polymer papers

Ultrasonic study of the interface between two grafted polymers

S. Akker and J. Arman*
Laboratoire de Physique des Matériaux Industriels, Centre Universitaire de Recherche Scientifique, Avenue de l'Université, 64000 Pau, France

and Ph. Monge
Service d'Etudes et de Réalisations Industrielles, Centre Universitaire de Recherche Scientifique, Avenue de l'Université, 64000 Pau, France
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When a sound wave is reflected by a multilayered system, minima of the reflection coefficient corresponding to the propagation of surface waves within the system are observed. We carried out reflectivity measurements on immersed plates made up of two grafted polymers, polyamide 12/poly(ethylglycidyl methacrylate). The experimental curves obtained are discussed and compared with the theoretical predictions to determine the characteristics of the interface between the two polymers.

(Keywords: ultrasound; interface; grafted polymers; reflection; multilayered system)

INTRODUCTION

The transmission and reflection of a sound wave by a multilayered system formed of elastic media is a vast subject, various aspects of which have been dealt with in a number of publications[1–10]. In particular, research has been conducted into the reflection of an oblique wave impinging on the plane interface between a fluid and the first medium of the system.

Resonance frequencies[11–14] can be observed by means of reflectivity measurements carried out at a constant angle of incidence.

Working at a fixed frequency, it is possible to demonstrate the existence of critical angles: the reflection coefficient presents minima for certain angles corresponding to the existence of a Rayleigh- or Lamb-type surface wave depending on the thickness of the system through which the sound propagates.

The theoretical aspect of the problem was examined in elastic media in order to establish dispersion curves yielding the phase velocity as a function of the frequency–thickness product. Reflectivity measurements were also carried out[15,16].

Experiments were performed on samples comprising a substrate covered with a fine layer of metal or adhesive and on bilaminar configurations involving two metal plates welded or bonded together[17–20].

Extending these studies to systems made up of viscoelastic media is useful to provide a non-destructive method to verify adhesion between two materials, or to determine the viscoelastic parameters of a layer within the system.

In this paper we present a comparative analysis of experimental results and the curves obtained from theoretical calculations for a particular configuration composed of two viscoelastic materials placed in contact, one of which is able to graft with the other.

* To whom correspondence should be addressed

THEORY

Reflection and transmission of a wave for an n*-layered system*

Establishing equations describing the reflection and transmission of a wave between a fluid and a multilayered system is based on the continuity of displacement and stress[2], or the pressure and acoustic impedance[15] at the interfaces between the different layers.

This study concerns the interaction between a plane acoustic wave and a system made up of n distinct elastic layers, which are assumed to be immersed in a fluid. Each layer is assumed to be homogeneous, isotropic, and of thickness d_j ($j = 1, 2, 3, \ldots, n$). The sound source is located in the $(n+1)$ fluid medium, and vibrates with angular frequency ω (*Figure 1*).

In the case of a harmonic wave, the velocity of particle displacement within a homogeneous medium is written in the form:

$$\boldsymbol{v}_j = \text{grad}\ p_j / i\omega\rho_j \tag{1}$$

in which ρ_j is the density of the medium j and p_j is the acoustic pressure defined for the medium j by:

$$p_j = (A_j e^{-i\beta_j z} + B_j e^{i\beta_j z}) e^{i(\sigma_j x - \omega t)} \tag{2}$$

in which A_j and B_j are constants and β_j, σ_j are given by:

$$\beta_j = k_j \cos\theta_j \qquad \sigma_j = k_j \sin\theta_j \tag{3}$$

k_j is the wavenumber given by $k_j = \omega/c_j$, where c_j is the velocity of the longitudinal wave in medium j.

θ_j is given by the Snell–Descartes law:

$$k_{n+1} \sin\theta_{n+1} = k_j \sin\theta_j \tag{4}$$

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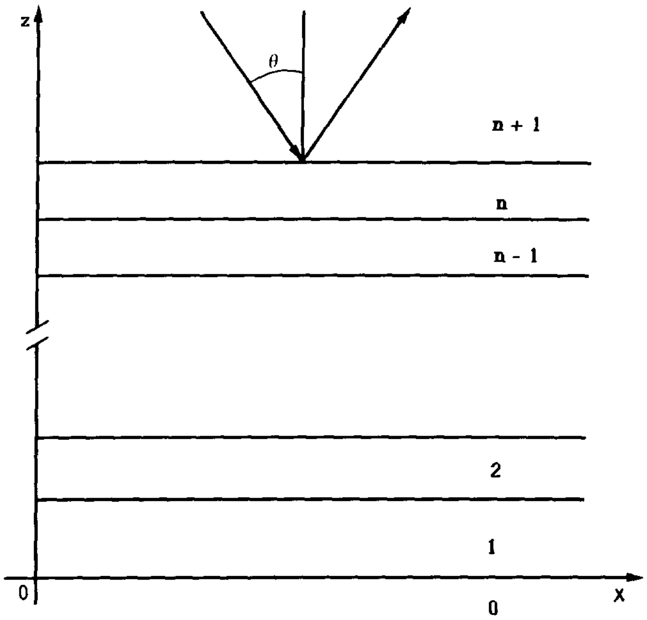

Figure 1 Schematic diagram of *n* elastic layers subjected to an incident acoustic wave from above

Figure 2 Geometry of the simplified problem

in which θ_{n+1} is the angle of incidence of the wave in the upper fluid $(n+1)$.

The acoustic impedance in the medium j is defined by:

$$Z_j = -(p_j/v_{jz}) \tag{5}$$

where

$$v_{jz} = (1/i\omega\rho_j)\left(\frac{\partial p_j}{\partial z}\right)$$
$$= (\beta_j/\omega\rho_j)(B_j e^{i\beta_j z} - A_j e^{-i\beta_j z}) e^{i(\sigma_j x - \omega t)} \tag{6}$$

in which v_{jz} is the component of $\boldsymbol{v}_j$ after z.

The boundary conditions of a wave from one medium to another can be expressed as zero variation of the acoustic pressure and impedance at the interface between the two media.

The configuration in *Figure 1* can be simplified to give the representation in *Figure 2* in which Z_m is the acoustic impedance of the medium formed by the $n-1$ layers and the lower fluid $(j=0)$.

The continuity of the acoustic impedance at $z=0$ and substitution of equations (2) to (6) can be used to establish a relationship between the constants A_n and B_n:

$$B_n/A_n = (Z_n - Z_m)/(Z_m + Z_n) \tag{7}$$

in which

$$Z_n = \frac{\omega\rho_n}{k_n \cos\theta_n} \tag{8}$$

Equations (2) and (6) to (8) are used to calculate the acoustic impedance of medium n at $z=d_n$, known as the 'input impedance' and defined by:

$$Z_{in}(n) = -(p_n/v_{nz})_{z=d_n} \tag{9}$$

$$Z_{in}(n) = \frac{(Z_m - iZ_n \tan k_{nz}d_n)}{(Z_n - iZ_m \tan k_{nz}d_n)} Z_n \tag{10}$$

Z_m is simply the input impedance of layer $(n-1)$: $Z_m = Z_{in}(n-1)$. Consequently, a recurrence relationship has been obtained yielding $Z_{in}(j)$ as a function of $Z_{in}(j-1)$, $(j=1, 2, \ldots, n)$.

The classical definitions of reflection and transmission coefficients are given by the expressions[15]:

$$R = \frac{(Z_{in}(n) - Z_{n+1})}{(Z_{in}(n) + Z_{n+1})} \tag{11}$$

$$T = \frac{2Z_{n+1}}{(Z_{in}(n) + Z_{n+1})} \tag{12}$$

Therefore, if the input impedance Z_{in} is known, R and T can be determined. A simple calculation gives an expression of Z_{in} for systems with two $(n=2)$ and three $(n=3)$ layers[15];

$$Z_{in}(2) = (A/B)Z_2 \tag{13}$$

in which

$$A = Z_0Z_1 - Z_0Z_2P_1P_2 - i(Z_1^2P_1 + Z_1Z_2P_2)$$
$$B = Z_1Z_2 - Z_1^2P_1P_2 - i(Z_0Z_2P_1 + Z_0Z_1P_2)$$

$$Z_{in}(3) = (C/D)Z_3 \tag{14}$$

where

$$C = (Z_0Z_1Z_2 - Z_0Z_2^2P_1P_2 - Z_0Z_2Z_3P_1P_3 - Z_0Z_1Z_3P_2P_3) - i(Z_1^2Z_2P_1 + Z_1Z_2^2P_2 + Z_1Z_2Z_3P_3 - Z_1^2Z_3P_1P_2P_3)$$

$$D = (Z_1Z_2Z_3 - Z_1^2Z_3P_1P_2 - Z_1^2Z_2P_1P_3 - Z_1Z_2^2P_2P_3) - i(Z_0Z_2Z_3P_1 + Z_0Z_1Z_3P_2 + Z_0Z_1Z_2P_3 - Z_0Z_2^2P_1P_2P_3)$$

The values of Z_j are impedances of the media j and the P_j are given by:

$$P_j = \tan(k_{jz}d_j)$$

in which d_j is the thickness of layer j.

EXPERIMENTAL

Experimental study of reflectivity was performed at fixed frequency, by varying the angle of incidence; angular analysis of the amplitude of the reflected signal yields critical angles θ_i for which the amplitude passes through a minimum, and this enables the phase velocities c_i of the plate's specific modes to be obtained. It should be recalled that the angle of incidence θ_i and the phase velocity c_i are connected by the Snell–Descartes relationship:

$$\sin\theta_i = c_{fluid}/c_i \tag{15}$$

The measuring cell is represented in *Figure 3*; it comprises a cylindrical vessel, with a sample holder fixed in the centre, mounted on a goniometer, and two adjustable transducer mountings. The transmitter is fixed to the goniometer platform; the movable receiver is rotated around the same axis as the sample. The transducers used have a central frequency of 2.05 MHz.

This apparatus limits the domain of angular exploration to the interval 15–70°, this limit being due to the space taken up by the transducer mountings. The immersion

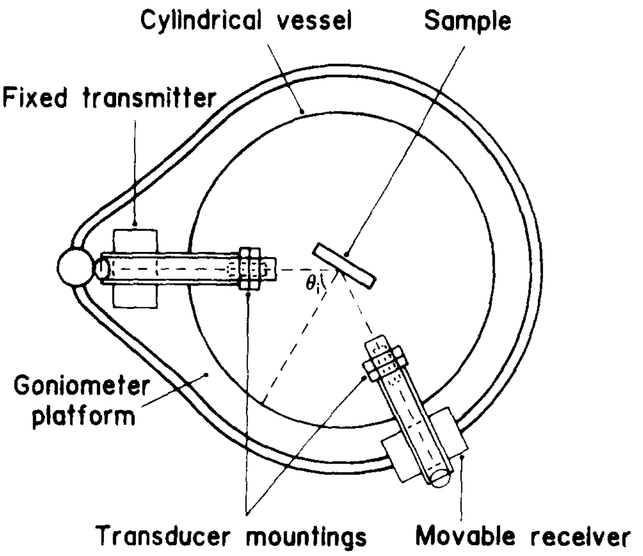

Figure 3 Experimental apparatus for determining reflected amplitude *versus* the angle of incidence

Table 1 Physical characteristics of the polymers

Material	Melting point (°C)	Density
Polyamide 12 (PA12)	176	1.01
Poly(ethylglycidyl methacrylate) (EMAG)	125	0.86

liquid (sound coupling medium) selected is silicone oil ($c_{fluid} = 1000 \pm 5$ m s^{-1}); this relatively low velocity makes it possible, in accordance with relation (15), to obtain a maximum number of specific modes.

For our material we chose polyamide 12 (PA12) and a poly(ethylglycidyl methacrylate) (EMAG), the physical characteristics of which are presented in *Table 1*. They were supplied to us in the form of granules. The samples are shaped by compression, under the combined action of pressure and temperature, in such a way as to produce rectangular plates of PA12 and EMAG of varying thicknesses between 1 and 5 mm. The PA12–EMAG assemblies are then made from these plates by bringing them into contact at the melting point of EMAG, where the opening of the glycidyl epoxide group causes a grafting phenomenon at the interface between PA12 and EMAG[21,22].

RESULTS AND DISCUSSION

Experimental results

Preliminary measurements obtained by reflection on plates of aluminium and copper yielded the critical angles determined by Knollman and Hartog[17].

The experimental apparatus was used to assess the acoustic characteristics of PA12 and EMAG; *Figure 4* represents the variations of longitudinal wave travel time as a function of sample thickness. The slope of the straight line gives the wave propagation velocity for each material. The characteristics measured are presented in *Table 2*. The precision on the velocity and attenuation can be estimated respectively to 20 m s^{-1} and 50 dB m^{-1} for the longitudinal measurements and to 25 m s^{-1} and 80 dB m^{-1} for the transversal ones. It should be stressed that the transverse velocities c_t in the two materials are lower than the velocity in the immersion fluid, which explains the absence of critical angle for the transverse wave.

Figures 5–9 display the measurements of reflected wave *versus* angle of incidence performed on a few of the samples selected for our study.

The curves in *Figures 5* and *6* relating to simple plates of PA12 and EMAG, 1.82 and 1.18 mm thick respectively, show the existence of two minima corresponding to angles smaller than the longitudinal critical angle for each sample. *Figures 7* and *8* concern a sample comprising both the above-mentioned plates; the number of minima observed depends on the first plate encountered by the incident wave. For PA12 (*Figure 7*), two minima were found for the 1.82 mm thick plate on either side of a third minimum. At the upper angles at the longitudinal critical

Table 2 Ultrasonic characteristics of the polymers

Material	c_l (m s^{-1})	θ_l (deg)	α_l (dB m^{-1})	c_t (m s^{-1})	α_t (dB m^{-1})
PA12	2160	27.5 ± 0.5	1510	850	1850
EMAG	1880	31.9 ± 0.5	1520	700	2750

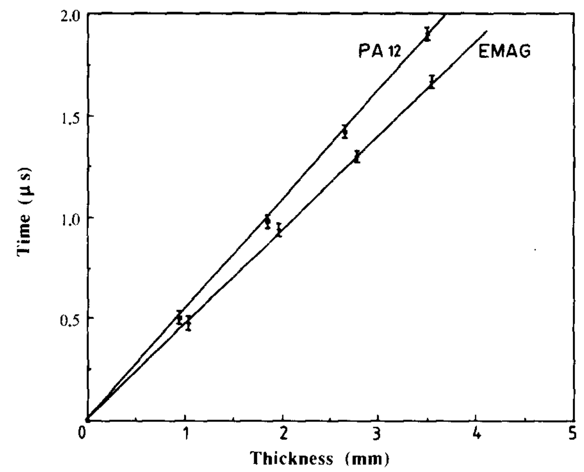

Figure 4 Longitudinal travel time display *versus* thickness of two plates PA12 and EMAG immersed in silicone oil

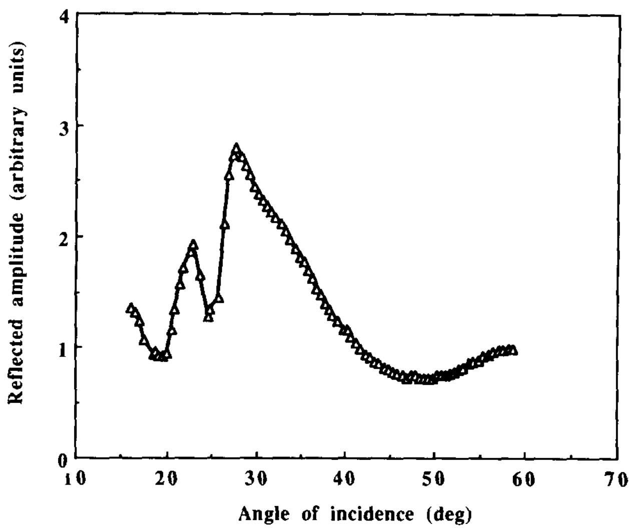

Figure 5 Reflected amplitude from a single PA12 1.82 mm thick plate immersed in oil as a function of the angle of incidence

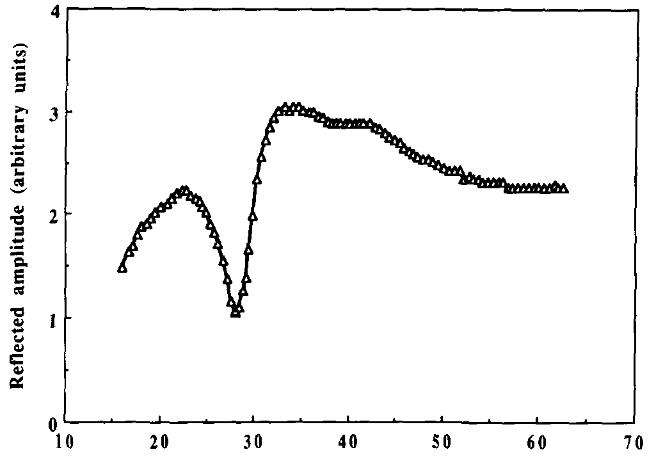

Figure 6 Reflected amplitude from a single EMAG 1.18 mm thick plate immersed in oil as a function of the angle of incidence

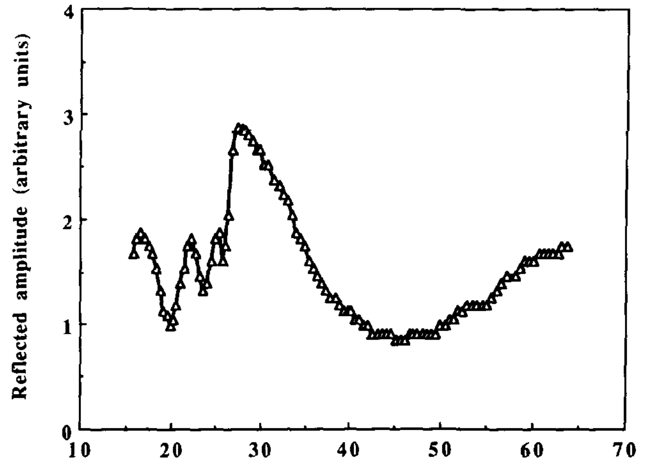

Figure 7 Reflected amplitude from a two-layered grafted sample PA12/EMAG immersed in oil as a function of the angle of incidence. The first plate encountered by the incident wave is PA12

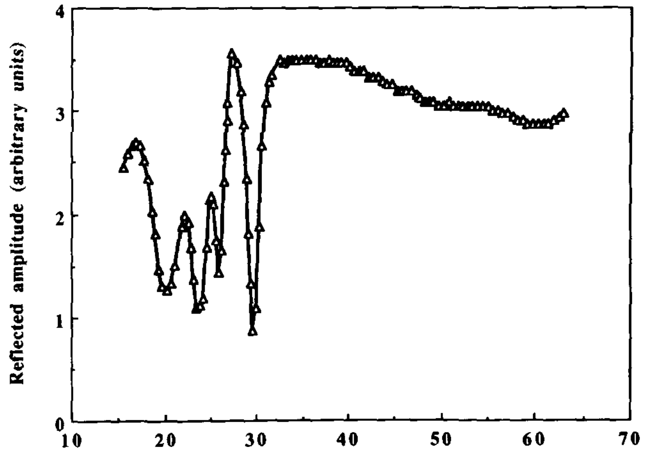

Figure 8 Reflected amplitude from a two-layered grafted sample EMAG/PA12 immersed in oil as a function of the angle of incidence. The first plate encountered by the incident wave is EMAG

angle, the curve coincides with that of PA12 alone. A symmetrical pattern of behaviour is observed if the plate first encountered by the wave is the EMAG plate (*Figure 8*), and since $\theta_{l(\mathrm{EMAG})} > \theta_{l(\mathrm{PA})}$, the minima angles for the two plates in isolation are observed. The two curves reveal the presence of an extra minimum with respect to each plate taken alone.

In order to allow comparison with grafted systems we constructed an assembly of two plates of PA12 and EMAG bonded by a thin layer of Araldite. The curve representing the reflected amplitude as a function of angle of incidence (*Figure 9*) has a different appearance, and particularly has minima and maxima which are less marked than those obtained for assemblies of two grafted polymers.

Discussion of the results

In the first part of this paper we presented a classical theory providing a quantitative description of the propagation of a plane sound wave in a configuration made up of an arbitrary number of elastic or viscoelastic layers[23–25]. This theory enables us to set up a model for the type of sample involved in our study.

A first approach to the problem consists in considering the configuration formed by the assembly of two plates of PA12 and EMAG as a two-layer system immersed in a fluid (in our case silicone oil).

Computation of relationships (11) and (13) can be used to plot the curve presented in *Figure 10* giving the modulus of the reflection coefficient *versus* angle of incidence. It can be observed that unlike the experimental data, the curve presents considerable variations beyond the longitudinal critical angle of EMAG ($\theta_{l(\mathrm{EMAG})}$).

This prompted us to introduce into the model a third layer between the first two and therefore to consider the system as a three-layered system. Relationships (11) and (14) can be used to calculate the reflection coefficient for such a configuration, provided the thickness, density and acoustic characteristics of the inter-layer are known. For the velocity and attenuation of the longitudinal wave, we selected respectively 2000 m s^{-1} and 1500 dB m^{-1}, which are values intermediate between the values corresponding to the two polymers. As regards density and thickness of the interfacial layer, the best fit between theoretical and experimental curves was obtained with a density of 0.95 (intermediate between the densities of the two polymers) and for a thickness of the interfacial layer of (0.09 ± 0.02) mm. As can be seen in *Figure 11*, the fit is not perfect but the shapes of the curves and the positions

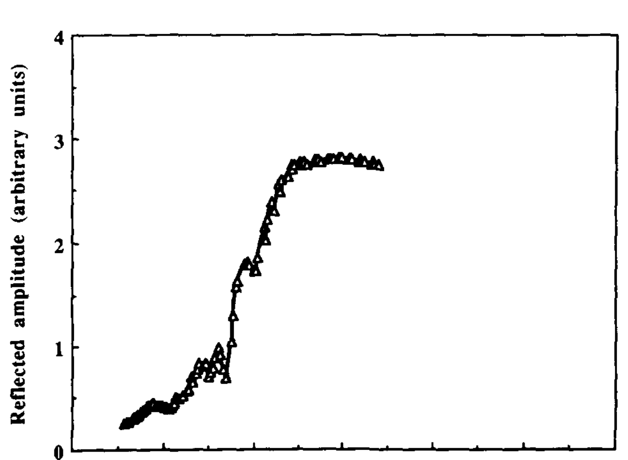

Figure 9 Reflected amplitude from a two-layered PA12/EMAG plate bonded by a thin layer of Araldite and immersed in oil as a function of the angle of incidence

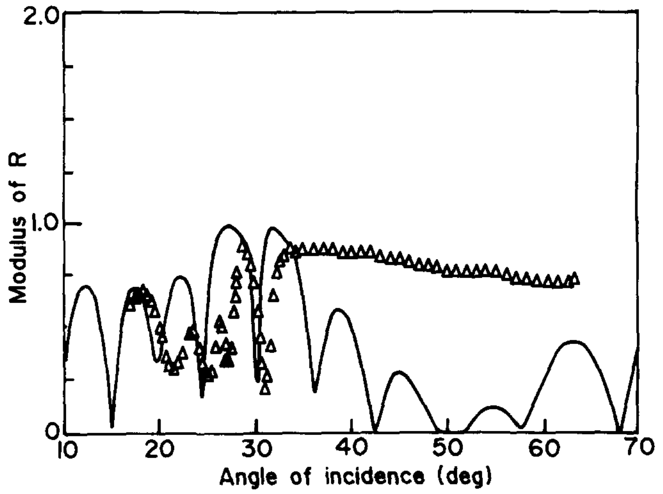

Figure 10 Comparison between reflected amplitude from a two-layered grafted sample EMAG/PA12 (*Figure 8*) and reflection coefficient computed with variable incident angle from a bilaminar configuration EMAG/PA12 immersed in oil

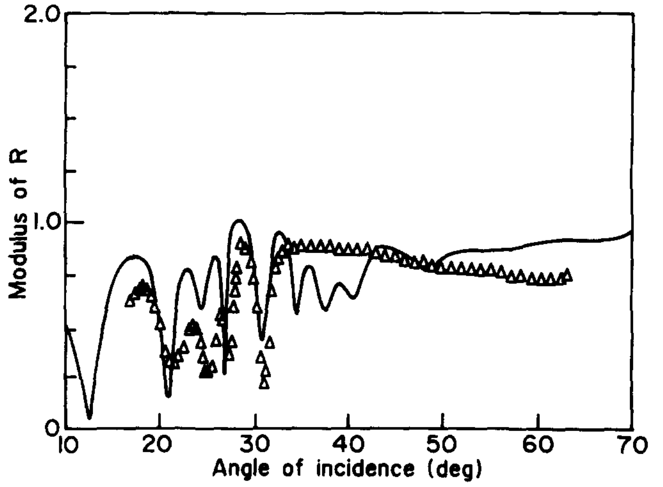

Figure 11 Comparison between reflected amplitude from a two-layered grafted sample EMAG/PA12 (*Figure 8*) and reflection coefficient computed with variable incident angle from a configuration EMAG/IZ/PA12 immersed in oil

of the minima are similar. In order to improve the model, it will be necessary to consider that the different media are also traversed by transverse waves. It will also be necessary to take account of propagation velocity gradients in the interfacial zone, as we have shown experimentally in another publication[26].

CONCLUSIONS

This study was carried out on a two-layer medium made up of two grafted polymers. Reflectivity measurements performed at oblique angles show the existence of minima, the number and position of which depend on the first material encountered by the incident wave. However, experiments carried out on the same polymers bonded together gave rise to different results.

A comparative study of curves obtained from a classical theory based on reflection of a plane sound wave at the interface between two media shows that the phenomenon of grafting introduces an interfacial zone, the properties of which differ from those of the two media in contact.

This study is not complete. Further measurements will have to be performed for varying sample thicknesses and percentages of glycidyl in the EMAG. We also hope to be able to refine the model in such a way as to achieve a more precise definition of the characteristics of the interfacial zone.

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NOMENCLATURE

d_j	thickness of layer j
$\boldsymbol{v}_j$	velocity of particle displacement
p_j	acoustic pressure
ρ_j	density
A_j, B_j	undetermined constants
k_j	wavenumber
Z_j	acoustic impedance
v_{jz}	component of $\boldsymbol{v}_j$ after z
θ_j	angle of incidence
Z_{in}	input impedance
c_l	compressional velocity
c_t	shear velocity
θ_l	longitudinal critical angle
R, T	reflection and transmission coefficients
c_{fluid}	velocity of the longitudinal wave in immersion liquid