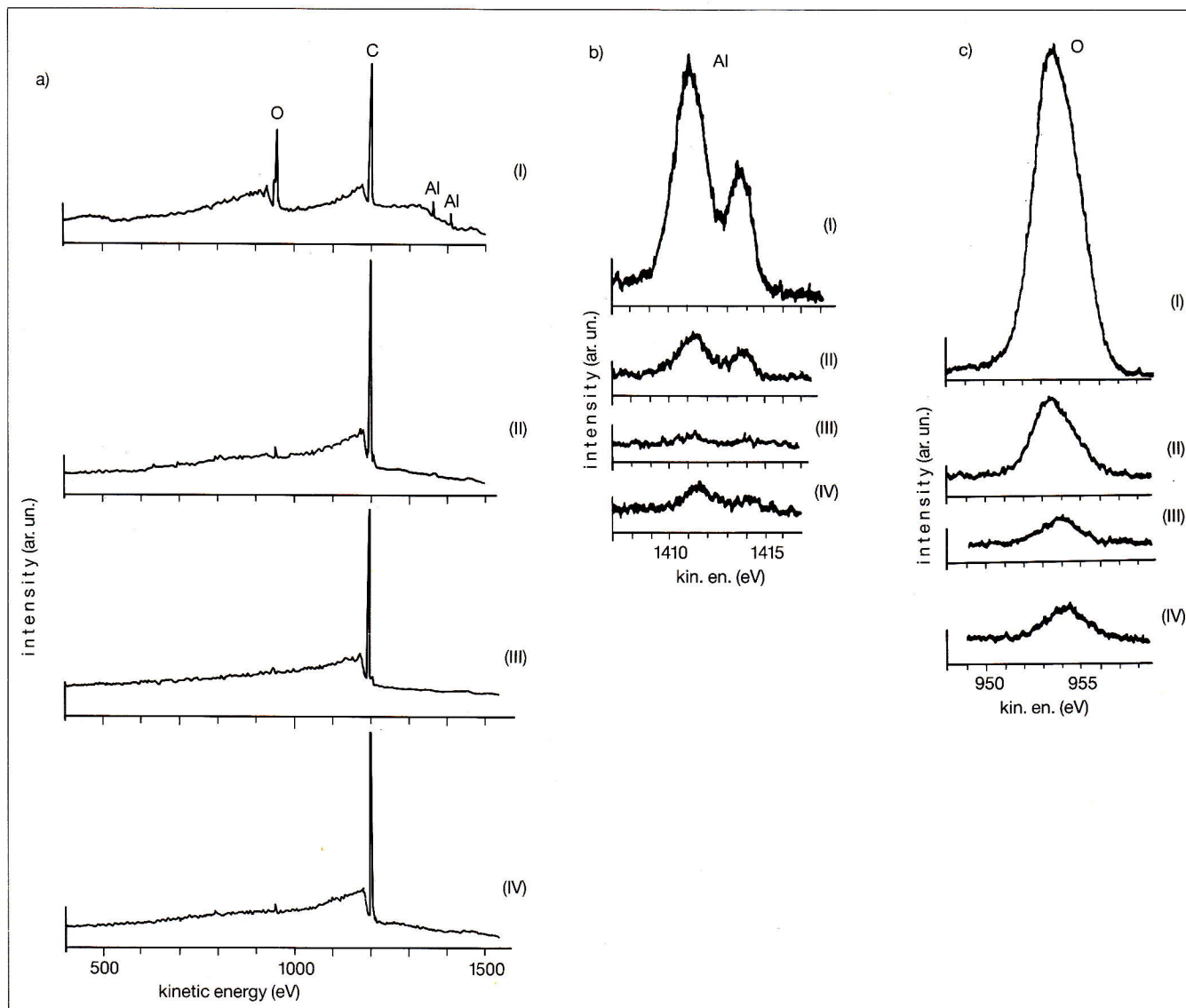


Fig. 4 - ESCA spectra (I, joints without filler; II, joints with 1% of filler; III, joints with 5% of filler; IV, joints with 10% of filler) showing:
a) general spectra of joints fracture zones;
b) aluminum peaks of the fracture zones;
c) oxygen peaks of the fracture zones.

following relation:

$$I_c + I_o = K_a$$

where (K_a) is a constant depending on the sampled joint area.

To compare ESCA data to results of other techniques, (I_c) values were related to filler percentage; a diagram is shown in Fig. 5. The curve filler % vs I_c , looks like the analogous curves showing filler % vs τ_{mx} (Fig. 2) and filler % vs A_0/A_1 (Fig. 12).

4. Ultrasonic scan

Ultrasonic investigation by the use of a C-Scan US 450 SLS instrument, with a focused probe, gives information about organic layer cohesion, inner homogeneity and adhesion uniformity (4).

Such techniques, monitoring the response to ultrasonic pulses, can detect even the smallest bond line porosity, gas bubbles or voids of order of magnitude $1 \mu\text{m}$, adhesion lack zones and filler aggregates near the

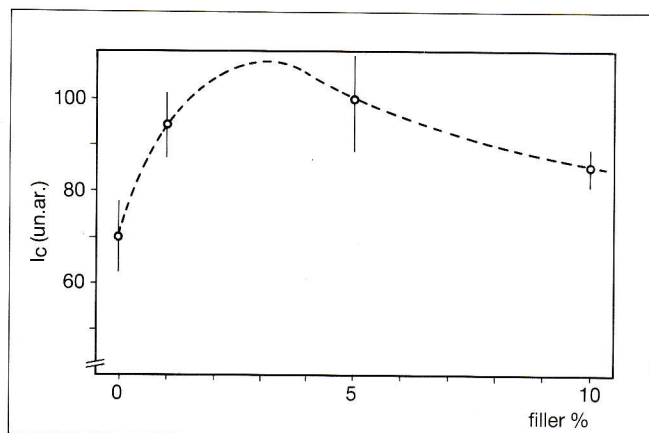


Fig. 5 - Carbon line intensity as a function of the filler percentage.

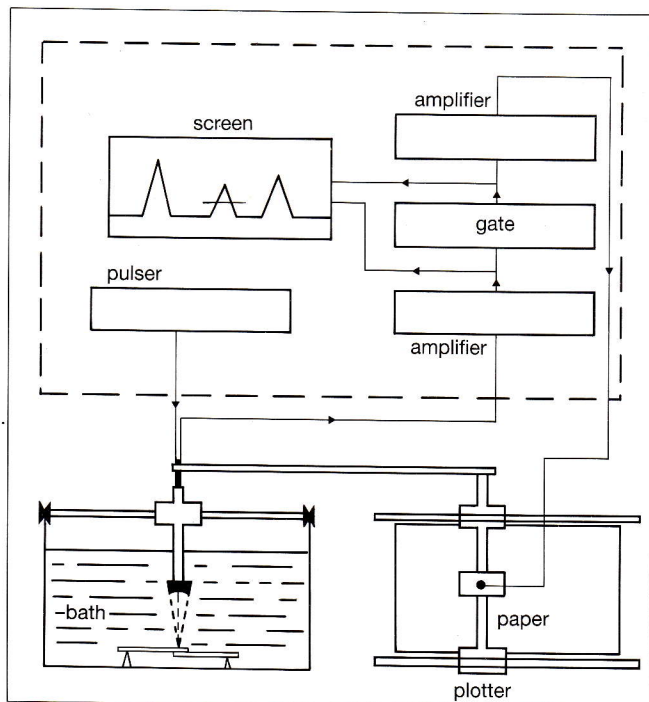


Fig. 6 - Ultrasonic C-Scan experimental system.

metal-adhesive interface.

Ultrasonic scan gives an actual sonographic map of junction bond line. Fig. 6 shows a diagram of the experimental system. Here a focused ultrasonic transmitting and receiving probe, working at 15 MHz, was used and the focal point was fixed on the adhesive layer.

The first ground echo was used as reference signal; in fact it is well detectable and travels twice through the adhesive layer. By an oscilloscope we can observe that ground echo amplitude varies depending on the junction type.

As it is shown in Figs. 7 a, b, c, sonography allows easy

Fig. 7 - Sonographs by comparison with the fracture zones photographs (5 mm thickness specimen on the leftside):

- a) joint with 1% of filler;
- b) joint with 5% of filler;
- c) joint with 5% of filler.

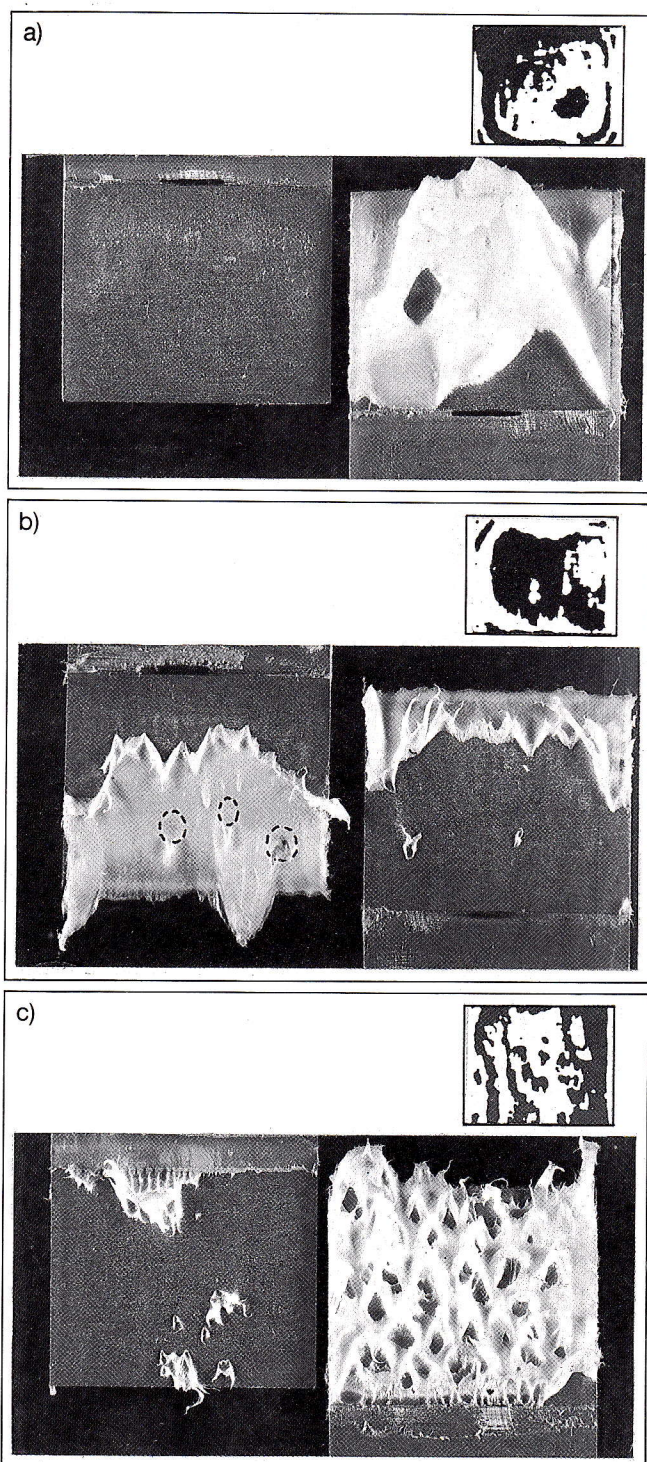


Fig. 8 - Sonographs of the interface zones:

a) joints without filler;
b) joints with 1% of filler;
c) joints with 5% of filler;
d) joint with 10% of filler;
frequency spectra analysis.



detection of weak boundary zones (besides larger macroscopic defects) which interrupt uniformity and continuity of metal-adhesive bonding interface (5) (1). Moreover a great likeness between non-destructive sonographies and morphology of the fracture surface becomes evident. At highest filler contents (5% and

10%) sonographies show the presence of zeolite aggregates at the interface zone (see Fig. 8). Thus sonographic map gives a detailed prediction of joint efficiency and failure sites.

5. Ultrasonic frequency spectra

Further investigation on adhesively bonded joints was carried out by analysing frequency response of through-transmitted pulses. Such a type of measurements are very sensitive to ultrasonic attenuation changes due to different acoustic impedance of joint interface (4) (1).

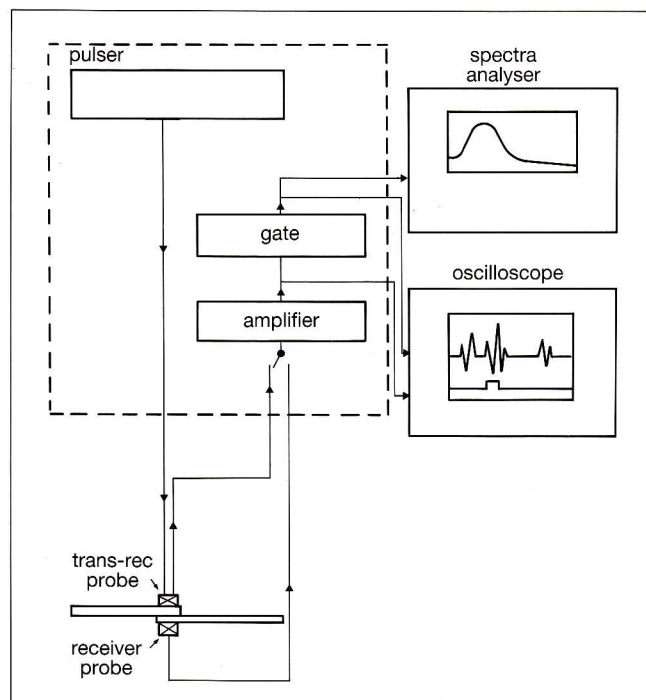
A block scheme of apparatus is shown in Fig. 9. There are two interesting signals: the transmitted one, indicated as (A_0) and the other one (A_1) reflected at the interface (Al-3 mm and adhesive layer).

These signals are shown in Fig. 10.

A complete examination of the whole junction area is not possible, due to transducer dimensions; thus a reliable comparison of signals for different samples requires a fine control of sampling conditions, i.e. sampling production and sampling area reproducibility.

For this purpose, a suitable support was designed to avoid shifts from the right sample position. In order to obtain a good-sample-transducer coupling,

Fig. 9 - Experimental system for ultrasonic frequency spectra analysis.



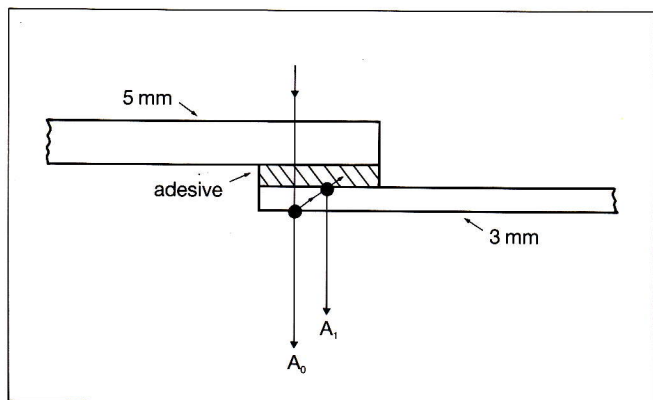


Fig. 10 - Transmitted (A_0) and reflected (A_1) signals for a sample.

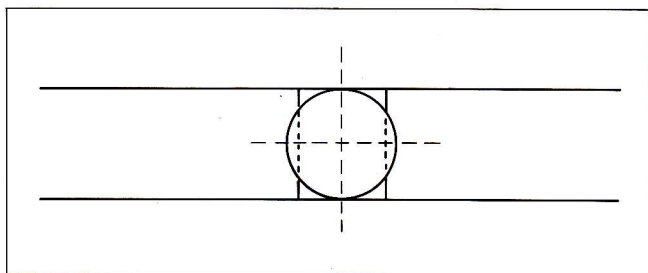


Fig. 11 - Joint surface (rectangular area) by comparison with the probe surface (circular area).

and with a good longitudinal wave transmission, mineral oil was interposed between sample and transducer surfaces.

Two 15 MHz-transducers were used for sample analysis, one as an emitter and another as a receiver, in direct contact with the specimens, having probes diameter of 10 mm and 22 mm respectively. Sampling area is about 76% of the whole joint surface (see Fig. 11).

Frequency spectra of both transmitted (A_0) and reflected (A_1) signals were found comparable for each set of joints with equally filled adhesive layer. For each sample set, A_0/A_1 ratio assumed similar values; a plot of A_0/A_1 mean values vs filler percentage is given in Fig. 12.

A non-monotonic curve is obtained with a maximum at 3-4% of filler content.

6. Ultrasonic amplitude spectra

Further investigation of adhesive joint properties was made by analysing amplitudes vs frequency variation of transmitted ultrasonic waves.

The frequency was varied in the range 0-20 MHz and the amplitude reached 2 Volts. In such a way power

absorption spectra were carried out. A block scheme of the experimental system is shown in Fig. 13.

Measurements were made in transmission mode, using a 10 MHz receiver probe and a 15 MHz transmitter. It should be taken into account the greater continuity of the continuous wave, respect to a sonic pulse, then the former undergoes little attenuation. Attenuation also depends on wave length, besides depending on the "physical obstacles" through specimen.

Spectra was registered by plotting amplitude (Volts) vs frequency (MHz).

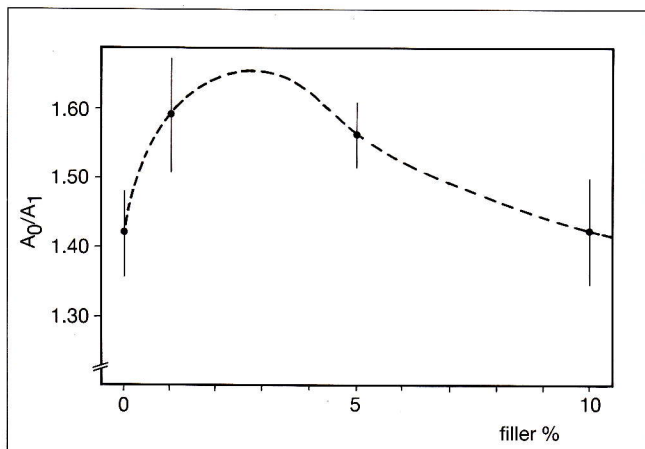


Fig. 12 - A_0/A_1 ratio as a function of the filler percentage.

Fig. 13 - Experimental system for ultrasonic amplitude spectra analysis.

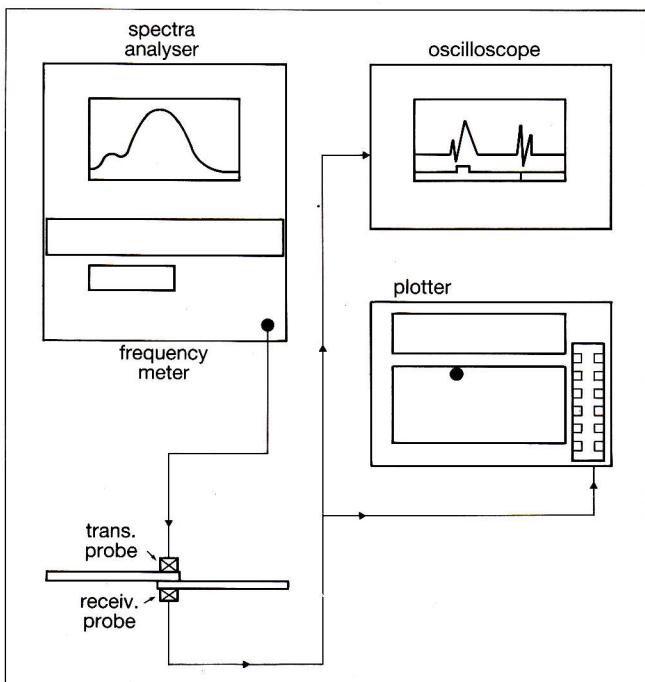
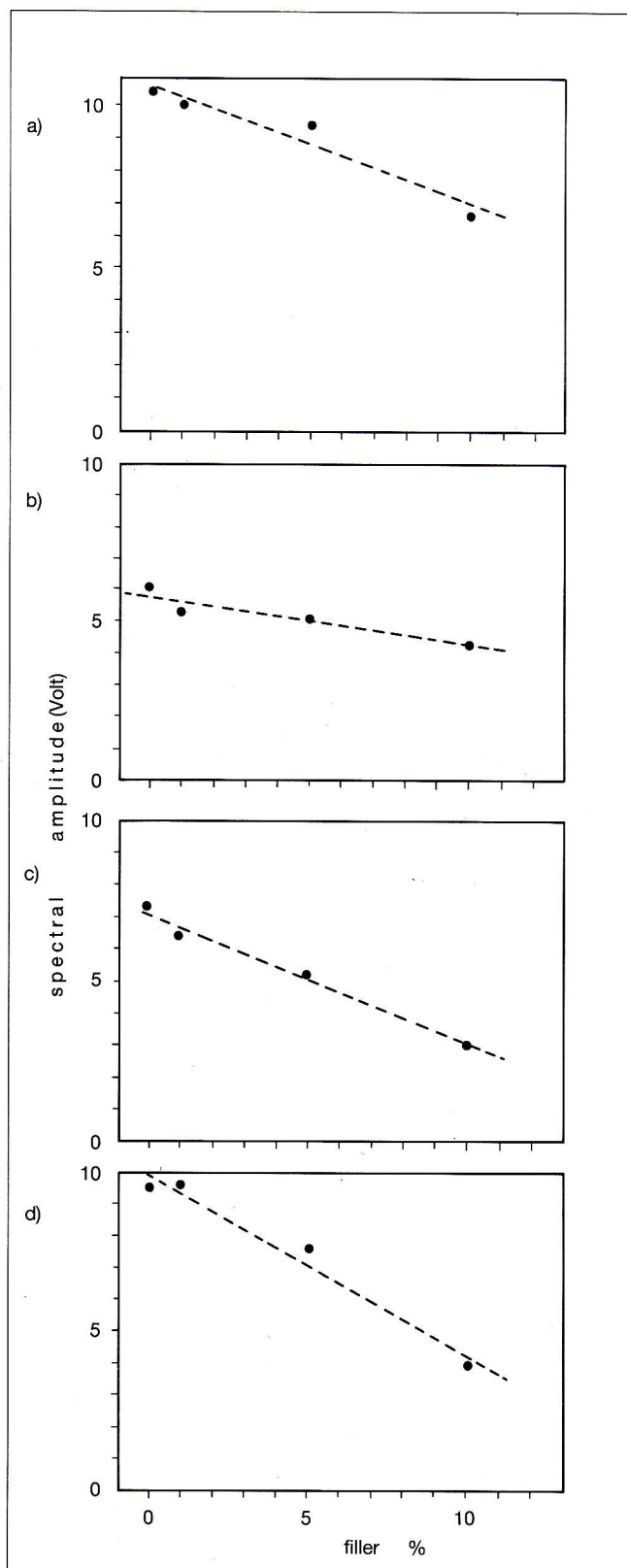


Fig. 14 - Spectral amplitude as a function of the filler percentage:
a) at 4.4 MHz; b) at 5.7 MHz; c) at 8.9 MHz; d) at 13.3 MHz.



Mean values of spectral amplitudes at four frequencies (4.4, 5.7, 8.9, 13.3 MHz) samples are linearly related to filler percentage in polyethylene, as Fig. 14 shows. Introductory that the filler granulometry is level into every samples, at different percentage and at all examined ultrasonic frequencies (from 4.4 to 13.3 MHz), it can be noticed, at all frequencies, the ultrasonic transparency decreases as filler percentage increases, but not uniformly.

Particularly it can be found:

- a general ultrasonic transparency minimum at 5.7 MHz; with 0% of filler, such a minimum is 0.6 times compared to the minimum at 13.3 MHz;
- the smallest absorbance reduction, at 5.7 MHz, as the filler percentage changes from 0% to 10%; moreover, you can find an absorbance maximum using a filler percentage lower than 10%;
- the greatest attenuation gradient, at 13.3 MHz, as the filler percentage changes from 0% to 10% (attenuation = 0 with 0% of filler, attenuation = 0.6 with 10% of filler);
- changing the wave frequency from 4.4 MHz to 13.4 MHz, the attenuation increase compared to the filler percentage increase becomes more noticeable (with the exception of the frequency of 5.7 MHz).

On the whole, it seems the ultrasonic bundle (that increases as frequency increases) decreases as the filler percentage increases. The anomaly found at 5.7 MHz makes guess at a close interaction between ultrasonic waves and the adhesive macromolecules.

7. Scanning electron microscope (SEM)

SEM investigation was carried out on fracture surfaces of lap-shear tested joints, in order to study failure morphology.

SEM photos were obtained with magnification ranging from 20 to 2000 times.

At highest filler content (5% and 10%), SEM shows a highly fibrous structure of residual polyethylene on Al surface where cohesive failure occurred (see Fig. 15).

This finding is related to higher mechanical strength of filled polyethylene. Besides fibrous structures, spheric particles of a few micron diameter are evident. These zeolite aggregates are randomly distributed, but preferentially adherent to polyethylene fibres. However ESCA analysis did not detect typical zeolite constituents; thus we can argue that zeolite particles are tightly bounded to an overlaying organic filled polyethylene layer (thickness more than 50 Å).



Fig. 15 - SEM photograph at 500 magnifications of a sample jointed by polyethylene holding 10% of filler.

Moreover with 10% filled adhesive, cratering zones become evident at failed interfaces. These craters could be related to local regions where fractures occur at $\text{Al-Al}_2\text{O}_3$ interface.

Conclusions

Ultrasonic tools, ESCA and SEM give complementary information useful to carry out a deeper understanding of adhesion phenomena.

An interesting correlation may be carried out from the surface chemical analysis section, owing to the physical significance of (I_c) and (I_o) ESCA-line intensities. It was established that $I_c + I_o = K_a$ (constant).

In order to have comparable graphic curves, $(K_a - I_o)$ values were related to τ_{mx} values, which resulted from lap-shear tests.

This relation (where K_a value was obtained by linear regression calculation of I_o and I_c , taking into account that $I_c = K_a$ when $I_o = 0$) gives a straight correlation (Fig. 16); thus a higher mechanical strength is found where larger cohesive failures occur (i.e. larger I_c values and lower I_o values).

On the other hand, ultrasonic maps evidentiate the appearance of zeolite aggregates in the boundary regions where adhesion is grater.

These observations are confirmed by SEM data. Thus both the techniques agree in correlate higher interface strength to higher filler content and the destructive method confirms the prevision of the non-destructive one.

Above results show that it is possible to realize a non-

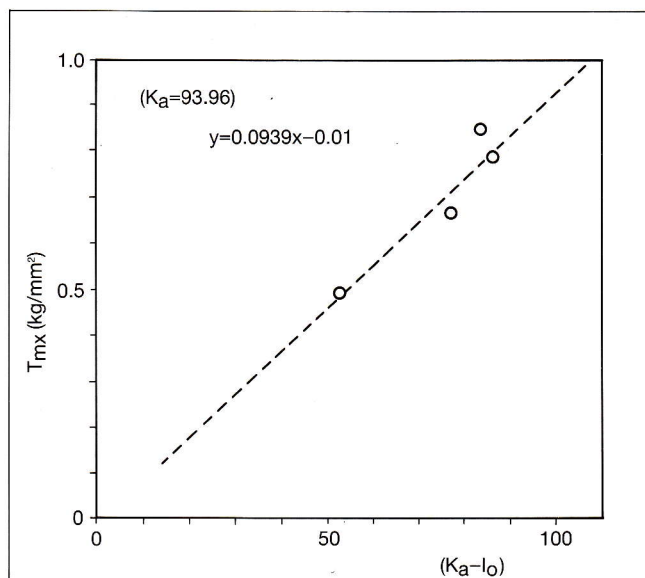


Fig. 16 - Specific maximum lap-shear stress as a function of the ESCA carbon line intensity.

destructive control test of adhesively bonded metal joints; in order to verify and then to improve joint performances, this work indicates a reliable tool, though certainly the method should be improved by more suitable devices.

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REFERENCES

- (1) Biggiero, G. and G. Canella. Ultrasonic testing for bond efficiency of carbon steel to stainless steel adhesive joints. *Int. J. of Adhesion and Adhesives*, 5 (1985), 143-148.
- (2) Ascarelli, P., G. Boccalon et al. Thermoplastic compositions based on non-polar organic polymers and zeolites in acid form. *US Patent NO. 4, 487, 810*, 1984.
- (3) Clark, D.T. The investigation of polymer surfaces by means of ESCA. In D.T. Clark and W.J. Feast (Ed.), *Polymer Surfaces*, John Wiley and Sons, New York, 1978, pp. 309-351.
- (4) Guyott, C.C.T., P. Cawley and R.D. Adams. The non-destructive testing of adhesively bonded structure: a review. *J. of Adhesion*, 20 (1986), 129-159.
- (5) Biggiero, G., G. Canella and A. Moschini. Ultrasonic scanning and spectrum analysis for inspection of bond efficiency of metal-to-metal structural adhesive joints. *NDT International*, April (1983), 67-73.