JOURNAL OF MATERIALS SCIENCE **35** (2000) 1931–1937

Influence of resin chemistry on water uptake and environmental ageing in glass fibre reinforced composites-polyester and vinyl ester laminates

ERIC BOINARD, RICHARD A. PETHRICK*
Department of Pure and Applied Chemistry, University of Strathclyde,
Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, UK
E-mail: r.a.pethrick@strath.ac.uk

JODY DALZEL-JOB
Structural Materials Centre, Defence Evaluation and Research Agency,
Rosyth Royal Dockyard, Dunfermline, Fife KY11 2XR, UK

COLIN J. MACFARLANE
Department of Ship and Marine Technology, University of Strathclyde, Henry Dyer Building,
100 Montrose Street, Glasgow G4 0LZ, Scotland, UK

Hand laid up glass fibre reinforced isophthalic polyester resin and transfer moulded vinyl ester resin composites were subjected to environmental ageing. Gravimetric measurements were performed on laminate samples exposed to air and distilled water at 30°C and 60°C. Complementary porosimetry measurements on the original and fully aged samples indicated significant changes in the structure arising on ageing. Blistering showed that hydrolysis and de-bonding at the fibre-matrix interface occurred in polyester laminate to a greater extent at 60°C than 30°C. Leaching of monomer residues led to an anti-plasticisation effect in vinyl ester laminate. The influence of the fabrication method on the ageing behaviour is observed through porosity measurements on aged samples.

1. Introduction

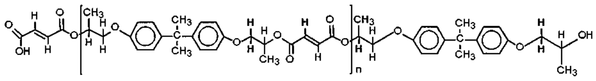
Glass fibre reinforced plastic [GFRP] thermoset composites are used extensively in structural applications [1]. In GFRP polyester and vinyl ester laminates, glass fibre cloth or fibre is used as the reinforcement. Reinforced materials have a higher resistance to crack initiated failure than the bulk resin, the crack being arrested by the fibre reinforcement. The great attraction of composites is their high specific strength to weight ratio. Many structures tend to be over designed to allow for uncertainties with regards to the loss of mechanical properties as a consequence of the ageing behaviour. Composites, however, find application where their unique characteristics of corrosion resistance, transparency to radar waves, ability to absorb impact and damping of vibrations are important.

Problems associated with achieving quality control during manufacture and a lack of knowledge of the way these materials age have limited their application. The fabrication processes are often labour intensive and the polymerisation processes difficult to precisely control in real environments. A lack of the ability to control the quality of the final product led designers to introduce large safety factors in marine applications, which disadvantage composites compared with conventional materials [2]. Glass fibre reinforced composites have the advantage of being non-magnetic and stable in a marine environment [3]. A good surface finish can be easily produced in these structures, which is aesthetically attractive, reduces drag and leads to low maintenance costs.

In this paper, the effects of water uptake and ageing on glass fibre reinforced polyester and vinyl ester resins composite structures are assessed.

1.1. Polyester resin

The term polyester resin applies to a variety of resins usually produced by the condensation of polybasic acids with polyhydride alcohols or from derivatives of these materials. The typical chemical structure of a bisphenol-A fumarate polyester resin is shown below.



The ester groups are potential weak points as they represent sites that are potentially sensitive to

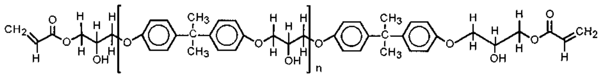
---

* Author to whom all correspondence should be addressed.

hydrolysis. Unsaturated bonds at the end and within the molecule are able to co-polymerise with styrene to form cross-links between neighbouring styrene chains. Polymerisation is achieved using free radical initiators [4]. Complete reaction of the styrene monomer and the polyester resin is rarely achieved and the matrix will contain trapped unreacted species. Residual monomer can act as a diluent that will lower the glass transition temperature [T_g] of the resin matrix. Microstructure in the form of gel particles, with dimensions of the order of 0.01–0.05 μm have been observed in polyester resins. As a consequence of the statistical nature of the polymerisation process, a heterogeneous cross-link density within the matrix material is generated [5]. Variation in the proportion of unsaturation as a result of changing from fumaric to maleic resins and also changes in the cure conditions lead to different degrees of heterogeneity being observed [6]. Increasing the hydrophobic content of the resin by the use of more styrene [7], will significantly influence the properties of the resins. Increasing the ratio of unsaturated to saturated acid [8] in the composition increases the density of cross-links and in turn alters the degree of restriction of the mobility of the polyester chains. A high cross-link density leads to a high T_g for the composite and a lower susceptibility to damage by water.

1.2. Vinyl ester resin

Vinyl ester resins were developed in the early 1960's, for application as matrix materials for the fabrication of GFRP [9]. Bearden and co-workers (1970) recognised later the advantages of vinyl ester resins in a corrosive environment and exploited their use in a range of applications. Vinyl ester resins are produced by the addition of an ethylenically unsaturated monocarboxylic acid to an epoxy backbone and are cured with styrene or other vinyl monomers. They possess similar thermal and mechanical properties to those of epoxy resins but have the advantage of a greater ease of processing. The typical chemical structure of a bisphenol-A vinyl ester resin is shown below.



The reactive vinyl unsaturations at the ends of the molecule allow the resin to cure rapidly and enable it to homopolymerise or copolymerise [10]. Since there are no ester groups present in the repeat unit of the molecule, vinyl ester resins have 30 to 50% fewer ester groups per unit of molecular weight than polyester resins and exhibit a much higher resistance to hydrolysis. The secondary hydroxyl groups in the vinyl ester molecule can interact with the hydroxyl groups present on the surface of glass fibre and improve wetting and bonding of the resin to the reinforcement. Polymerisation is usually achieved using free radical initiators and styrene as a reactive diluent [9]. Chain growth continues until all unsaturation has been removed or until vitrification occurs.

1.3. Effects of water on glass fibre reinforced polyester and vinyl ester resins

The stability resin-glass interface depends on a combination of chemical bonding and non bonding physical interactions [11]. The formation of an interpenetrating network and co-polymerisation of the coupling agent with the matrix significantly influences the susceptibility to ageing in water [12]. Silane coupling agents [13] can improve the stability of the interface between the glass fibres and the polymer matrix when resistance to hydrolytic cleavage is required.

Hydrolytic degradation occurring in GFRP materials is associated with hydrolysis of the matrix and fibre, and destabilisation of the fibre-matrix interface. Absorption of moisture will lead to a lowering of the T_g of the polymer matrix by plasticisation. The modulus of the matrix material is reduced by water absorption and the elastomeric range is shifted to lower temperatures; it decreases the transverse flexural strength and tear strength [14], but also increases the energy dissipation capacity [15]. Chemical reactions can lead to the generation of water soluble low molecular weight substances that have the capability of generating an osmotic pressure and producing blisters [16]. Bubbles, cracks and glass fibre packing caused by internal stress can also cause blistering which is accelerated by poor inter-laminar bonding near the surface of the composite [17].

Hydrolysis of the resin results in main chain scission and an increased susceptibility to further chemical attack. Vinyl esters based on bisphenol A-fumarate resins are less vulnerable to hydrolysis since they only contain terminal ester groups, than polyester resins. Environmental stress corrosion cracking [ESCC] of glass fibres is the result of the delayed brittle fracture of stressed fibres under the influence of an aggressive environment [11]. In the presence of water, ESCC of glass fibre is caused by a stress-assisted hydrolysis of the silica fibre. Water attacks the surface of the glass fibre promoting pitting and producing free alkali hydroxide groups that can further degrade the silica structure [12]. The free hydroxide groups can also catalyse hydrolysis of the ester groups in the resin [9]. Destabilisation of the fibre-matrix interface is the combined effect of hydrolytic decomposition of chemical bonds between the resin and matrix and swelling of the matrix causing a loss of physical interactions and dewetting [12].

Plasticisation of the matrix occurs when water interacts with the resin through polar interactions and hydrogen bonding and causes an increase in the free volume. As a result the T_g of the resin is reduced at a rate of approximately 20 K for each 1% of water absorbed [11]. However, in some cases exposure to elevated temperature has been shown to increase the T_g [18].

Non-Fickian water diffusion behaviour has been observed in fibre glass reinforced thermosets and ascribed to the effects of heterogeneity [19]. Initially water diffuses mainly in the resin matrix but can enter the matrix via capillary action if voids exist next to the fibres. A small amount of water will become absorbed at the fibre-matrix interface. After the total water absorption has approached the saturation point, matrix degradation may occur and leading to an increase in the rate of water absorption. Weight loss in the form of water-soluble residues takes place and can be observed after a few hours of exposure to a moist environment [20]. After long periods of exposure a change in the rate of water uptake can occur together with no clear saturation level and is associated with a continuous degradation of the matrix and de- bonding of the fibre-matrix interface [2].

2. Experimental methods

2.1. Materials

The laminates used in this study were prepared from woven-rowing E glass fibre reinforced thermoset resins. Two different types of composite were produced:- (i) a 50% weight glass fibre hand lay-up reinforced unsaturated isophthalic polyester resin laminate (Crystic 489/Y0530, Scott-Bader Ltd) and (ii) a 70% weight E glass fibre reinforced vinyl ester resin laminate (Derakane 411 Dow Chemicals) manufactured using the Seamann Composites Resin Infusion Moulding Process (SCRIMP). In the SCRIMP samples, the glass fibre layers (up to 20) are placed in an airtight bag and the wetting of the fibres is ensured by drawing the resin into the layers under vacuum. This process achieves a better wetting of the fibre and produces a laminate with a higher fibre content. Since the SCRIMP process uses a vacuum, a better quality laminate is produced and trapped air bubbles are avoided to a large extent. One of the disadvantages of the method is that monomer is trapped and cannot escape by evaporation. With the hand lay-up technique there is a tendency to entrap air, however the residual monomer is lost by evaporation. The laminates were cured at room temperature and not post-cured prior to the investigation. The samples used were produced at DERA Farnborough and were obtained by machining 7 mm thick samples from a plate which had an original thickness of 20 mm supplied by Messrs. Vosper Thorneycroft, Southampton.

2.2. Gravimetric measurement

The pristine machined samples were placed in a dessicator at room temperature in order to avoid moisture absorption. Two groups of identical samples were used in the study. The first group of samples was firstly aged in an air-circulated oven at 30°C and 60°C in order to assess the possible loss of low molar mass fragments. Once these samples had reached a constant dry weight, they were exposed to distilled water. The second group of samples were exposed to distilled water at 30°C and 60°C and when they had reached equilibrium, were then allowed to undergo desorption in an air circulated oven. The fan extraction system in the oven produced a stable relative humidity which was assumed to be low enough not to influence the desorption behaviour of the samples. Gravimetric measurements were performed by removing the samples from the ageing environment and in the case of those immersed in water, rapidly dried with tissue paper to remove excess water and immediately weighed using an electronic balance (Mettler AJ100) which has an accuracy of ±0.1 mg. The samples aged in water spent 20 to 30 seconds out of their environment; the samples aged in air spent up to 60 seconds out of the oven. The times for the weighing experiments were assumed to be sufficiently short not to influence the values of the mass measured. A constant measurement procedure was used throughout.

2.3. Dynamic mechanical thermal analysis (DMTA)

A Polymer Laboratories Dynamic Mechanical Thermal Analyser MkIII was used to test selected laminate samples. The single cantilever mode operating at a frequency of 1 Hz was used in the measurements, with a 64 μm peak to peak displacement and a rate of heating of 5°C/min from 25°C to 175°C.

2.4. Porosimetry

A Micromeritics Autopore II 9220 was used for the porosity measurements. Using a pressure range from 35 kPa to 420 MPa, pore sizes from 30 to 0.003 μm were investigated.

3. Results and discussion

3.1. Initial characterisation of the laminates

GRP laminates are cured at ambient temperature and the reaction is usually incomplete. The laminate will contain unreacted monomer that can act as a plasticiser for the matrix structure and lower the observed glass transition temperature, T_g. In the case of polyester hand lay-up laminates, much of the styrene is released during the fabrication process, whereas in the SCRIMP lay-up process the monomer will be retained by the vacuum bag. Monomer release is suppressed by the vitrification of the sample during the cure process.

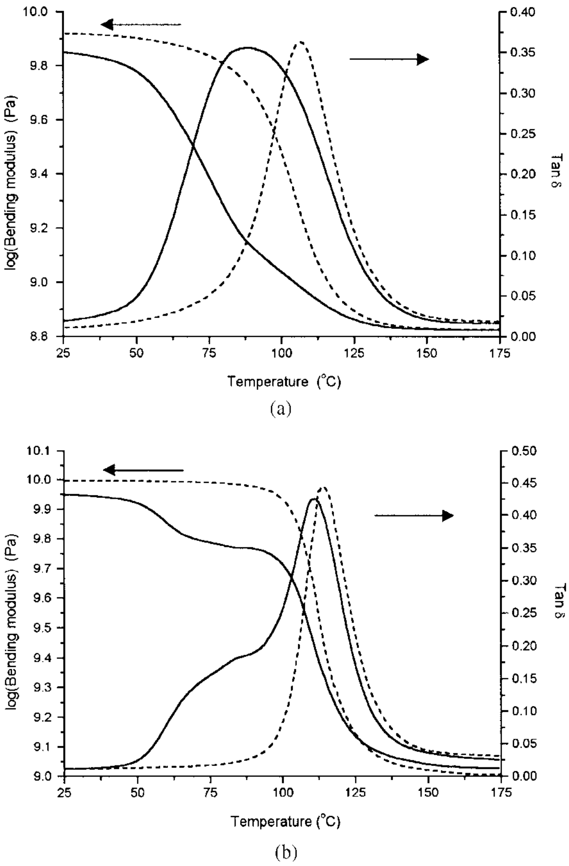
DMTA measurements were carried out on as received laminates, Fig. 1. A repeat of the DMTA scan after the sample has been heated to 175°C during the first cycle, indicates significant changes in both the modulus and the tan δ traces consistent with advancement of the state of cure. The T_g of the polyester laminate, Fig. 1a, increases from 88°C to 106°C, after the first temperature scan. The area under the tan δ peak decreases between the first and second temperature scans and the modulus of the laminate at low temperature increases. All these characteristics imply that the laminate as it was received is not fully cured and the first temperature scan up to 175°C post-cured the resin. Similarly, the vinyl ester laminate exhibited, Fig. 1b, a characteristic decrease in the area of the tan δ peak and an increase of the modulus between the first and second temperature scans.

3.2. Ageing studies

3.2.1. Polyester laminate

3.2.1.1. Gravimetric measurement. The polyester samples subjected to exposure to water at 30°C eventually reached an equilibrium uptake value of about 0.70 wt %, Fig. 2a. The apparent larger amount of water lost during the desorption process implies a loss of unreacted monomer and possible degradation of the laminate. The negligible amount of matter desorbed during ageing in air compared to the extra amount desorbed after exposure means that the effect of water on the laminate is the main factor responsible for the weight loss. A gradual increase observed in the rate of water uptake after 12 weeks exposure of the same material immersed at 60°C, Fig. 2b, shows evidence of another degradation mechanism becoming operative. Hydrolysis of the resin leading to reduction in the crosslink density is one possibility and is supported by the observation of a change in colour of the laminate. An alternative theory is that debonding at the fibre-resin interface is occurring permitting additional water uptake to occur in this void region. Evidence for the latter mechanism was the observation of a blistering at the surface of the laminate. Exposure of the polyester laminate to water at 60°C results in the appearance of additional mechanisms of degradation from those operational at ambient temperature of 30°C. This has particular implications for the artificial or accelerated ageing of such material at elevated temperature. The greater rate of absorption after ageing in air compared with the absorption of ‘as received’ samples is due to an increase of the porosity of the laminate caused by the loss of monomer during ageing in air.

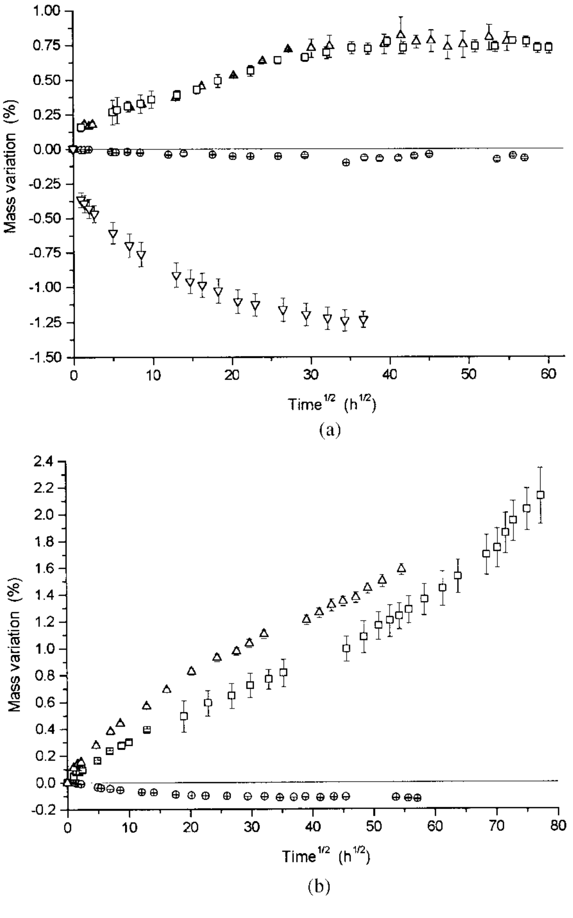
3.2.1.2. Dynamic mechanical thermal analysis. DMTA of aged polyester laminate, Fig. 3, demonstrates that anti-plasticisation and hydrolysis processes



(a)

(b)

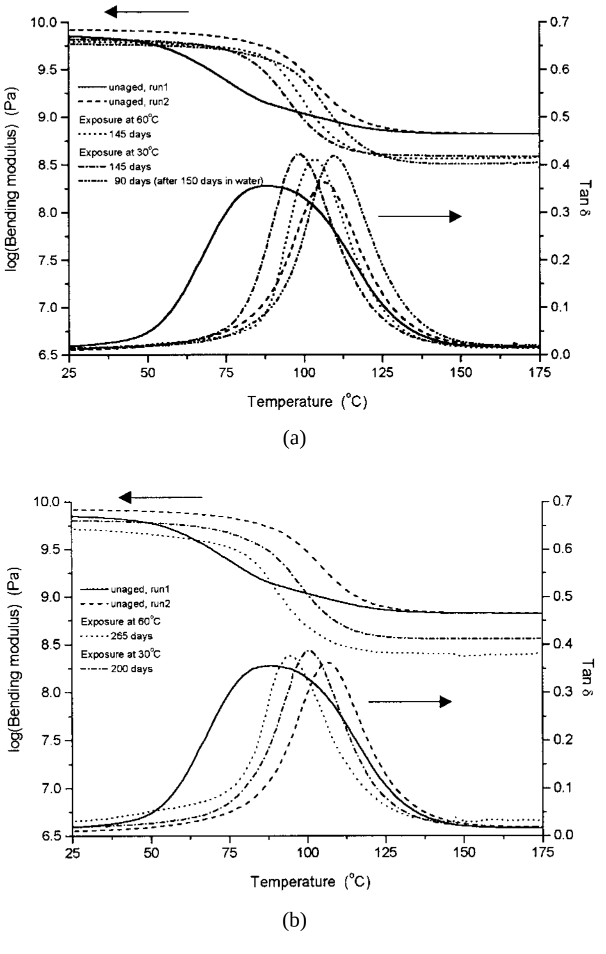
Figure 1 DMTA of (a) polyester and (b) vinyl ester laminate. (— first cycle, - - - - second cycle).



(a)

(b)

Figure 2 Sorption of 7 mm thick polyester laminate exposed to distilled water at (a) 30°C and (b) 60°C. □ absorption, ○ desorption during ageing in air, △ absorption after ageing in air, ▽ desorption after ageing in water.



(a)

(b)

Figure 3 DMTA of polyester laminate after ageing in (a) air and (b) water.

are occurring. The former is shown by the increase of the T_g of the polymer, without significant increase of the modulus at low temperature, the latter by a significant decrease of the modulus at high temperature. The increase of the T_g is not a consequence of an increase of the crosslinking of the material, otherwise the high temperature modulus would not decrease. The significant decrease of the bending modulus observed at high temperature implies that decrease of the bonding between the resin and the fibre in the laminate has occurred. Indeed, the influence of the bonding between the matrix and the fibre on the mechanical properties of the laminate is greater at high temperature. The variation observed in the DMTA results are due to the leaching of 'free', non-crosslinked monomer residues that were acting as plasticiser in the laminate. Fig. 3a indicates that the greatest increase in the T_g is shown by the sample aged for 150 days in water followed by 90 days in air at 30°C. This implies that a combination of ageing in water and air has a greater effect on the laminate than the ageing in air or water, even at 60°C.

3.2.1.3. Porosity measurement. The aim of the porosity measurements was to assess the possible variation of the sample porosity due to the leaching of unreacted monomer on the laminate structure. Porosity measurements shown in Fig. 4 were performed on unaged samples and samples exposed to water at 75°C for 12 weeks. A marked increase in porosity of the laminate occurred in the pore diameter range of 0.03 to 10 μm that corresponds approximately in size of the inter-fibre spacing. This is in agreement with the gravimetric curve at 60°C, where a change in the rate of water uptake after about 12 weeks indicates the appearance of degradation of the laminate. Above the interfibre range, the presence of cavities or bubbles produced during manufacturing are shown and the variation between both samples is probably due to a different density of these defects in the samples. Below this range is the scale of the microstructure of the resin. It has been suggested that polyester resins have a microstruture consisting of microgel particles embedded in a less densely crosslinked phase [21]. Leaching of uncured monomer, will increase the porosity of the laminate.

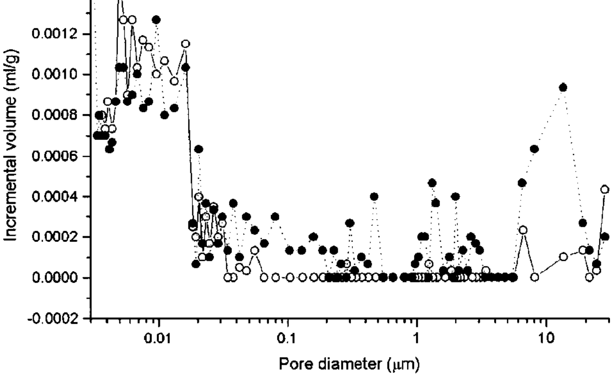


Figure 4 Porosity of polyester laminate. ○ 'as received', ● exposed to distilled water.

3.2.1.4. Discussion. An analysis of all the results obtained for the polyester laminate leads to the following conclusions concerning the ageing of the material in the conditions defined for this work.

i. The monomer residues act as plasticiser in the laminate. The anti-plasticisation effect observed during ageing occurs when residues leach out of the material. An increase in the modulus implies that the laminate becomes stiffer during ageing and therefore looses some of its capability to absorb shock and damp vibrations.

ii. A certain degree of debonding occurs in the laminate during ageing and correlated with a decrease of the high temperature modulus. It is not possible to determine whether the debonding occurs between the fibre and the matrix or between the fibre and its coating.

iii. Hydrolysis of the laminate occurs during ageing. This is shown by a loss of weight of the laminate after exposure to water that is greater than the weight lost during ageing in air. The loss in air can be correlated with the loss of unreacted monomer trapped in the glass.

3.2.2. Vinyl ester laminate

3.2.2.1. Gravimetric measurement. An entirely different situation was observed for the vinyl ester laminate. The 30°C absorption curve, Fig. 5a, shows an initial net

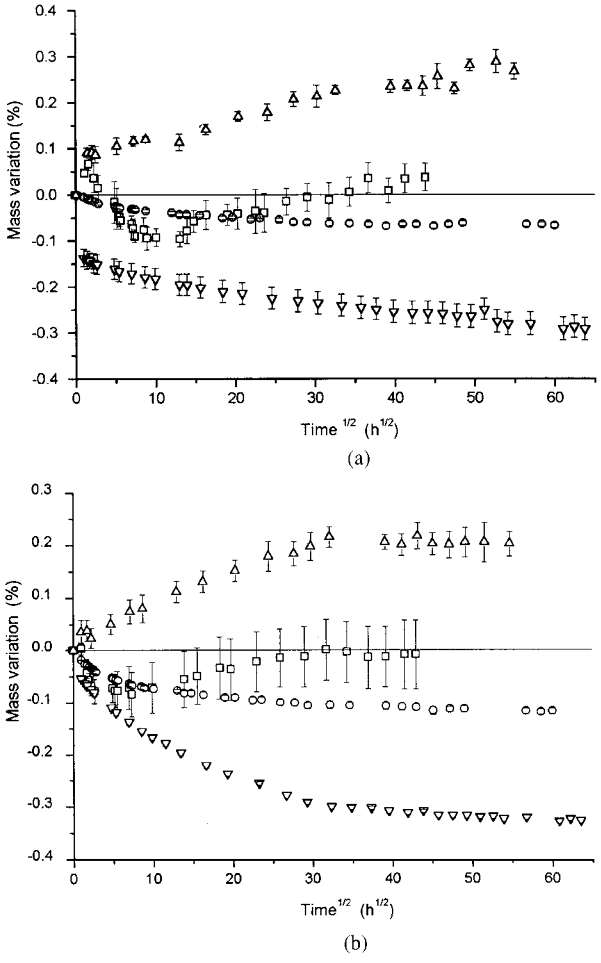
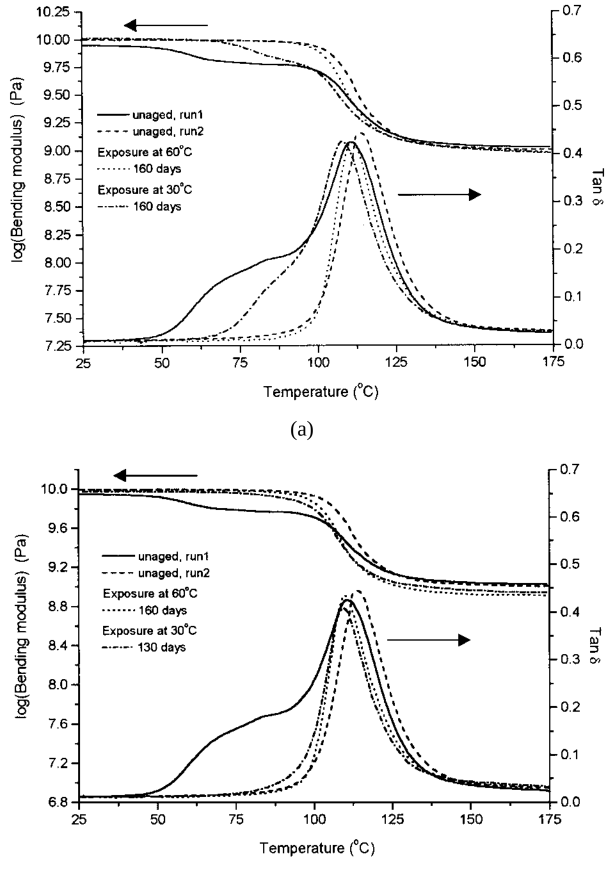


Figure 5 Sorption of 7 mm thick vinyl ester laminate exposed to distilled water at (a) 30°C and (b) 60°C. □ absorption, ○ desorption during ageing in air, △ absorption after ageing in air, ▽ desorption after ageing in water.

mass gain caused by water uptake, followed by a net mass loss over the period of the first 5 days of exposure. It is believed that the initial net mass gain is due to the adsorption of water on the surface of the sample. The leaching of low molar mass material from the sample caused the net mass loss. Diffusion of water in the sites left empty by the leached material is believed to be responsible for the mass increase. The laminate exposed after ageing in air does not present any weight loss at the start of the exposure to water. Ageing in air will have allowed monomer residues trapped during the processing of the laminate to leach out. The amount of water desorbed after ageing is similar to the amount absorbed after ageing in air added to the loss in weight during ageing of the samples in air. This observation implies that no leaching due to hydrolysis is occurring during exposure to water. The amounts absorbed and desorbed after ageing in water of vinyl ester laminate at 60°C, Fig. 5b, are similar to the data obtained at 30°C.

3.2.2.2. Dynamic mechanical thermal analysis. The DMTA curves, Fig. 6, show only an anti-plasticisation effect: an increase of the T_g and decrease of tan δ peak area. Leaching of monomer residues is probably responsible for this effect. No debonding seems to occur, as the modulus of the laminate at high temperature does not vary. As could be expected, the effect is greater at 60°C than 30°C and greater after exposure to water. The effect of the water ageing occurs much faster as the same level of ageing is reached after about half the time of exposure to air.



(a)

(b)

Figure 6 DMTA of vinyl ester laminate after ageing in (a) air and (b) water.

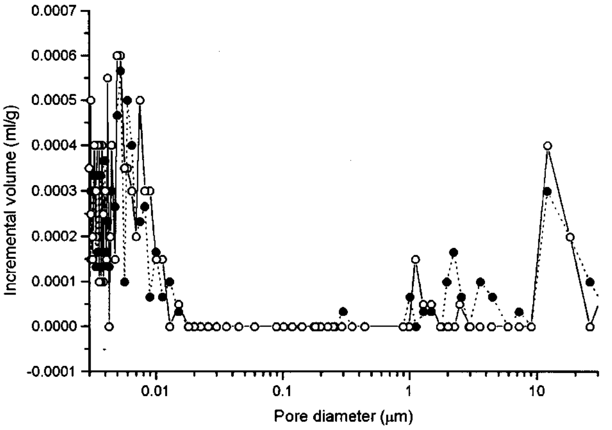


Figure 7 Porosity of vinyl ester laminate. ○ 'as received', ● exposed to distilled water.

3.2.2.3. Porosity measurement. The vinyl ester samples showed no variation in porosity after exposure, Fig. 7, in agreement with the gravimetric measurement. The observation that the vinyl ester laminate did not show any variation in its modulus at high temperature after ageing correlates well with the absence of an increase in porosity, showing that the fibre-matrix interfacial bond and degree of crosslinking have been maintained. This result is also consistent with the results of the gravimetric measurement showing that the amount of water absorbed after ageing in air is equivalent to the amount of water desorbed after ageing in water.

3.2.2.4. Discussion. An analysis of all the results obtained for the vinyl-ester laminate leads to the following conclusions concerning the ageing of the material in the conditions defined for this work.

i. As for the polyester laminate, the monomer residues act as plasticiser in the laminate. This is shown by the anti-plasticisation effect, that is the disappearance of the DMTA peak at 75°C and the decrease of the tan δ peak area.

ii. No degradation process seems to occur during ageing. The observed behaviour is consistent with water occupying sites generated by the leaching of unreacted monomer.

iii. As there is no significant increase of the porosity of the laminate after ageing in water at 75°C, it can be assumed that delamination processes have not occurred. This observation agrees with the DMTA data that show no decrease of the modulus at high temperature.

4. Conclusions

DMTA analysis on samples tested as soon as received showed that both polyester and vinyl ester laminates contained non-uniformly dispersed styrene monomer residues. An anti-plasticisation process due to leaching of monomer residues during ageing in air of the polyester laminate occurs in conjunction with degradation of the fibre-matrix interface. Ageing in water showed degradation by hydrolysis of the resin and of the fibre-resin interface yielding debonding between the fibre and the matrix and blistering of the laminate surface. The degradation of the interface between fibre and matrix led to a significant loss in the reinforcement initially provided by the fibre. These processes are responsible for the observed increase in porosity of polyester laminate exposed to water.

Degradation of the vinyl ester composite in the same conditions appeared more restricted. An anti-plasticisation process, due to leaching of monomer residues was the only degradation process observed. The influence of this phenomenon seemed, however, limited since no significant variation of the porosity of the laminate could be observed.

The following conclusions can be drawn from the comparison of the polyester and vinyl ester results. The vinyl ester laminate (a) absorbs less water than the polyester laminate but (b) presents a greater loss of weight during ageing in air. This was expected as the porosity of the vinyl ester is much lower than the one of the polyester laminate and the vinyl ester composite is processed under vacuum. The rate of water absorption of the polyester laminate at 30°C is twice the rate of the vinyl ester laminate which implies that the polyester laminate will reach water absorption equilibrium quicker and therefore the effect of ageing will be felt sooner than in the case of the vinyl ester laminate. The sorption of both laminates could not be defined as Fickian, despite some similarities in behaviour in some cases. Porosity measurements present a better crosslinked structure for the vinyl ester laminate, since the variation of the incremental volume is less than half that observed for the polyester laminate. Furthermore, the upper limit of the microstructure range due to the heterogeneity of the crosslink density is 0.02 μm for the vinyl ester resin, whereas it is 0.05 μm for the polyester one.

Acknowledgements

One of us (E.B.) wishes to thank the U.K. Ministry of Defence for the provision of a maintenance grant in support of this study.

References

1. A. B. STRONG, in "High Performance and Engineering Thermoplastic Composites" (Technonic Publishing Company Inc., 1993).
2. A. LAGRANGE and R. JACQUEMET, in Proceedings of the 45th Annual Conference of the Composites Institute, session 8-B (The Society of the Plastics Industry Inc., 1990).
3. A. MARCHANT and R. F. PINZELLI, in "Looking Ahead for Materials and Processes" (Elsevier Science Publishers B. V., Amsterdam, 1987) p. 257.
4. V. R. KAMATH and R. B. GALLAGHER, in "Developments in Reinforced Plastics—1," edited by G. Pritchard (Applied Science Publishers, London, 1980) p. 121.
5. R. A. PANTHER, in "Handbook of Polymer-Fibre Composites," edited by F. R. Jones (Longman Scientific and Technical, Harlow, 1994).
6. W. E. DOUGLAS and G. PRITCHARD, in "Developments in Reinforced Plastics—1," edited by G. Pritchard (Applied Science Publishers, London, 1980) p. 231.
7. T. HUNT, in "Developments in Reinforced Plastics—1," edited by G. Pritchard (Applied Science Publishers, London, 1980) p. 59.
8. R. S. LENK and J. C. PADGET, *Eur. Polym. J.* **11** (1975) 327.
9. T. F. ANDERSON and V. B. MESSICK, in "Developments in Reinforced Plastics—1," edited by G. Pritchard (Applied Science Publishers, London, 1980) p. 29.
10. R. E. YOUNG, in "Unsaturated Polyester Technology," edited by P. F. Bruins (Gordon and Breach Science Publishers, 1976) p. 315.
11. F. R. JONES, in "Handbook of Polymer-Fibre Composites," edited by F. R. Jones (Longman Scientific and Technical, Harlow, 1994).
12. E. P. PLUEDDEMANN, in "Silane Coupling Agents," 2nd ed. (Plenum Press, New York and London, 1991).
13. G. W. EHRENSTEIN, A. SCHMIEMANN, A. BLEDSKI and R. SPAUDE, in "Handbook of Ceramics and Composites, Vol. 1," edited by N. P. Cheremisinoff (M. Dekker, New York, 1990).
14. R. A. PETHRICK, *Eur. Polym. J.* **26** (1990) 853.
15. E. G. WOLFF, in "Handbook of Polymer-Fibre Composites," edited by F. R. Jones (Longman Scientific and Technical, Harlow, 1994).
16. F. CHEN and A. W. BIRLEY, in "Handbook of Polymer-Fibre Composites," edited by F. R. Jones (Longman Scientific and Technical, Harlow, 1994).
17. L. S. NORWOOD and E. C. HOLTON, in Proceedings of the SPI Composites Institute's 46th Annual Conference, Washington, 1991, session 8-B.
18. L. C. BANK, T. R. GENTRY and A. BARKATT, *J. Reinforced Plast. Comp.* **14** (1995) 559.
19. T. MORII, T. TANIMOTO, H. HAMADA, Z. MAEKAWA, T. HIRANO and K. KIYOSUMI, *Composites Science and Technology* **49** (1993) 209.
20. J. W. CHIN, T. NGUYEN and K. AOUADI, *J. Appl. Polym. Sci.* **71** (1999) 483.
21. F. R. JONES, M. MULHERON and J. E. BAILEY, *J. Mater. Sci.* **18** (1983) 1522.

Received 2 February
and accepted 21 September 1999