JOURNAL OF MATERIALS SCIENCE 21 (1986) 3633–3637

Hydrothermal ageing of CSM-laminate during water immersion – an acousto-ultrasonic study

K. K. PHANI, N. R. BOSE
Central Glass and Ceramic Research Institute, Calcutta 700 032, India

Acousto-ultrasonics represents a very attractive and promising technique for detecting flaws and studying degradation of composite material. Studies of damage under hydrothermal ageing incurred by random fibre-reinforced laminates have been carried out with this technique. It is shown that the "stress wave factor" is a sensitive indicator of random fibre composite strength reduction due to a hydrothermal effect. The same study can be used for the estimation of strength from the data generated under accelerated conditions.

1. Introduction

The effect of environment on composite properties is of great interest in the effective design of polymer matrix composites. Thermal and moisture exposure may lead to a number of undesirable effects such as polymer degradation, fibre–matrix debonding, chemical attack of the fibre surface, etc. [1–4]. Reinforced plastic structures, especially those fabricated by hand lay-up from random mat reinforcement (CSM), frequently contain defects such as resin-rich regions and voids, creating additional defects at the microstructural level during service. Thus assessing the accumulation of damage through non-destructive evaluation (NDE) methods and other techniques is of prime importance for building more economical, but safe, structures.

Two widely used NDE methods for verification of composite integrity as well as degradation due to service conditions are ultrasonic and acoustic emission techniques. The detection of flaws in composites by the conventional pulse-echo ultrasonic technique is difficult due to scattering and it is often difficult to correlate a detected flaw with the overall performance of the composite. Additionally, evaluation of strength loss after ageing may depend on sensing subtle changes that are distributed throughout the material rather than isolated flaws [5]. On the other hand, the acoustic emission (AE) technique can be used to evaluate the integrity of the material as a whole [6, 7] but it has two problems. Firstly, the material structure must be put under stress to produce spontaneous emissions from induced flaw growth and it is difficult to evaluate the effect of this stress on the life of the material being tested, especially in the case of composites. Secondly, the microstructure of a composite exerts a dominating influence on the observed AE signals and no direct correlation can be made between microstructural failure events and the amplitude distribution of the acoustic emission observed [8]. As a consequence, useful information from AE patterns of any composite structure can be derived only if there is already a substantial background knowledge of the behaviour of similar structures under known conditions.

The acousto-ultrasonic technique combines advantageous aspects of both acoustic emission and pulse-echo ultrasonics and at the same time overcomes the problems mentioned above associated with these techniques [5]. All the morphological factors that govern or contribute to material performance are quantitized in terms of a "stress wave factor", which is defined later. The stress wave factor is essentially a relative measure of the efficiency of energy dissipation in a material and reflects the combined effect of flaws or other material anomalies that exist in the volume of material being examined. Strong correlations between stress wave factor and ultimate and interlaminar shear strength in composite laminates have already been reported in the literature [9–14]. This paper reports a study on the degradation of CSM laminates in water at different temperatures through this technique, and correlates the degradation process with the stress wave factor.

2. Equipment and experimental procedure

2.1. Equipment

The experimental equipment comprises an Instron 1185, Universal testing machine (100 KN), Brookefield constant temperature bath Ex.200, and an acousto-ultrasonic test instrument, Model 206 AU, of AET Corporation, USA.

The model 206 AU (Fig. 1) is composed of three main sections: the pulser section, the acoustic emission section and the display section. Using a broadband transducer, the pulser section injects ultrasonic pulses into the composite materials. Each pulse produces simulated stress waves that resemble acoustic emission events. The receiving transducer relays the signals back to the acoustic emission section, where they are electronically processed. The display section consists of an oscilloscope which displays the continuously repeating bursts of simulated stress waves and includes a $3\frac{1}{2}$ digit LED display which can be selected

0022–2461/86 $03.00 + .12

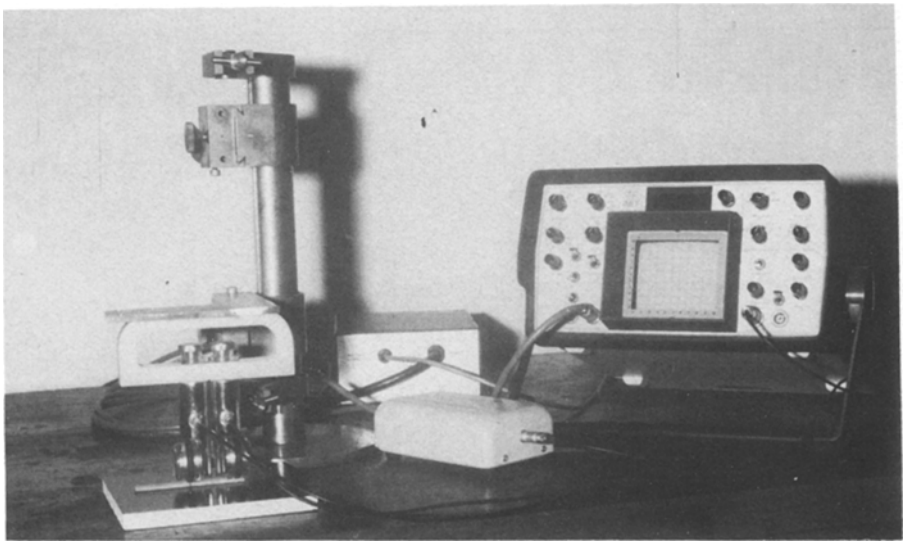

Figure 1 AET model 206 AU with wheeled sensor fixture.

to give counts, events, threshold voltage and signal level (rms) voltage.

2.2. Experimental procedure

All data reported in this paper were generated on random mat reinforcement specimens prepared from large panels, which were fabricated using three layers of E-glass CSM (density 450 g m^{-2} manufactured by FGP Ltd, India) and isophthalic polyester resin (HSR 8131 manufactured by Bakelite Hylam Ltd, India) by a standard hand lay-up technique. Methyl ethyl ketone peroxide and cobalt naphthanate were used as catalyst and accelerator, respectively. The laminates were cured in laboratory atmosphere for 72 h and then post-cured at a temperature of 100° C for 4 h. The nominal thickness of the finally cured laminate was 2.4 $\pm$ 0.4 mm having a glass content of 36.4% as determined by burn-out method. Flexure test specimens of length 80 mm and width 10 mm were cut from these panels and the edges were smoothed by sanding.

Each specimen was subjected to measurements of the acoustic-ultrasonic stress wave factor by placing the receiving transducer at the centre of the specimen. The instruments were set up in the following manner: Gain 50 dB, threshold voltage 0.25 V, (auto mode operation) pulse rate 2000 sec^{-1}, pulse energy 50 V, gate width 187.2 μsec. This was kept the same in all subsequent measurements. 40 specimens were tested dry in three-point flexure employing the Instron machine at a displacement rate of 2 mm min^{-1} which was maintained the same for all tests. 90 specimens were kept in boiling distilled water. Of these, 10 samples were drawn at random after a specified number of hours of boiling. They were again subjected to stress wave factor measurement and flexure test after cooling to laboratory temperature. The flexural strength was calculated by using a standard beam formula and reported as the average of 10 values.

The procedure was repeated for water temperatures of 60 and 42° C.

In the stress wave factor measurement simulated stress waves were repeated at a fixed rate, r (2000 sec^{-1} in this study) with each successive burst identical to its predecessors. After amplification, the received signals were sent to a counter that registered the number of oscillations, n, in each burst exceeding a fixed threshold voltage. The counter was reset automatically after a predetermined time interval, g (1 sec in this study) and the previous count was held in a memory and digitally displayed. The displayed count assumed a constant value soon after the probes were placed on the specimen. The number that was displayed, $E = grn$, is defined as the stress wave factor. This value is normalized relative to the maximum E value found for all specimens, i.e. $N_{swf} = E/E_{max}$. E and N_{swf} are both relative and depend on factors such as probe pressure, signal gain, reset time, threshold voltage, repetition rate. All these factors have been kept constant in this study.

3. Experimental results

The average flexural strength, σ, values obtained after different ageing times at 100° C are plotted against the normalized stress wave factor, N_{swf}, in Fig. 2. The plot indicates a monotonic increase of σ with N_{swf}. The linear regression curve fitted to the data had a coefficient of determination of 0.97 and gave the relation.

$$\sigma = 204.3\ N_{swf} + 62 \qquad (1)$$

correlating σ and N_{swf}.

The average normalized stress wave factors at different ageing times at 60° C were calculated and then the flexural strength values were computed from Equation 1 obtained from data at 100° C. The calculated values as well as those measured at different ageing times along with its percentage deviation from the measured strength, are given in Table I. As can be seen from Table I, agreement between the two strength values are extremely close with a maximum deviation of about 10% for 24 h strength values.

An analysis of the values of normalized stress wave factors at different ageing times (t) at 100° C showed a linear relationship between $\ln N_{swf}$ and t with a coefficient of determination of 0.96. Thus a relation of type $N_{swf} = A \exp(-bt)$ where A and b are

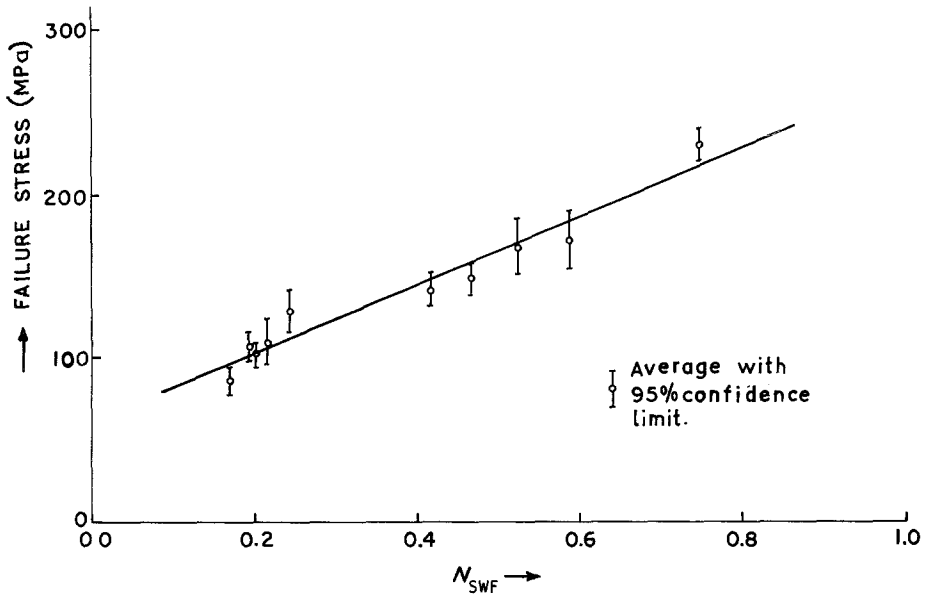

Figure 2 Flexural strength as a function of normalized stress wave factor for specimens aged in water at 100° C.

constants, is fitted to the data following the method given by Lewis [15] yielding the relation

$$N_{swf} = 0.717 \exp(-7.436 \times 10^{-3} t) \quad (2)$$

Combining Equations 1 and 2 the strength degradation with hours of ageing in water at 100° C is given by

$$\sigma = 146.5 \exp(-7.436 \times 10^{-3} t) + 62 \quad (3)$$

A similar analysis of the data at 42° C gives the relation

$$N_{swf} = 0.721 \exp(-5.836 \times 10^{-4} t) \quad (4)$$

For values of t up to 300 h, the equation can be approximated to

$$N_{swf} = 0.721 - 4.208 \times 10^{-4} t \quad (5)$$

Equations 2 and 5 have been plotted in Fig. 3. Equation 4 is again combined with Equation 1 to give the relation:

$$\sigma = 147.3 \exp(-5.836 \times 10^{-4} t) + 62 \quad (6)$$

for strength degradation at different ageing times in water at 42° C. It can be seen that Equations 3 and 6 are almost identical, except the exponent of the exponential term. For the range of values of t studied here, Equation 5 can be approximated by the relation

$$\sigma = 209.3 - 0.086 \quad (7)$$

without any appreciable error. This equation is linear and plotted in Fig. 4 along with Equation 3.

4. Discussion

As mentioned earlier, the stress wave factor may be described as a measure of the efficiency of stress wave energy transmission. The sending transducer injects a repeating series of ultrasonic pulses into the material. Each of these pulses produces simulated stress waves that resemble acoustic emission in the material [16, 17]. The receiving transducer intercepts some of the simulated stress wave energy that radiates from the point of injection. Any defect of discontinuity present in the material under investigation leads to the attenuation of energy with consequent reduction in the energy received by the receiving transducer.

Thus attenuated stress wave energy flow corresponds to decreased fracture resistance [9]. The correlation given by Equation 1 supports this view. In a random fibre composite the strength is predominantly controlled by the efficiency of the load transfer at the interface between the fibre and the resin matrix, i.e. the shear stress at the interface and the orientation of the fibres with respect to the loading axis [18]. A good bond between the fibre and the resin at the interface with the maximum number of fibres oriented in the

TABLE I Flexural strength of CSM-laminates kept in water at 60° C

Time in water at 60° C (h)	Average flexural strength, measured (MPa)	Flexural strength, calculated (MPa)	Deviation from measured strength (%)
264	190	193	+1.6
240	197	196	−0.5
216	199	204	+2.5
192	205	205	0
168	205	203	−0.97
144	221	197	−6.3
72	212	196	−7.5
48	216	202	−1.6
24	222	200	−9.9

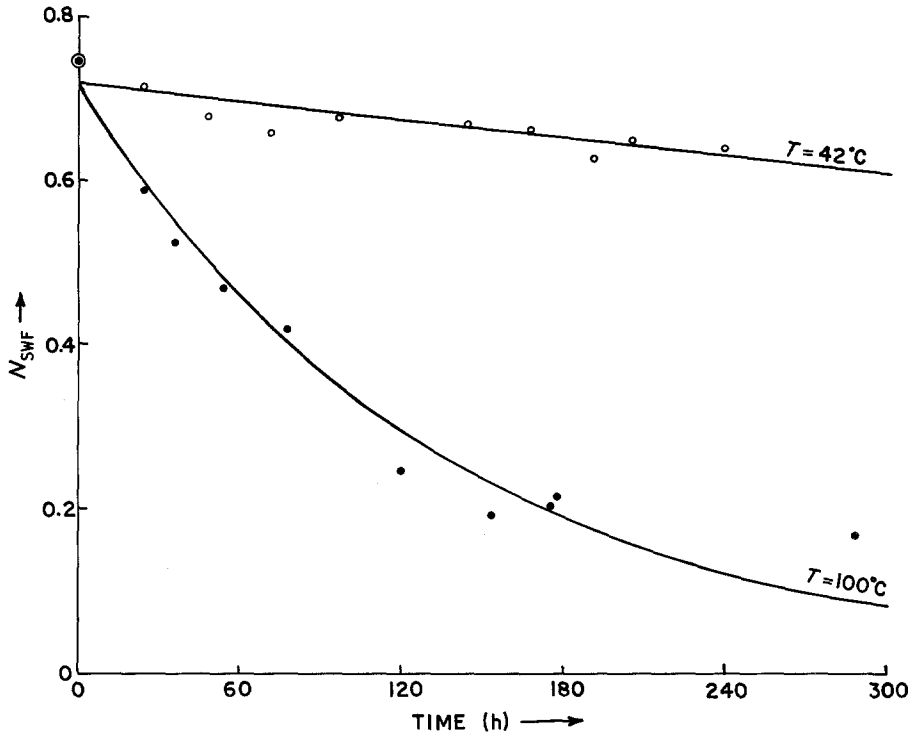

Figure 3 Stress wave factor as a function of ageing time at 100 and 42° C.

direction of load will lead to higher strength. Both of these factors will contribute to more efficient transfer of stress wave energy (high stress wave factor values) since the intimate contact between the fibre and the resin will reduce the loss of energy, and also attenuation is less along the direction of fibre orientation.

On ageing in water the polyester component in the laminate is subjected to water attack. The water acts as a swelling agent and plasticizes the resin. In the presence of traces of salts, the resin acts as a semi-permeable membrane and the resulting osmotic pressure within the resin leads to cracking [19]. The reinforcing E-glass fibres may give rise to alkaline hydrolysis products making the interface more hydrophilic, and three distinct but inter-related effects [3], may occur.

1. Penetration of water into the resin will promote crack growth in the individual fibres resulting in weakness.

2. Radial stress due to resin swelling along with osmotic pressure caused by penetration of water will lead to fibre debonding, increase in transfer length and consequent weakening of the composite.

3. Increase in viscoelasticity due to plasticization of resin will result in further increase in transfer length decreasing the efficiency of load transfer at the interface.

The swelling process, as mentioned above, inflicts irreversible damage on the composite. Moreover, the swelling rupture of the resin and fibre–resin interface exposes the fibres to a highly humid atmosphere which when coupled with the swelling-induced tension in the fibres can lead to severe stress corrosion of the glass fibre. Ishai [2] has observed experimentally for glass-fibre reinforced and unfilled epoxy specimens that the problem of stress corrosion of the reinforcement is further aggravated when the specimens are exposed to hot water. Hot water promotes attack on the glass

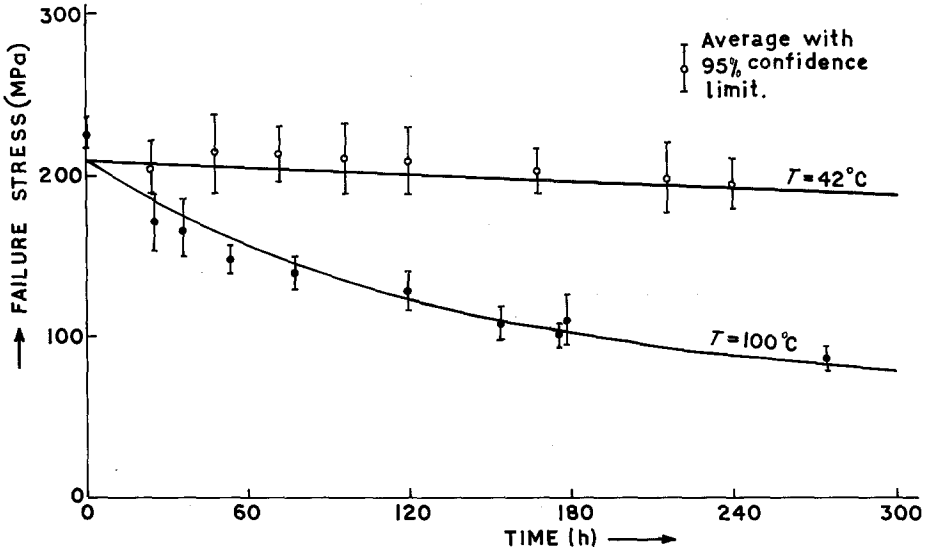

Figure 4 Flexural strength as a function of ageing time at 100 and 42° C.

fibre surface and the interface coupling agent, with consequent leaching and removal of glass constituents [1]. All these contribute to the reduction of the strength of the fibre. Since, for a given volume fraction of fibre, the composite strength is predominantly dependent on the factor

$$\sigma_f\left(1 - \frac{l_c}{l}\right) \quad (8)$$

where σ_f is the fibre strength, l_c and l are the load transfer length and fibre length, respectively, any reduction in σ_f and increase in l_c will contribute to the reduction in strength of the composite.

On the other hand, stress wave energy transmission in these composites takes place from the matrix to the discontinuous fibres through the interface. The fibre, having a higher modulus of elasticity, transmits stress wave energy more efficiently than the matrix. Thus a debonded or weak interface attenuates the energy more, thereby transmitting less energy to the fibre.

The ageing of fibre also makes it less efficient in transfer of stress wave energy. Both these factors reduce the simulated stress wave energy at the receiving transducer and give low values of stress wave factor. Thus the correlation that was obtained probably arose because stress wave propagation is predominantly controlled by the fibre–resin interface which, in turn, controls ultimate strength in the composite tested.

The close agreement between the measured strength values and those predicted from the correlation obtained for ageing at 100° C for the degradation of composite at water temperatures of 60 and 42° C, indicates that the stress wave factor provides a means of rating the deterioration process on a time and temperature scale. The lower value of the exponent of the exponential term in Equation 6 is expected since at lower temperature the degradation will occur at a much lower rate.

Equations 3 and 6 can be put into the form

$$\sigma(t) = \sigma_\infty + (\sigma_0 - \sigma_\infty) \exp(-t/\tau)$$

where t is exposure time and σ_0 and σ_∞ are the composite strength at the times 0 and ∞, respectively, and τ is a characteristic time dependent on temperature. This equation is identical to that describing the environmental degradation of interlaminar shear strength in carbon fibre epoxy composite [20–22] indicating that the interfacial effect is the controlling factor in the degradation of random fibre composites.

5. Conclusions

The hydrothermal degradation of CSM-laminates was evaluated nondestructively through an acousto-ultrasonic technique. The method involved characterization of stress wave propagation in the material. This measurement yielded the stress wave factor which was used to determine the rate of the degradation process.

Specific conclusions drawn from this study may be summarized as follows:

1. The stress wave factor is a sensitive indicator of random fibre composite strength reduction due to hydrothermal effects.

2. For a given system, stress wave factor readings can be used for the estimation of strength from the data generated under accelerated conditions.

3. In a random fibre composite the hydrothermal degradation process is predominantly controlled by the interfacial phenomena.

Acknowledgements

The authors are grateful to Dr S. Kumar, Director, Central Glass and Ceramic Research Institute, for his keen interest in this work and kind permission to publish this paper. Thanks are due to Mr A. K. Moitra also of the Institute for carrying out some of the strength measurements and M/s FGP Ltd, India for supplying the reinforcement for this study.

References

1. K. H. G. ASHBEE and R. C. WYATT, *Proc. Roy. Soc. A* **312** (1969) 553.
2. ORI SHAI, *Polym. Eng. Sci* **15** (1975) 491.
3. J. AVESTON, A. KELLY and J. M. SILLWOOD, in "Advances in Composite Materials", Vol. I, edited by A. R. Bunsell, C. Bathias, A. Martrenchar, D. Henkes and G. Verchery (Pergamon, Paris, 1980) p. 557.
4. B. DEWIMILTE, J. THORIS, R. MAILFERT and A. R. BUNSELL, *ibid.*, p. 597.
5. A. VARY, "Mechanics of Nondestructive Testing" (Plenum, New York, 1980) p. 123.
6. T. J. FOWLER and R. S. SEERPELLINI, *Chem. Eng.* October (1980) 145.
7. *Idem, ibid.*, November (1980) 293.
8. M. G. PHILIPS and B. HARRIS, in "Advances in composite materials", Vol. II, edited by A. R. Bunsell, C. Bathias, A. Martrenchar, D. Henkes and G. Verchery (Pergamon, Paris, 1980) p. 998.
9. A. VARY and R. F. LARK, *J. Test. Eval.* 7 (4) (1979) 185.
10. A. VARY and K. J. BOWLES, Proceedings 33rd Annual Conference of the Society of the Plastics Industries Sec. 24-A (Society of the Plastics Industry, Inc., New York, 1978) p. 1.
11. A. VARY and R. F. LARK, NASA, Lewis Research Centre, Ohio, NASA, T.M. 78846 (1978).
12. A. VARY and K. J. BOWLES, *Polym. Eng. Sci.* **19** (1979) 373.
13. J. H. WILLIAMS Jr and N. R. LAMPERT, *Mat. Eval.* December (1980) 68.
14. J. H. WILLIAMS Jr and B. DOLL, *ibid.* May (1980) 33.
15. DAVID LEWIS III, *Ceram. Bull.* **57** (1978) 434.
16. D. M. EGLE and A. E. BROWN, *J. Acous. Soc. Amer.* **57** (1975) 591.
17. *Idem, J. Test. Eval.* **4** (3) (1976) 196.
18. H. L. COX, *Br. J. Appl. Phys.* **3** (1952) 72.
19. K. H. G. ASHBEE, F. C. FRANK and R. C. WYATT, *Proc. Roy. Soc. A* **300** (1967) 415.
20. J. C. HALPIN, H. W. POLLEY, *J. Comp. Mater.* **1** (1967) 64.
21. J. C. HALPIN, J. R. KOPF and W. COLDBERG, *ibid.* **4** (1970) 462.
22. D. H. KAELBLE, P. J. DYNES and E. H. CIRLIN, *J. Adhesion* **6** (1974) 23.

Received 4 September
and accepted 18 December 1985