RESIDUAL STRENGTH OF POLYESTER COMPOSITES

CHEMICAL STRUCTURE DESIGN FOR FAILURE PREVENTION UNDER DYNAMIC LOAD

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Laboratory accelerated aging of polyester composites was performed in order to establish environmental sensitivity of the dynamically loaded interphase layer. Life prediction and structural significance of failure mode is interpreted in terms of matrix properties and degree of chemical bonding to the fibre. Analysis of service conditions, includes peak load occurence and environmental degradation rate, because of their large influence upon structural integrity. Non destructive evaluation of remaining life of composites under service conditions is surveyed. Chemical structure design principles for resin and fibre bonding mechanism are proposed.

COMPOSITE MATERIALS FAILURE MODES

In composite materials under dynamic load, there are a number of failure modes, such as delamination, cracking of matrix, debonding and fibre breaking. These failure modes do not combine to form a single self-similar crack normally found in metals but instead they form a very complex damage state.

Fibre breaking is seldom observed and delamination is the macroscopic result of matrix cracking, almost always combined with fibre debonding.

Properties of cured unreinforced resin can be taken as parameter for matrix cracking prediction, but fibre debonding is usually responsible for local strain concentration that leads to matrix cracking. In fact mechanical load transfer from one fibre to another is based on the interfacial bond. Nevertheless not much work is performed and published on evaluation and characterization of the bonding layer by itself. The objective of present work is to set up relationships between the molecular structure of the bonding layer and the long term mechanical behaviour of the composite.

Matrix dominated properties of composite have already been detailed by a number of authors, like Yang et al. (1), Pritchard and Rhoades (2), Williams and Rhodes (3) among others. This author's aproach is somewhat more empirical in the sense that the method generally used can hardly account for the interphase degree of bonding to the matrix.

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CHEMICAL BONDING OF THE FIBRE

Bond strength between the matrix and the glass fibre reinforcement is of vital importance for the mechanical performance. The author has attempted to correlate bonding strength with type and amount of organic reaction taking place at the bonding layer during matrix polymerization.

The kinetic study of the chemical reaction taking place at the bond layer was the basis for the development of two new binding agents for glass fibre that are being now extensively tested after some outstanding results obtained at the preliminary tests.

Long term mechanical performance can be predicted on the basis of test after accelerated conditioning, but the degree of chemical degradation of the bonding layer is less simple to evaluate. The long term environmental effect was simulated on samples treated by a chemical process in which the polymer is removed, but the bond layer was preserved and analysed. This testing procedure emphasizes the organic reaction mechanism that takes place at the bond layer on aging. Correlation with tensile testing after conditioning, was obtained (Fig. 3).

Chemical Resistant Polyester Resins. Some resins of the neopentyl glycol type although presenting good physical adhesion to termoplastics have a remarkable low reactivity on binding to glass fibre organic surface layer. This can be interpreted as a steric effect attributable to structure bulkiness. Preliminary results indicate that when a long chain unsaturated silane is used as coupling agent in glass fibre surface treatment, chemical adhesion increases. However in the case of epoxy--polyester bisphenolic type resins, the use of epoxy-funtional silane doesn't improve the adhesion, and this may be ascribed to premature epoxy ring opening during glass surface treatment.

Experimental

Laminates were produced by conventional hand lay-up methods using unsaturated Polyester Resins and E Glass Fibre Mat. Commercial resins used for the preparation of laminates:

Crystic 196 High performance Polyester Resin.

Crystic Q 586 Chemically resistant Flexible Resin. The Glass Fibre Mat used was prepared from E Glass and several surface treatments were used in order to improve chemical adhesion to the polyester. Laminates produced with powder bounded E Glass mat are hereafter refered as Laminates P, and the ones produced with emulsion bounded E Glass mat are refered to as laminates E.

Mechanical Testing: Most experimental results were obtained using an Instron 1185 testing machine with pertinent accessories. Impact tests were conducted on a heavy duty Variable Impact Tester model 1615, from Braive Instruments (Liege) and performed according to ASTM standard D 2794.

LIFE PREDICTION

Models for life prediction under fatigue failure conditions were analysed and compared with available experimental data in order to assess reliability of each method.

Models reported to be in good agreement with experimental results are the following:

Fatigue Fracture Model	Hashin and Roten(4)
Linear Damage Accumulation Model	Gerharz (5)
Wear-out Model	Halpin el al (6)
Delamination Propagation Model	Ratwani and Kan (7)
Strength Degradation Analytical Model	Yang and Liv (8)
Extreme Value Distribution Model	Bompas-Smith (9)
Mechanistic Model	Kulkarni el al. (10)

Structural Integrity Assessment

Structural Integrity of composites can be assessed at any time of its life by non destructive methods. The more relevant ones have been described by Harris (11) and can be mentioned here:

Radiographic Methods	Thermographic Methods
Microwave Methods	Dynamic Mechanical Analysis
Eddy Current Methods	Ultrasonic Methods
Acoustic Emission Monitoring	

Local integrity of fibre to matrix bonding has not, to the author's knowledge, been directly assessed by any one of these methods, but the use of ESCA (Electron Spectroscopy for Chemical Analysis) for bond surface analysis seems to be a promising technique, Dilks (12), specialy if a Dynamic Depth Profiles Version is used. Also the Inelastic Electron Tunnelling Spectroscopy can be used as a very useful tool for fibre bonding evaluation Conyn (13).

CHEMICAL STRUCTURE DESIGN

Unsaturated Polyester Resin

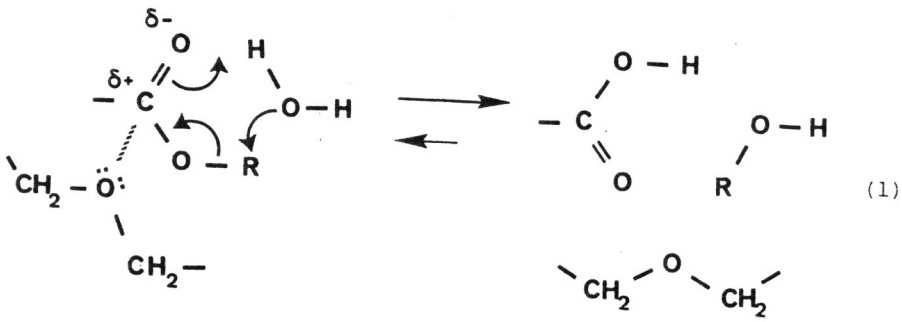
Mechanical properties of Glass Reinforced Polyester (G.R.P.). depend greatly on the matrix (crosslinked copolymer of polyester styrene) and on the strength of the interphase resin-reinforcement. In a previous work, macromolecular structure and mechanical behaviour relationships for self-reinforced polyester resins was presented, Bordado (14). The accurate temperature control required to induce self-reinforcement during radical polymerization of polyester resin with adequate structure is not a simple scale up problem, and large samples are difficult to obtain.

Flexible Resin: Chemical Design Principles

In order to obtain a good impact resistance, and to reduce fatigue failure probability, is common procedure to blend the main resin with a calculated amount of flexible resin. This procedure generaly gives good results on short term tests but environmental degradation gives rise to a shorter life, always predictable by accelerated conditioning (aging).

Most of the flexible resins commercially available have, either a low molecular weight or an ether linkage, and therefore susceptible to hydrolysis. Ether linkage is not by itself easily

broken, but electron pair (sp^3 non bonding orbital) of oxygen is able to assist carbonyl group, acting therefore as a catalyst of ester hydrolysis (either intramolecular or intermolecular assistance).



(1)

The outlined reaction may take place as a step by step mechanism entropically more likely to occur in a low mobility system as a solid polymer.

In order to minimize changes in matrix properties throughout testing and accelerated conditioning, the flexible resin used in these experiments (Crystic Q 586) is a high molecular weight, low insaturation polyester resin, with a flexible but sterically hindered glycol residue in the structure.

Residual Strength of Laminates

Residual interlaminar strength of impacted laminates, can be related with the delaminated area, Dorey (15), by the relation:

$$\tau_c \simeq k \; K_c \; (A)^{-1/4} \qquad (2)$$

Where A is the area of delamination, K_c is the intrinsic fracture thoughness and K is a parameter dependent of resin to fibre adhesion, that, for standard reinforcements can be related with the resin bonding ability.

After the first delamination (incipient) the laminate acquires a new form of energy dissipation (additional vibration mode) and then the residual strength and delaminated area holds constant for impact energy increment. (Fig. 5 and 6).

CONCLUDING REMARKS

Powder binder E glass mat gave consistently better performance than emulsion binder one, as a result of a greater degree of chemical bonding to the matrix.

Emulsion bounded fibres, less strongly bounded to the matrix undergo gross plastic deformation of the composite, even for low levels of bounding degradation and always weaker behaviour on compression. For high levels of degradation, emulsion bounded fibres show consistently some retention of strength level, that can be attributed to the stickiness of the interphase degradation products. (Fig. 2).

AKNOWLEDGEMENTS

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GLOSSARY OF SYMBOLS

A	= Area of delamination
ASTM	= American Society For Testing and Materials
C	= Carbon (structural formulae)
C 196/P	= Laminate with Crystic 196 and powderbounded glass mat
C 196 T/P	= Laminate with toughened Resin and powderbounded glass mat
ESCA	= Electron Spectroscopy for Chemical Analysis
H	= Hydrogen (Structural formulae)
K	= Empirical parameter
K_c	= Intrinsic fracture thoughness
O	= Oxygen (structural formulae)
Sp^3	= Hybrid atomic orbital
$\delta+$	= Partial positive charge
$\delta-$	= Partial negative charge
τ_c	= Residual Interlaminar Strenght

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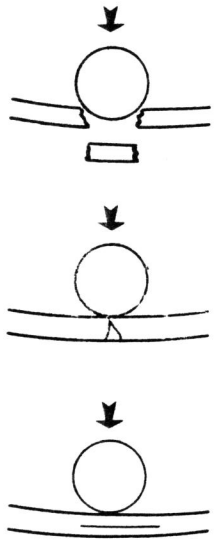

Figure 1 : Primary failure modes for G.R.P. laminates under dropweight impact

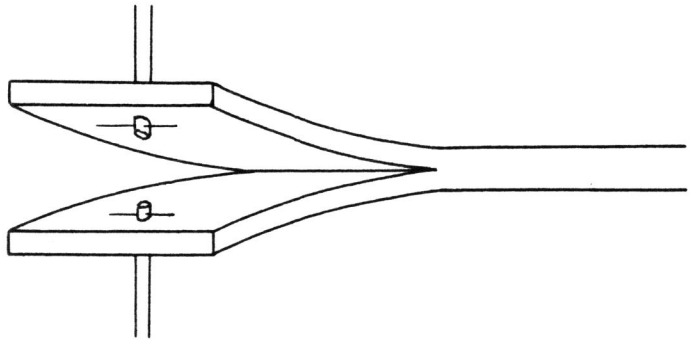

Figure 2 : Schematic outline of inter-laminar adhesion evaluation method

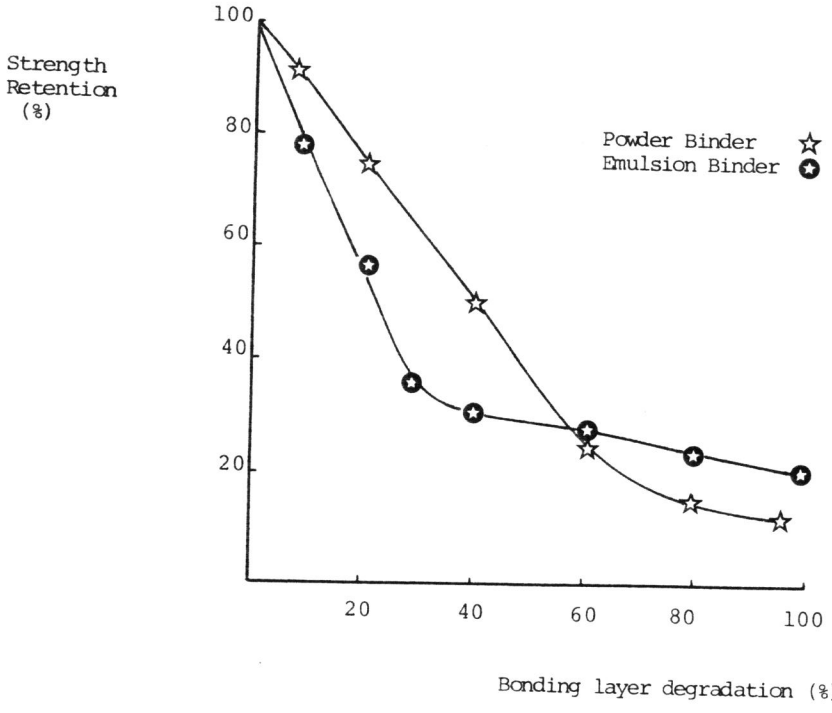

Figure 3 : Correlation of Srength retention with bonding layer degradation for polyester/chopped strand glass mat composites

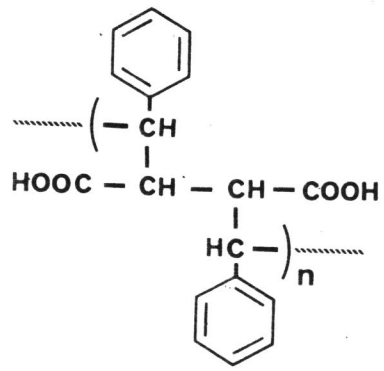

Figure 4 : Polymeric structure of degraded polyester

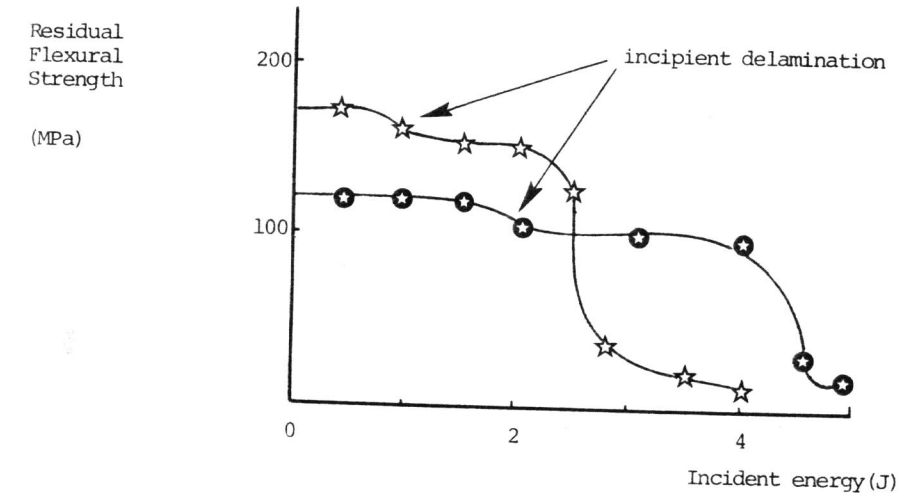

Figure 5 : Effect of resin on Flexural strength of G.R.P. after dropweight impact

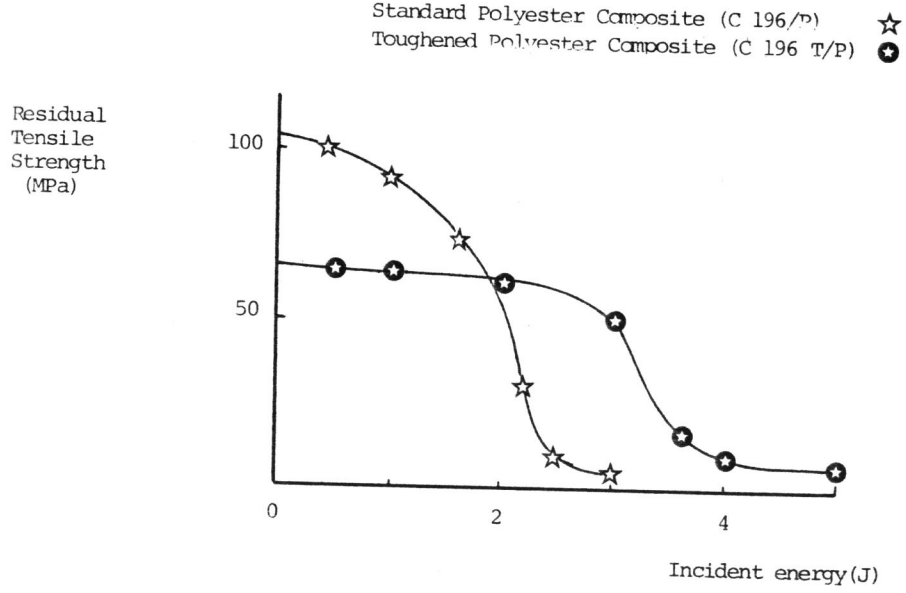

Figure 6 : Effect of resin on tensile strength of G.R.P. after dropweight impact