

Acoustic scan analysis of the morphological evolution of a vinylester resin near a surface

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The acoustic analysis of the morphological evolution, from the surface to the bulk, of a vinylester resin cured in contact with two types of surfaces, i.e. aluminium and air, has been studied. The analysis was also performed as a function of styrene monomer content of the uncured resin. The existence of a thick layer, in which the vinylester network is deeply affected due to the relative variations of polystyrene and vinylester polymer from the interface to the bulk, was first demonstrated by microscopical Fourier transform–infrared spectroscopy. Secondly, this structural evolution was analysed by means of an acoustic scan technique, allowing the variations of the mechanical properties of the vinylester network to be estimated as a function of the distance from the interface. A good correlation was obtained between spectroscopic and acoustic results.

1. Introduction

It is well known nowadays that interfaces and interfacial layers could play an important role in determining the final performances of multimaterials, such as fibre-reinforced composites, because when these materials are subjected to stresses, load transfer from one solid to another takes place through such contact zones. Hence, it is of great importance for subsequent mechanical analyses to determine precisely the physical and chemical structure of these interfacial zones, as well as their mechanical properties or gradient of properties. In the case of polymer–substrate junctions, the properties of the polymer, depending on its nature, could be strongly affected by the presence of the substrate: for example, the existence of a transcrystalline layer near the substrate surface in the case of thermoplastic semi-crystalline polymers, structural changes of the network due to over- or under-concentration of cross-linking agents near the interface in the case of thermosetting resins.

In a recent paper [1], Fourier transform–infrared spectroscopy (FT–IR) and ^{13}C nuclear magnetic resonance (NMR) revealed the existence of a thick interfacial layer (100–300 μm) in vinylester resin cured in contact with different materials, whatever their nature (glass, aluminium, air, ...) or geometry (plates, fibres). This “interphase” stems from the variation of the relative concentrations of polystyrene and vinylester

polymer from the substrate surface to the bulk, leading to a structural evolution of the polymer network. Such a variation is due to the diffusion, during curing, of styrene monomers towards the bulk of the resin. New investigations on these types of interfacial layers by means of acoustic scan analysis were performed in the present work. Only two kinds of “model substrates” were used: aluminium (in fact, natural aluminium oxide) and air. First, the existence of interphase was demonstrated by FT–IR analysis and, then the variation of the mechanical properties of the resulting network from the interface to the bulk was examined by means of an acoustic scan technique. In both cases, the effect of the initial styrene monomer content in the polymer was determined.

2. Experimental procedure

2.1. Materials

The vinylester resin (Derakane 411, Dow Chemical) was based on diglycidyl ether of bisphenol A (DGEBA) groups with a methacrylate function located on chain ends. The cross-linked network of this resin was obtained by reaction of the prepolymer with a given amount of styrene monomer (usually 45% by weight). The initial content of styrene was varied from 35–55 wt %. The mixture was cured at room temperature using 2 wt % of a 50 wt % solution

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of methylethyletherketone peroxide in dimethylphtalate, 0.3 wt % cobalt octoate (Akzo) and 0.6 wt % of a 10 wt % solution of dimethylaniline in styrene. Post-cure was carried out at 90 °C for 4 h, then 120 °C for 4 h. The resulting network exhibited a heterogeneous structure constituted by an internodular phase enriched in polystyrene (PS) with the other phase enriched in vinylester (VE) [2, 3]. Before curing, the mixture was poured into a small aluminium cup. Therefore, the cross-linking process was carried out in contact with aluminium oxide at the bottom and with air at the top. Both interfaces were thus analysed.

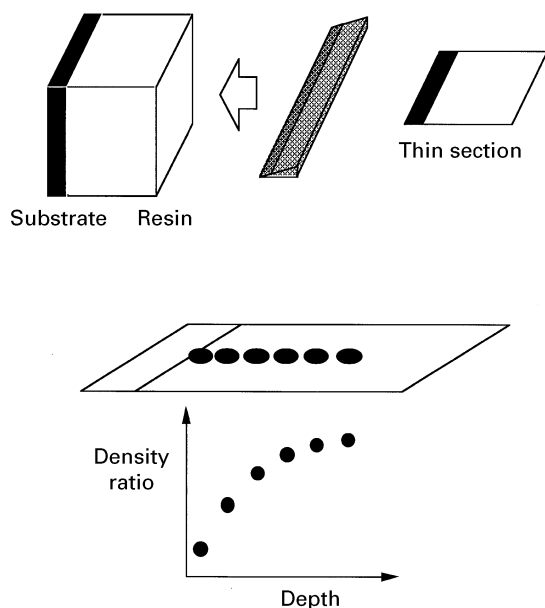


Figure 1 Schematic representation of the sectioning method for FT-IR analysis.

2.2. FT-IR measurements

The infrared analysis of the cured polymer was performed with a Bruker IFS-88 FT-IR spectrometer equipped with a microscope and a narrow bandpass mercury cadmium telluride detector. Thin sections of the polymer were cut in the direction perpendicular to the respective interfaces (aluminium or air interfaces; Fig. 1). These sections were 10 μm thick to allow a transmission analysis with the infrared microscope. Spectra were recorded at varying distances from the interface, using a beam diameter comprised between 30 and 50 μm , at a resolution of 4 cm^{-1} and by averaging about 200 scans. The evolution of the optical density ratio 700/1608 of the infrared bands at 700 and 1608 cm^{-1} , corresponding respectively to styrene-based entities and to DGEBA aromatic groups, was determined. This ratio was therefore representative of the content of polystyrene and residual styrene monomer in the matrix.

2.3. Acoustic scan analysis

Prospects displayed by microacoustic techniques [4–6] visualizing local variations of elastic modulus, led to the use of the scanning acoustic microechography for the present study of our samples. The analysis was performed by means of an acoustic micro-scan homemade apparatus, schematically represented in Fig. 2. The principle of the analysis was as follows. The sample to be analysed was immersed in water which acted as a coupling fluid. An incident acoustic pulse wave, generated by a focusing transducer (Fig. 3) with a small conical incident angle (13.5°), was reflected at the water/sample interface due to the difference between the mechanical properties of both media in contact. The frequencies generated by the transducers were relatively low, i.e. 15 or 25 MHz in the present

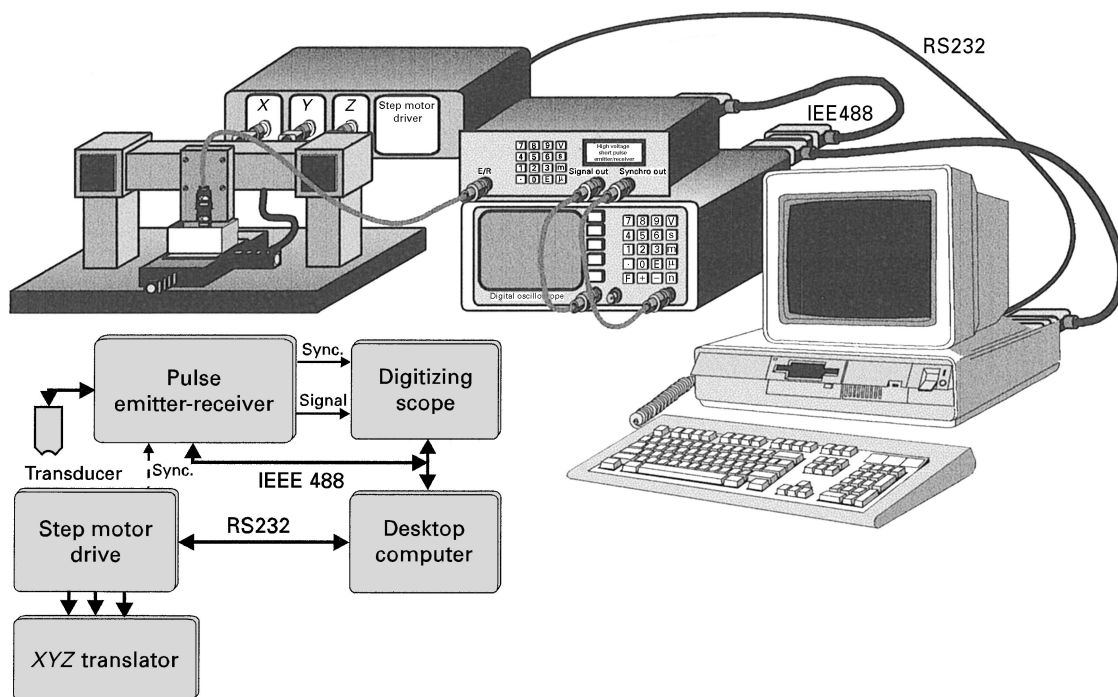


Figure 2 Schematic representation of the acoustic micro-scan device.

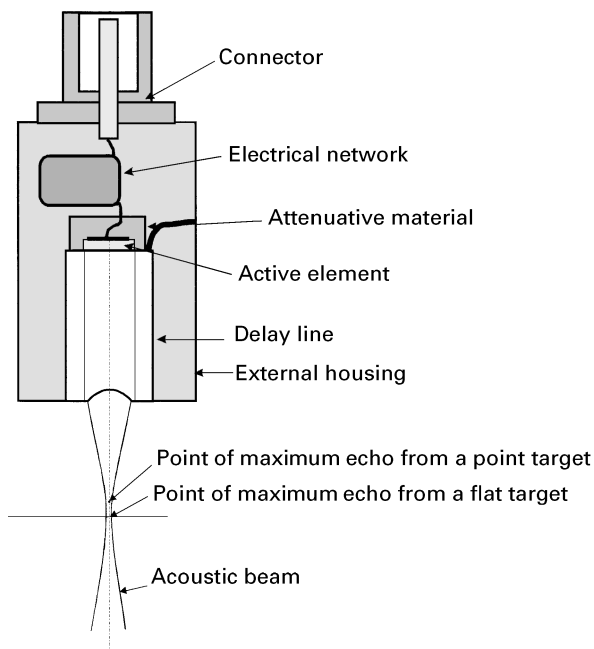


Figure 3 Schematic representation of an acoustic focusing transducer.

case. The pulse width of the generator was set to a shorter duration than half a period of the resonance frequency, f , of the transducer and the pulsation frequency was determined in order to avoid the overlapping of the reflected signals. In the case of a 13 mm focus length, the delay between the emitted signal and its echo was about 17 μs . Thus, a pulsation frequency value of 5 kHz (200 μs) was chosen. In addition to the resonance frequency, f , the most important characteristics of the transducer were the aperture diameter, D , and the focus length, F . Hence, the diameter, d , of the spot (at -6 dB) at the focus point is given by [7]

$$d = \frac{FV}{Df} \quad (1)$$

where V is the propagation rate of the longitudinal waves in the coupling fluid. In our case, the diameter of the focal spot was approximately 125 μm , for $f = 25$ MHz, $D = 6$ mm and $F = 13$ mm. To choose the working frequency, a compromise has to be made between resolution and sensitivity, assuming that the sensitivity decreases when a transducer with higher resonance frequency is used.

Neglecting the effect of the transverse waves, the apparatus allowed us to determine directly the energy of the reflected beam and then the coefficient of reflection, R , of the interface, knowing that the amplitude of the measured electrical signal was proportional to the acoustic pressure. In fact, the output signal is proportional to the integral of the product of the reflection coefficient and the pupil function in a square, taken over the semi-aperture angle of the lens. Because this angle is quite small (13.5°) and the reflection coefficient is practically constant over this range, it can be considered, to a first approximation, that the output signal is proportional to the reflection coefficient, R . The error incurred is a priori less than about 1% in this

range. This reflection coefficient, R , or reflectivity, of the interface, for a normal incidence, is expressed as a function of the acoustic impedance, Z , of both media in contact (subscripts w and s for water and solid respectively), according to

$$R = \frac{Z_s - Z_w}{Z_s + Z_w} \quad (2)$$

with $Z = \rho V$, the acoustic impedance of a given material being equal to the product of its density, ρ , with the rate, V , of acoustic wave propagation inside it. For longitudinal waves, this rate of propagation, V , is given by

$$\begin{aligned} V &= \left(\frac{E}{\rho}\right)^{1/2} \left[\frac{(1-\nu)}{(1+\nu)(1-2\nu)}\right]^{1/2} \\ &= \left(\frac{K}{\rho}\right)^{1/2} \end{aligned} \quad (3)$$

where K , E and ν are the bulk modulus for uniaxial deformation, elastic modulus and Poisson's coefficient of the solid, respectively. It is worth mentioning that all these mechanical properties are usually frequency-dependent and, thus, can be greatly affected by the experimental conditions of the acoustic experiment and, certainly, very different from those determined on the bulk material subjected to quasi-static deformations. Because water was always used as the coupling liquid, Z_w was a constant ($Z_w = 1.48 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ at 20°C) and, thus, all the variations of the surface reflectivity, R , were directly related to the variations of the mechanical properties of the solid material. In fact, although the acoustic analysis was performed on "half-space" specimens, only a thin superficial layer of the material was concerned, the thickness of this layer being of the order of the wavelength, i.e. about 100 μm for a frequency of 25 MHz.

Experimentally, a focusing transducer (V324 SU for 25 MHz and V260 SM for 15 MHz, Panametrics), allowing analysis of a small surface area of maximum diameter equal to about 130 μm (focal spot diameter, Fig. 3), was used. Only the maximum amplitude of the acoustic signal was taken into account. Acoustic imaging of the sample surface was obtained by scanning, using a computer-controlled XY table. Each elementary measurement was materialized in the resulting images by a coloured pixel representing a square area of size $12.5 \times 12.5 \mu\text{m}^2$. Sixteen different colours, each of them corresponding to a given level of surface reflectivity, were used. In addition, it was also possible to determine profiles of the variation of surface reflectivity in one direction (along a line) by converting each colour into reflectivity data. These latter were calculated from an arbitrary level and, thus, only comparative data were obtained. The precision of the measurement was estimated on the order of 2% according to the following reasoning. The reflected signal, after amplification and peak value extraction, is converted into a 6 bits digital value (64 enabled discrete states). Assuming that the peak voltage remains into the 0–1 V range of the analogical digital converter, we can expect an accuracy of $1/64$ V, i.e. less than 2% of the full-scale value. To avoid acoustic diffusion

phenomena due to surface roughness, samples were usually embedded into an epoxy resin and polished before analysing.

3. Results and discussion

3.1. FT-IR results: existence of an interphase

FT-IR analysis of thin sections cut near the bottom of the sample in contact with the aluminium surface, on the one hand, and near the top of the same sample in contact with air, on the other hand, leads to the determination of the evolution profile of polystyrene (including residual styrene monomer) in the polymer from both surfaces to the bulk. Such evolution profiles are presented in Fig. 4, where the optical density ratio 700/1608 (PS content) is plotted against distance from the interface. It immediately appears that, in agreement with previous results [1, 8] and whatever the nature of the interface considered, strong variations of the content of styrene-containing entities are observed from the surface to the bulk. Near the interface, the PS content seems to be very low. This PS content increases with the distance from the interface to reach a plateau value at a depth on the order of 300 μm . In a previous paper [1], such a variation has been clearly confirmed by the determination, as a function of depth, of the conversion rate of vinyl groups contained in the prepolymer by means of solid-state ^{13}C NMR. A thermal effect leading to a diffusion phenomenon of styrene monomer from the surface to the bulk during the cross-linking process has been invoked to explain the existence of such an interphase. It is clear that the VE cross-linking reaction is exothermic (exotherm temperature reaches about 140 $^{\circ}\text{C}$ in the core of the samples) and always started in the bulk of the specimen. Hence, due to a higher rate of cross-linking in the core, it is conceivable that diffusion of styrene monomer could occur, leading finally to the establishment of a concentration gradient in the skin. Such a process, however, is yet not clearly understood nor quantified. It is also worth mentioning that, in the case of the free surface of the specimen in contact with air, because styrene monomer exhibits a low vapour pressure, the evaporation of these monomers during curing can additionally affect the profile of PS content near the interface.

Nevertheless, all these results indicate that the morphological structure of the polymer network in the interfacial zone is deeply affected by the variations of the relative concentrations of both VE and PS components. This leads to a decrease in the density (because the density of pure VE resin is higher than that of PS) and to an increase in the elastic modulus of the network from the skin to the core of the sample, as experimentally determined in previous studies [1, 8]. The problem of the variation of mechanical properties of the polymer in the interfacial layer is now revisited by means of acoustic scan analysis.

3.2. Acoustic scan analysis

3.2.1. Preliminary observations

A block of resin was first cut in two equivalent parts in a direction perpendicular to the interfaces and one of

both resulting new surfaces is slightly polished and analysed by the acoustic micro-scan method. The acoustic image obtained by scanning and corresponding to the side of the sample in contact with air is presented in Fig. 5. A uniform variation of colours (or levels of grey) is clearly observed from the surface to the bulk. Each measurement of the surface reflectivity during scanning corresponds on the graph to an elementary coloured square of size 12.5 μm . Therefore, although the scatter on the location of the sample edge is large, the thickness of the altered interphase could be estimated to be equal to about 400 μm in good agreement with previous FT-IR results. Similar observations are obtained for the side of the sample in contact with aluminium. According to Equations 2 and 3, such a variation is related to the evolution, as a function of depth, of the density, Young's modulus and/or Poisson's coefficient of the resin. At this stage of the study, it is impossible to determine which physical or mechanical parameter of the resin is mainly responsible for this variation. From present FT-IR and previous NMR [1] analyses, it is known that the existence of such an interphase is related to the local concentration of styrene-containing entities (mainly

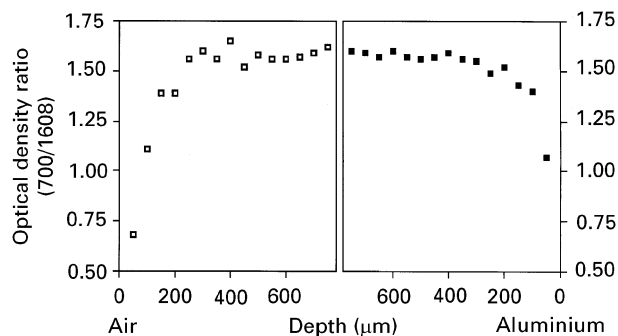


Figure 4 FT-IR analysis of a vinyl ester resin (styrene content 45 wt %) cured in contact with air and aluminium.

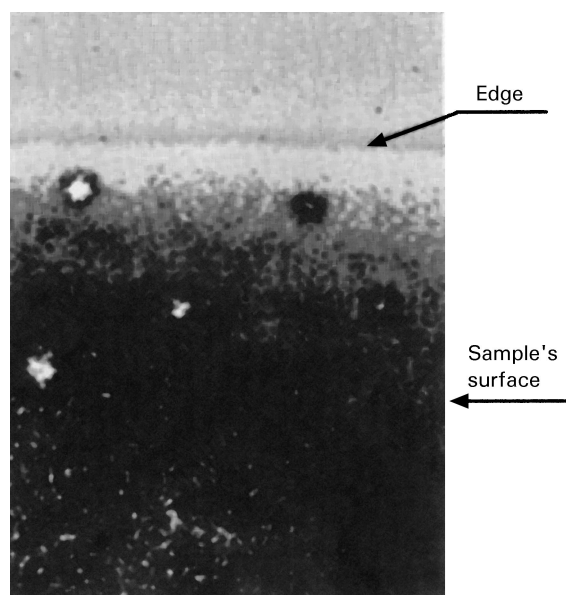


Figure 5 Acoustic image of the interphase near the surface of the resin (styrene content 45 wt %) in contact with air.

PS). Hence, it is first necessary to determine the acoustic properties of bulk resin based on different initial contents of styrene monomer. This is examined in the next section.

3.2.2. Effect of styrene content on the acoustic reflectivity of vinylester resin

Four samples of vinylester resins containing different initial contents of styrene monomer, i.e. 35, 40, 46 and 50 wt %, cut in the bulk of larger specimens, embedded into the same block of epoxy resin and polished, were simultaneously analysed by acoustic scanning. The resulting images obtained with a frequency of 15 MHz are presented in Fig. 6. Because the colours (level of grey) of the specimens are clearly different, it is obvious that average reflectivities of the samples are different and, therefore, vary with styrene content.

The variation of the average acoustic reflectivity of the vinylester resin versus styrene content is plotted in Fig. 7. It appears that this acoustic reflectivity seems to decrease linearly with styrene content in the

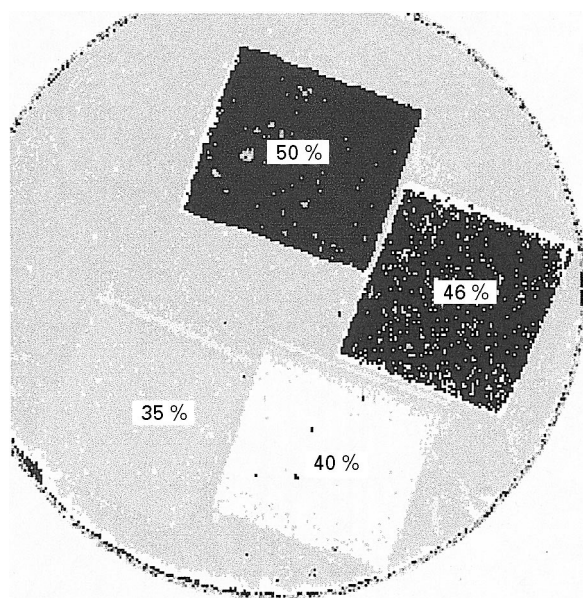


Figure 6 Bulk acoustic reflectivity of vinylester resins for different styrene contents ranging from 35–50 wt %.

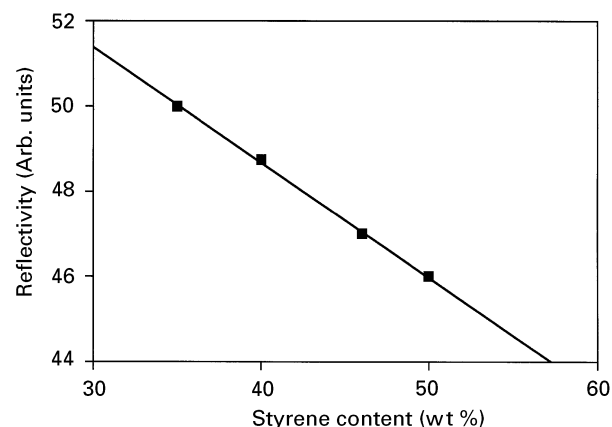


Figure 7 Variation of bulk acoustic reflectivity of vinylester resins with styrene content.

interval considered. A least-square linear fitting method applied to these data leads to a high value of the fitting coefficient, r , close to 0.9995, indicating that the decrease is actually linear. To a first approximation, this straight line can be considered as a master curve, allowing us to estimate the variation of styrene content as a function of depth in the interfacial layers previously pointed out.

As an example, a profile of acoustic reflectivity, measured along a line perpendicular to the interface, of a specimen containing 45 wt % styrene (similar to that presented in Fig. 5), from the surface cured in contact with air to the bulk, is given in Fig. 8. This profile indicates clearly that the surface reflectivity of the vinylester resin decreases from the surface to the core in good agreement with the fact that the concentration of styrene-containing entities (PS) increases in the same direction. Hence, using the master straight line given in Fig. 7, it is possible to estimate the variation of PS content versus the depth in such an interphase, although the scatter in the results is large. The results are presented in Fig. 9. They clearly show that the PS content increases smoothly from the surface to reach, at a depth of the order of 400–500 μm , about 40–45 wt %, as expected. The extrapolation of the variation at a depth equal to zero leads to an estimated “surface concentration” of PS equal to about 20–25 wt %, i.e. half that in the bulk. Similar results were obtained on all the samples, whatever the side studied, in contact with air or with aluminium. Apart from the thickness of the interphase, which could vary with the experimental conditions and the nature of the substrate in contact with it, such profiles of PS content variation are in good agreement with those obtained previously in vinylester resin in contact with glass plates and determined from the variation of the density of the resin [8]. In particular, about the same estimated value for the “surface concentration” of PS (20 wt %) is obtained.

It is known [2] that the bulk density, ρ , decreases, whereas the elastic modulus, E , of the resin increases with the content of styrene monomer initially added to the uncured polymer. The density of our samples linearly decreases as a function of styrene content, from 1151 (35 wt % PS) to 1133 kg m^{-3} (50 wt % PS).

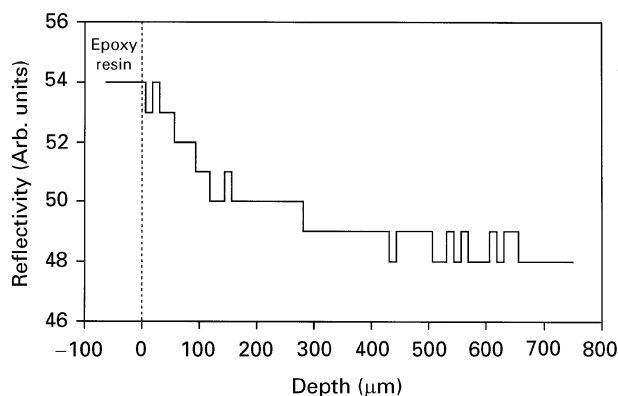


Figure 8 Variation of acoustic reflectivity with depth from the surface (initially in contact with air) to the bulk of a vinylester resin (styrene content 45 wt %).

According to Equations 2 and 3, the linear decrease of surface reflectivity, R , with this styrene monomer content, or, in other words, with PS content in the cured resin, indicates that necessarily the impedance, Z_s , of the resin also decreases. It can be considered that the Poisson's coefficient, ν , of the resin is kept constant [9] and close to 0.40, whatever the PS content. Thus Z_s is equal to $(k\rho E)^{1/2}$, where k is a constant, although it is worth mentioning that a small variation of ν could significantly affect the value of this coefficient. Therefore, to a first approximation, all the results show that the increase in the elastic modulus of the resin with PS content is not able to compensate the decrease of its density, ρ , in the same conditions. The dependence on the PS content ($[PS]$) of the acoustic impedance Z_s of the resin can be written as

$$Z_s \approx (k\rho E)^{1/2} \approx \frac{\alpha[PS] + \beta}{\gamma[PS] + \delta} \quad (4)$$

where α, β, γ and δ are factors depending on acoustic impedance, Z_w , of water, and slope and intercept at the origin of the straight line corresponding to the variation of R versus $[PS]$. Hence, in principle, knowing the variation of ρ versus $[PS]$, the corresponding variation of the Young's modulus of the resin could be determined for a given frequency of the incident acoustic beam. However, in practice, because reflectivity data are calculated by comparison with an arbitrary level, it is difficult to obtain accurate values of elastic modulus from direct acoustic measurements. In the near future, by analysing the total acoustic signal and not its maximum amplitude as it has been done until now, it could be possible to reach absolute values of the surface reflectivity, and thus direct measurements of Young's modulus of solids, provided that both density and Poisson's coefficient of these solids are known. Nevertheless, in previous studies [2, 8] the variation of the elastic modulus of bulk vinylester resin as a function of styrene content (or $[PS]$) has been determined and fitted according to the following empirical law

$$E \approx -4.23 + 0.309[PS] - 0.003[PS]^2 \quad (5)$$

where E is in GPa and $[PS]$ in wt %. However, it is worth mentioning that this relationship was established for styrene content ranging from 35–55 wt % and, thus, its validity for any other value of styrene content can be controversial.

Therefore, the results presented in Fig. 9 can lead to the estimation of the gradient of elastic modulus of the vinylester network in the interfacial layer, according to Equation 5. The resulting variation of E as a function of depth from the interface is given in Fig. 10. It can be observed that the Young's modulus of the polymer near the surface is as low as about 1 GPa, while the expectable value of E of about 3.5 GPa for the resin containing 45 wt % styrene [2] is reached in the bulk. It is worth mentioning that quite similar results were obtained by Knollman and Hartog [10] for shear modulus of epoxy resin on aluminium substrates and measured by an ultrasonic Rayleigh waves method as a function of the layer thickness of the

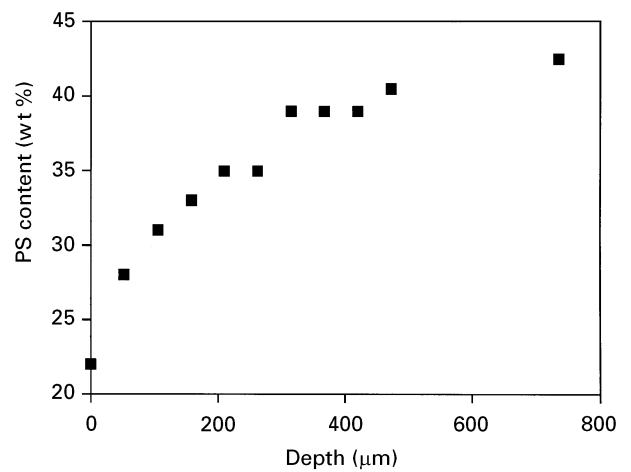


Figure 9 Variation of polystyrene concentration with depth from the surface to the bulk.

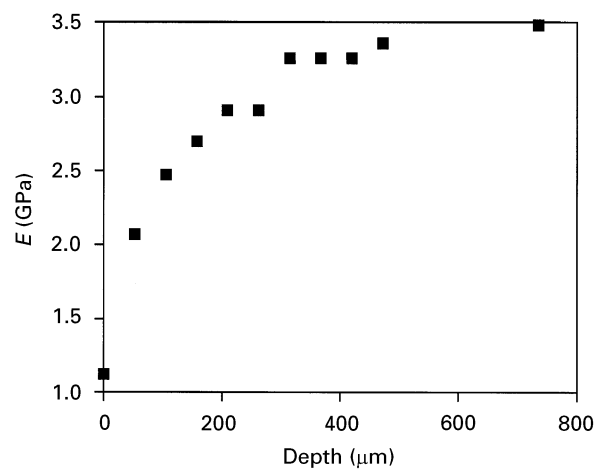


Figure 10 Estimated variation of the elastic modulus of the resin as a function of depth from the surface to the bulk.

epoxy adhesive. It is thus clear that such a pronounced variation of the mechanical properties of the vinylester network in the interfacial region can strongly affect all the subsequent load-transfer phenomena in multi-materials involving such a resin, for example glass fibre-reinforced composites.

3.2.3. Thickness of the interphase

Another phenomenon concerning the thickness of the interfacial layer as a function of styrene content is observed. Although the scatter on such a quantity is large (of the order of $\pm 50 \mu\text{m}$), it appears clearly in Fig. 11 that the extent of the interphase at both types of surfaces, i.e. in contact with air and aluminium, depends strongly on the initial styrene monomer content. The thickness of the modified zone seems to increase with styrene content, from about 100–500 μm . However, a sudden drop of this thickness is clearly evinced for a styrene content close to 50 wt %. This can be compared to previous observations [2] showing that the consumption rate of carbon–carbon double bonds of VE polymer during curing reaches its highest values, in other words the cross-linking reaction is more efficient, for styrene contents ranging

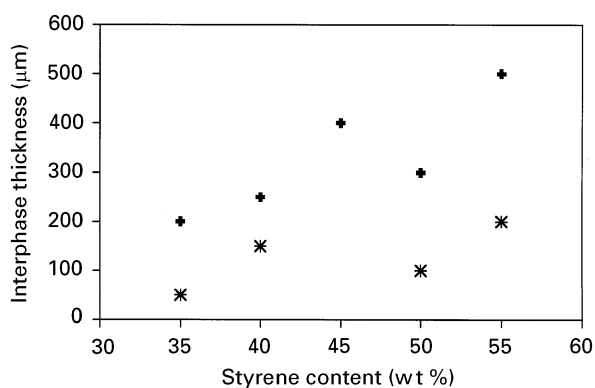


Figure 11 Variation of the interphase thickness at both sides (in contact with (+) air and (*) aluminium) of specimens with styrene content.

from about 45–50 wt %. Such results seem to indicate that the process of styrene diffusion from the specimen surface to the bulk during curing is strongly related to the complex phenomena of homopolymerization and cross-linking, taking place first in the core of the specimen and then extending from the bulk towards its edges. Finally, as already stated, the fact that the interphase thickness is larger for the side of the sample in contact with air than for that in contact with aluminium, can be attributed to the evaporation of styrene monomer in the former case, because of the low vapour pressure of this product.

4. Conclusion

In the present study, the existence of thick interphases in vinylester resins in the vicinity of a substrate surface (aluminium) as well as of its free surface (in contact with air) was first confirmed by means of microscopical FT-IR spectroscopy. Such interphases stem from the variations, as a function of depth from the surface to the bulk, of the relative concentrations of vinylester polymer and styrene-containing entities, due to the migration of styrene monomers towards the core during the cross-linking process, as previously proposed [1]. Then the evolution of physical and mechanical properties of the resulting resin network were studied by means of an acoustic micro-scan technique. This method allows us to analyse locally the acoustic reflectivity of specimen sections, cut perpendicular to both

interfaces. Images, obtained by scanning near the edges of all the samples studied, clearly confirm the existence of these interfacial layers. The measurement of the average acoustic reflectivity of bulk vinylester resins, containing different amounts of styrene monomers before curing, leads to the determination of the variation profiles of polystyrene concentration, after curing, from the surface to the bulk. It appears that, in each case, the polystyrene content increases smoothly from a value of about 20 wt % near the surface to reach, at a depth ranging from 100–500 µm, its actual level, i.e. 45 wt % for the standard case. An estimation of the variation of the elastic modulus of the resin, from the surface to the bulk, and based on previous data relating the elastic modulus of a vinylester resin to its polystyrene content, is also proposed. Moreover, it is observed that the thickness of the interfacial layer is dependent on the initial styrene content, indicating that the process of diffusion of styrene monomer from the specimen surface to the bulk is strongly affected by the polymerization and cross-linking chemical reactions during curing. Finally, this study clearly shows that the acoustic scan technique is a powerful tool to analyse the morphological variations of polymer materials, in the bulk or near a surface.

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