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Comparison of ultrasonic reflectometry and FTIR analysis for thermal ageing effect detection for paint films on steel plates

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Ultrasonic reflectometry has been successfully used to detect in a non destructive way the curing effect of thermal ageing up to 110°C for epoxy paint films on steel plates. From simulations, a specific acoustic mode has been selected for its higher sensitivity to variations to the longitudinal and transverse velocities of the film compared to potential plate thickness fluctuations. Experiments have confirmed the presence of this acoustic mode generated around 38° using conventional plane sensors with a working frequency of 5 MHz in immersion configuration for coated samples with an average film thickness of 100 µm. Next, from thermal ageing tests performed at different temperatures on three identical samples, ultrasonic reflectometry measurement have revealed the kinetics of the curing effect after paint application from the shift of several degrees of the position of this so-called surface paint mode. This variation can last one or two weeks for the sample at room temperature, few days at 80°C and less than one day for 110°C and, in this last case, with a lower final value indicating an higher hardening level. At the end of these tests, comparisons of FTIR spectra for these three samples have confirmed differences of their epoxy network.

1 Introduction

Polymer paints are used for many industrial applications such as protection against corrosion but these coatings can present ageing effect due to severe conditions or long term service. Their molecular structures and their physical properties may change progressively requiring non destructive evaluation. For instance, a lack of elasticity will generate an embrittlement risk of the paint film. As longitudinal wave and shear wave velocities are directly related to elastic modules, ultrasonic means are potentially interesting to evaluate the mechanical properties of materials in order to control the film elasticity.

To investigate these potentialities, samples were made of steel plates with a thickness of 1.5 mm coated with a single epoxy film with a thickness around 100 µm. Characterisation of the longitudinal and transverse velocities of these paint coatings from direct time of flight measurement would require high frequency transducers as high as 100 MHz to avoid echo overlapping. Moreover, in polymer materials, ultrasound damping is generally high with a square law dependence increasing with frequency. Moreover, the film thickness has to be known to calculate these velocities.

Ultrasonic reflectometry can measure directly longitudinal and transverse velocities for bulk materials from detection of sharp variations of reflection for specific angles. For coated plates, these critical angles depend on the elastic properties of the plate and of the coating. Their positions change also versus frequency and thicknesses. The aim of this work is to find the most sensitive mode for paint evaluation using simulation and experimental results. This sensitivity will be tested to detect the damage of paint coating on steel plates submitted to thermal ageing. Infra Red spectrometry will be used to confirm evolution of the molecular epoxy network at the sample surface when variations are detected by ultrasonic reflectometry to identify the degradation mechanisms.

2 Simulation results and research for the most sensitive conditions

When an ultrasonic wave arrives on a fluid-solid interface, a reflection happens. Its value can be predicted using the Brekhovskikh model for multi-layered materials. To get the simulation parameters, the properties of the steel plate have been measured using classic ultrasonic echography. For the paint film, a 130MHz transducer has been used to measure the coating thickness and next its

longitudinal velocity from time of flight measurement. Its mass density has been measured from hydrostatic weighing method on a few millimeter thick paint bulk sample with parallel plane sides in order to also estimate its transverse velocity at lower ultrasonic frequency by echography. These data are reported on the Table 1.

material	longitudinal velocity (m/s)	transverse velocity (m/s)	mass density (kg/m ³)	thickness (mm)
Steel	6000	3240	7870	1.45
Paint	2400	1050	1155	0.1

Table 1: parameters of the coated sample for simulations

With this plane wave model for multi-layered media, various guided modes propagating in the steel-coating plane structure are predicted with critical angles lower than the steel plate equivalent Rayleigh mode value. Indeed, beyond this angle, a total reflection of the incident wave is obtained when all the contributions of the energy emitted from the sample to the fluid are added in particular for evanescent waves. In experiments, this situation will be almost impossible to achieve due to the finite size of the ultrasonic receiver. Moreover, sensor diffraction will occur. For this reason, an assumption of the pressure field pattern has been taken into account. In this condition, the simulation shows various modes with angular positions very similar to the Lamb modes detected for the same steel plate without coating (see the Figure 1). On the other hand, a new mode appears for an incident angle of 36° approaching the theoretical paint Rayleigh velocity.

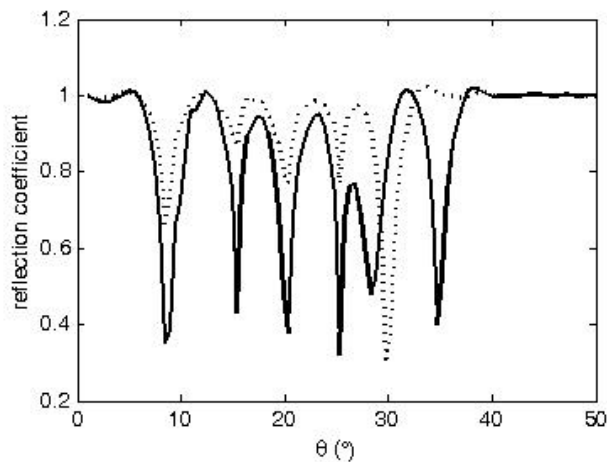


Figure 1: comparison of theoretical reflection coefficient for a steel plate with/without the paint (with paint: full line; without paint: dotted line)

From simulations, this last mode has been proved to be the most sensitive to the presence of the paint layer. For this reason, we will call it the “surface paint mode” as opposed to the “plate modes” due to their small sensitivities to variations of the layer properties. Indeed, as illustrated on the Figure 2, a variation for instance up to +/-20% of the longitudinal velocity of the paint has induced a large shift of the surface paint mode whereas the plate modes have been only slightly modified. On the legend of this graph, 0.8 corresponds to a 20% decrease of the paint longitudinal velocity.

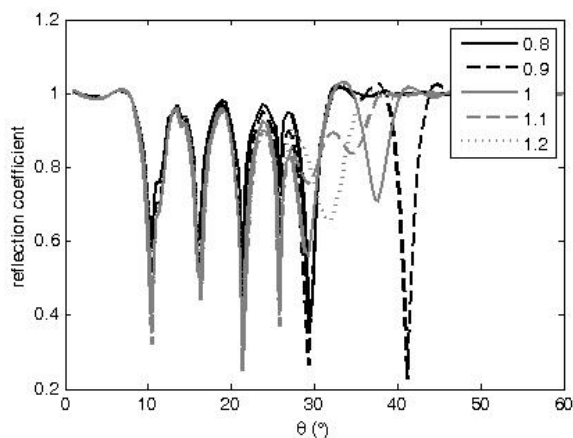


Figure 2: simulated amplitude of the reflection coefficient for different values of the longitudinal velocity of the paint layer.

3 Acoustic experimental results

3.1 Experimental settings

For experiments, the coated plates are immersed in a water tank. Two transducers are used with a frequency centre around 5 MHz and a bandwidth between 4 and 7 MHz. One transducer is used as transmitter; the other one is the receiver. Both transducers are moved simultaneously using a step motor. The incident angle can vary from 8° to 45° with a resolution around 0.1°. For each angle, the echo pattern issued from the wave reflection at the sample

surface is saved. Then, with a Fast Fourier Transform, its frequency spectrum is obtained in order to detect variations of the acoustic reflection angular dependence for any given frequency within the sensors bandwidth. This procedure can not give access to the absolute value of the reflection coefficient but the positions of the smallest values of the measured spectral amplitude correspond to the critical angles of the acoustic modes generated in the sample. All the spectral amplitudes are systematically divided by their highest value for normalisation.

3.2 Comparison between experimental and simulation results

In the Figure 3, an experimental curve is compared to the simulation result. The dashed line is the normalized amplitude spectrum at the sensor central frequency whereas the solid line corresponds to the theoretical module of the reflection coefficient at the same frequency. The angular positions of the sharp valleys are in correct agreement in particular for the plate modes, probably because the plate simulation parameters have been more accurately measured compared to the paint film ones.

The surface paint mode is present on the experimental curve as one of the lowest valley which is not the case on the simulation results. The transducer design used seems to be more sensitive to the nature of the surface paint mode than expected.

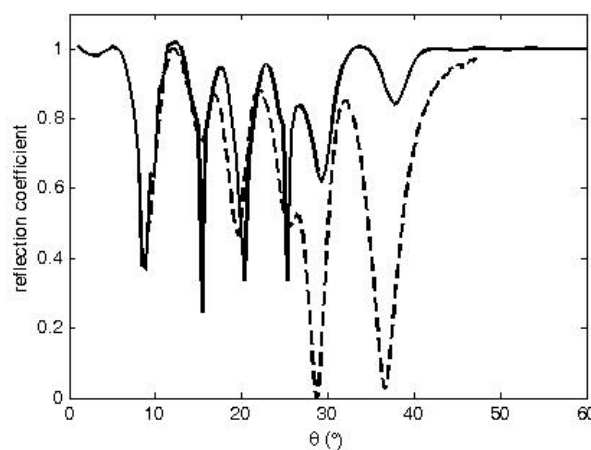


Figure 3: comparison between the simulation result (solid line) and experience (dashed line) for 5 MHz frequency

3.3 Observation of the curing process of paint after application for different temperatures

For samples elaboration, a paint volume was elaborated with a 1.1 ratio of epoxy and amide. Next, three samples issued from the same steel plate have been coated with this paint using a manual applicator to get an homogeneous layer with a constant thickness around 100 µm. After a manufacture recommended curing time of 2 days at room temperature, two of these samples were aged respectively at a temperature of 80 °C and 110°C, whereas the last one stayed at ambient temperature. Then, each sample was daily characterized twice using our ultrasonic reflectometer.

The Figure 4 shows the superposition of the results for the sample aged at room temperature for the first week of test.

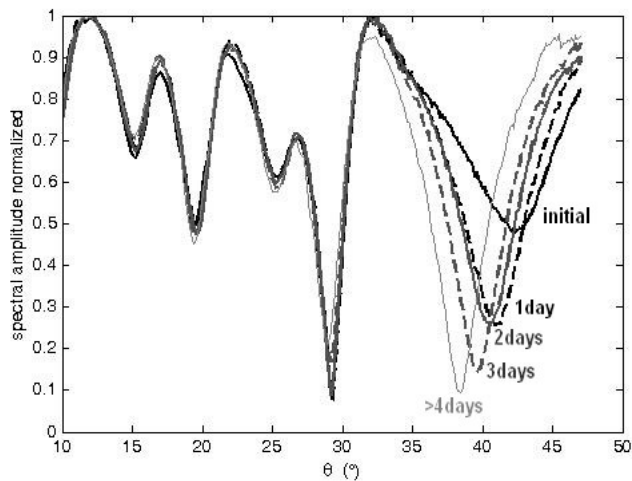


Figure 4: evolution of the spectral amplitude for the surface paint mode for the first week of the curing test at room temperature

As expected, under incident angles lower than 32° , the plate modes do not change while the angular position of the surface paint mode shifts gradually to lower values with a variation of several degrees. There is also a clear effect on the amplitude of this valley. From measurement control, the layer thickness is known not to have changed. Moreover, from simulations, it has been demonstrated that variation of the coating mass density can not explain such a decrease of the surface paint mode angle. This shift is consequently the sign of an increase of the acoustic velocities of paint that is to say an increase of its Young's modulus, the paint becoming harder after the polymerisation. This gradual variation reaches a first limit around 37° after seven days and later decrease down to 35° .

The same effect is present for the sample heated at 80°C but lasts only few days.

The sample aged at 110°C reaches after just few hours a value of only 32° for its surface paint mode. This level is lower than the minimal value measured for the two previous samples aged at ambient temperature and at 80°C . This film has become harder than the two other ones but no sign of damage appears later even after 80 days of thermal ageing.

4 FTIR evaluation

FTIR analysis gives access to the chemical structure of the material surface from absorbance variations of the electromagnetic spectrum induced by excitation of harmonic vibrations for specific wavelengths corresponding to particular molecular structures. For epoxy network, thermal ageing is known to give rise to oxidative degradation identified by researching specific oxidation products.

The three samples have been tested with FTIR after 65 days of thermal ageing (in reflection mode, Bruker IFS66 V/S spectrophotometer). These spectra are compared in the Figure 5.

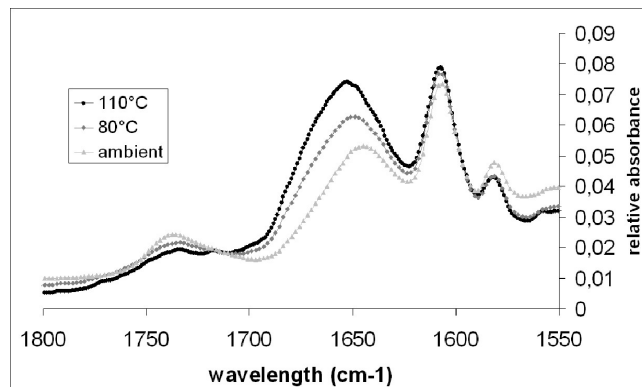


Figure 5: FTIR spectra of the samples after 65 days of thermal ageing at 25°C , 80°C and 110°C

A clear difference is observed for the peak at 1659 cm^{-1} corresponding to amide formation corresponding to the crosslink density. In a same time, oxidation process can be followed by the peak at 1720 cm^{-1} corresponding to carbonyl formation. The latter is associated to a chain scission process, which leads to elastic modulus changes and to embrittlement process.

Unfortunately, FTIR analysis has not been performed all along the thermal ageing tests. Nevertheless, these investigations after 65 days show that all the three paint films become differentiated for the infra red absorbance spectra, whereas the two samples aged at ambient temperature and at 80°C have got the same surface paint mode angle by ultrasonic spectroscopy. Further investigations have to be done to correlate molecular structure information and macroscopic elastic measurement.

5 Conclusion

Ultrasonic reflectometry has demonstrated its ability to detect or to investigate curing effects after coating applications for an epoxy film on a steel plate using conventional ultrasonic sensors. As predicted from simulations, the detection of the position variations of a specific critical angle around 5 MHz enables to detect modifications of the elastic properties of the coated layer. Applied to thermal ageing experiments, this technique has revealed the differences of the kinetic of the paint film curing process. Thus, for ambient temperature and 80°C tests, the epoxy layer has reached an equivalent level of elasticity after one or two weeks, whereas this film is much harder after just one day at 110°C . These tests are still under way for longer term ageing evaluation.

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