

The chemistry and properties of a new generation of toughened epoxy matrices

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Novel polyurethane-based liquid polymers, used in conjunction with the more conventional epoxy resin/reactive liquid polymer adducts, offer the ability of formulating matrix systems having superior toughness than before; an important criterion when considering, for example, the fatigue resistance of modern composite materials and bonded structures. Such matrices can be used in their own right as structural adhesives for bonding a wide range of metallic, non-metallic and sandwich substrates and structures. On the other hand, combined with glass, carbon or aramid fibres, they can yield prepregs which translate the tough adhesive properties of the matrix into the final composite component.

Key words: toughened epoxies, polyurethane modifier; blend synergy; matrix properties; structural adhesives; composite prepregs

For some considerable time, polyurethanes (PUR) and polyurethane prepolymers have been used to give flexibility to epoxy resin formulations, especially those for use as sealants and mastics¹⁻³. Likewise, functional rubbers — particularly those based on butadiene and/or copolymers of acrylonitrile and butadiene — have been used to impart toughness⁴⁻⁶ and have led to the relatively modern generations of so-called 'toughened epoxy' structural adhesives.

This paper outlines the chemistry behind and the properties of a new generation of matrix materials for both structural adhesive and composite use, where, as a result of recent research work, the best properties of each modifier can be incorporated into the formulated system.

Background chemistry and toughening mechanisms

Polyurethanes and/or their prepolymers, by the very nature of their structure, are able to produce a high degree of flexibility in the cured epoxy system by modifying the otherwise rigid and essentially brittle continuous phase. However, this is usually at the expense of creep resistance, stiffness and thermal stability and hence polyurethanes are more generally used in sealants rather than structural adhesives.

On the other hand, pre-reacted adducts of epoxy resins and carboxy-functional liquids (or, occasionally, solid acrylonitrile-butadiene polymers (e.g., Hycar CTBN, Hycar 1072, etc.)) (Fig. 1) are initially compatible with the formulated, epoxy-based matrix system but, on cure, phase separate to form a dispersion of rubber-based particles within the cured bulk. The energy absorption characteristics of these particles enables a considerable degree of toughness to be built into the relatively brittle matrix. The continuous phase (i.e., the cured epoxy) is therefore left essentially unchanged, hence preserving its desired performance as far as stiffness, high load-bearing capability, creep resistance and thermal stability are concerned.

Whilst the major drawbacks associated with polyurethane modification of structural matrices are fairly obvious, those related to rubber toughening are not so straightforward. Firstly, the degree of toughness imparted to the cured system, as evidenced by static and dynamic (impact) peel resistance, has often been insufficient when temperatures below about -40 to -50°C are encountered on static peel testing and generally across the whole temperature band on impact testing. Further, in many instances when such matrices are used in conjunction with glass, carbon or aramid fibres to produce structural composites, the toughening mechanism appears to function less efficiently —

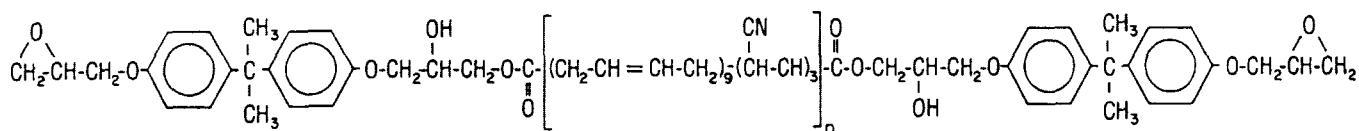


Fig. 1 A typical adduct of an epoxy resin and a carboxyl-terminated acrylonitrile-butadiene liquid rubber

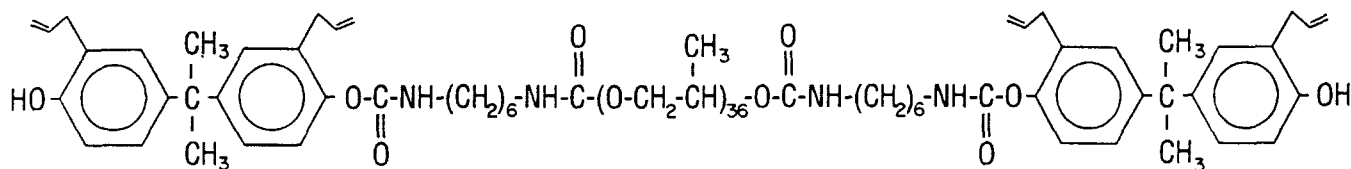


Fig. 2 A typical phenolic-tipped polyurethane liquid rubber

possibly due to the very small free volume between the fibres reducing the degree of phase separation — leading to a diminution of the expected properties.

However, recent research work at Ciba-Geigy⁷, addressing the problems associated with impact peel performance of toughened structural adhesives, has identified a range of novel liquid polymers based on phenolic-terminated polyurethanes (Fig. 2 shows a typical structure) which can be used in conjunction with simple adducts of epoxy resins and carboxyl-terminated acrylonitrile-butadiene liquid rubbers to great effect. Provided that the polyurethane:rubber ratio used lies within the optimized range⁷, then the chemistry and nature of the precipitated phase is altered; this allows a degree of blend synergy to take place and leads to an improvement in the adhesive shear properties, compared with a standard CTBN-toughened system, coupled with a marked increase in peel strength, particularly under dynamic loading conditions (Fig. 3).

Blend synergy — toughening mechanisms

As has been stated, blend synergy appears to be the key to improved performance, and Mülhaupt and Powell's initial work⁷ has shown the importance of

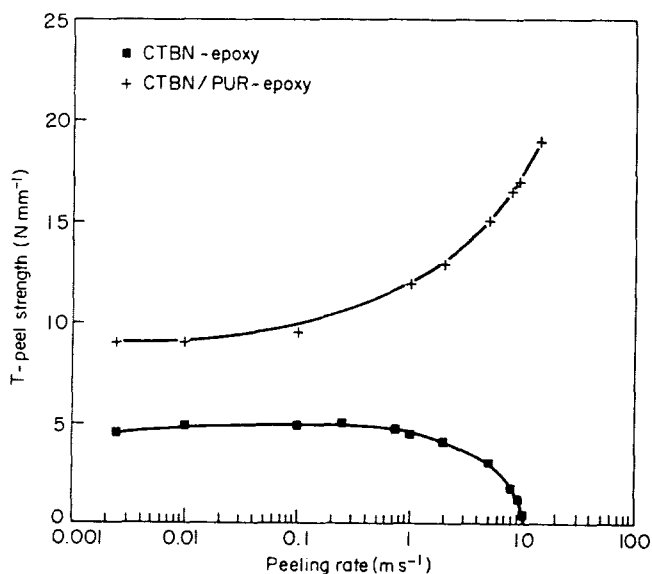


Fig. 3 T-peel strength vs. peeling rate: comparison of CTBN-toughened epoxies with CTBN/PUR-toughened epoxies

compatibility between the two modifying polymers in attaining this condition. Compatibility can be obtained by careful 'tailoring' of the polyurethane chemical structure as well as optimizing its ratio with the liquid nitrile rubber. The degree of compatibility can be further enhanced if both polymers contain reactive groups (as shown in Figs 1 and 2) which can co-cure to form a microphase having interpenetrating rubber networks: a typical mechanism is represented in Fig. 4.

When all the conditions are optimum, the nitrile rubber/epoxy adduct, instead of having a distinct, separate phase, is incorporated into the polyurethane microstructure, resulting in the formation of a novel non-continuous microphase that has a somewhat similar bimodal distribution to that seen with standard CTBN toughening but with what appears to be a slightly larger upper limit on particle size. The micrographs in Fig. 5 show how similar these precipitated phases are.

It is believed, however, that it is the polymer which is retained by the continuous phase that produces the marked changes in the physical properties of the cured matrix. Various hypotheses have been put forward as to the toughening mechanisms associated with this phenomenon; some are briefly outlined below.

- Sufficient blended polymer is held in the continuous phase or is present as a co-continuous phase to toughen the whole matrix without detriment to the system's glass transition temperature (T_g), stiffness, load-bearing capabilities, etc.
- The modification to the continuous phase is such as

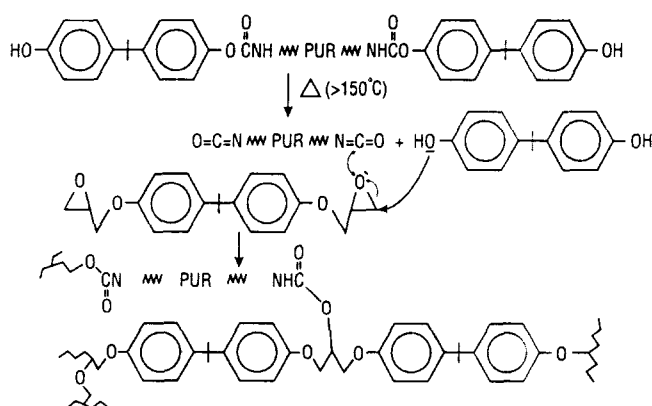


Fig. 4 Typical reaction mechanism between CTBN/epoxy adducts and phenolic-tipped PUR

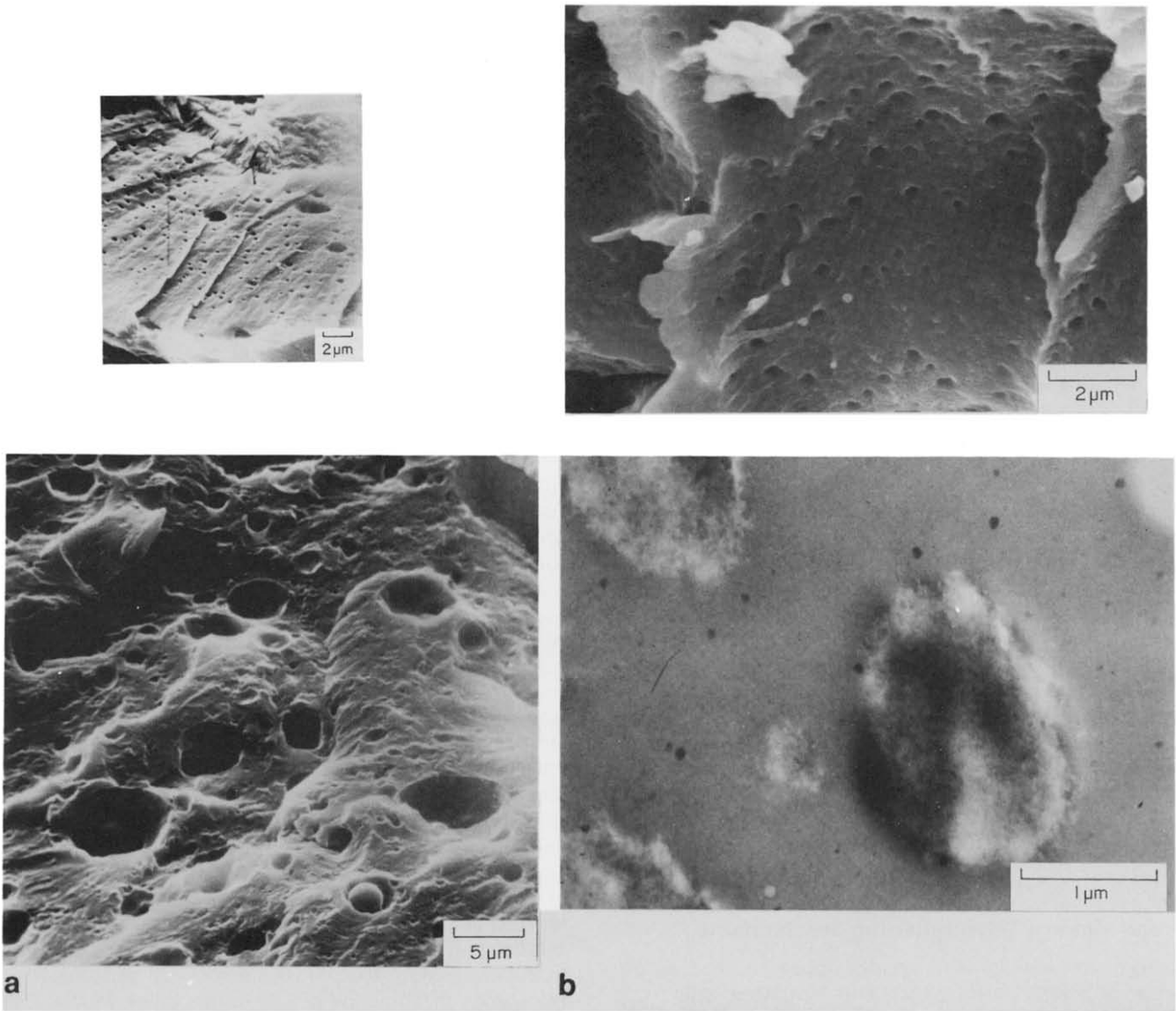


Fig. 5 Scanning electron micrographs of fracture surfaces through: (a) conventional CTBN-toughened epoxy matrices; and (b) novel CTBN/PUR-toughened epoxy matrices

to improve the 'bond' between it and the precipitated phase, this possibly being achieved by the presence of a so-called spinodal decomposition where there is a series of intermediate phases between the continuous and the precipitated whose compositions vary between 'epoxy-rich' to 'polymer-rich'^{8,9}.

- A co-continuous phase is formed having a structure comprising discrete particles of the interpenetrated rubber networks whose particle size is on the nanometre rather than the micrometre level. With the much higher incidence of energy absorbing particles, it would be expected that such a zone would have a more immediate and efficient response to a propagating crack, hence leading to improved toughness. This mechanism could also explain the excellent toughness-related results obtained on composite structures, discussed below.
- A combination of any or all the above hypotheses.

Properties of structural adhesives and composites

As indicated above, this novel toughening process was developed to improve the impact resistance of structural adhesives, particularly those for use in the automotive industry. It has now proved possible, by extensive development work, to formulate matrix systems utilizing this concept that are suitable for composite use as well as to produce similar systems which can be used as structural film adhesives for aerospace applications.

Matrix properties

As has already been stated, the conventional toughened epoxy systems are successful because the increase in toughness is achieved without sacrificing thermal, stiffness and load-bearing properties. It is important,

therefore, that any novel, improved toughening system does not achieve its goal at the expense of any/all of these properties nor at the expense of ease of processibility.

Comparison of the rheological, reactivity and thermal properties of this novel matrix system with a more conventional toughened epoxy shows that such a goal can be attained (see Figs 6-8); similar dynamic viscosities, gelation times, glass transition temperatures and loss moduli of the cured matrices being obtained.

Properties of structural adhesives

It is proving possible to utilize this blend synergy concept to formulate 120°C-curing structural film adhesives having significantly higher degrees of toughness. The comparative data presented in Table 1 indicate an improved peel strength profile for the novel adhesive over the temperature range of -55 to +80°C. Comparison of the lap shear profile between 22 and

100°C shows that the thermal properties are, indeed, not adversely affected by this novel form of toughening. Further, such adhesives perform well when bonding both sandwich and composite structures.

Properties of composite structures

Potentially, one of the most important features of this new generation of epoxy matrices is their ability to be used in composite structures (with aramid, carbon and particularly glass reinforcement) at up to 60% volume fraction (V_f) which, in the latter case, means up to 75% W_f . Not only can the matrix translate well the properties of the reinforcing fibres into the cured composite, as evidenced by the flexural strength and ultimate tensile strength values shown in Table 2, but even at these high fibre volume fractions the prepreg can utilize the properties of the matrix to act as an adhesive in its own right (Table 2). Further, such a matrix, by capitalizing on its improved toughness, is able to give the final composite structure enhanced performance as far as fatigue and impact-related properties are concerned.

Current work along these lines has culminated in the development of a series of adhesive prepreps which now form the basis of the 'Aerospace ARALL' range of fibre-reinforced aluminium laminates¹⁰⁻¹². The glass-fibre reinforced version, in particular, produces an engineering material (GLARE¹³) having such strength, durability and resistance to fatigue and damage that

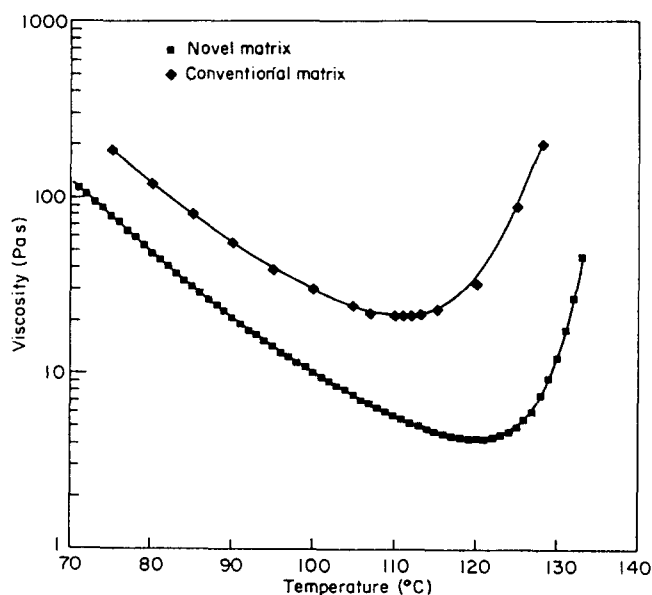


Fig. 6 Rheology of matrix materials: Rheometrics RDS determination in cure mode

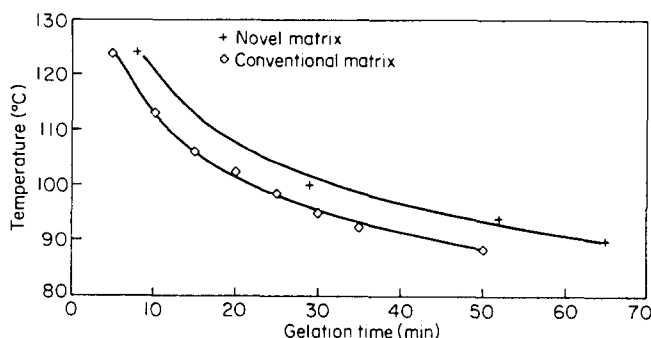


Fig. 7 Gelation times: Koffler Heizbank determination

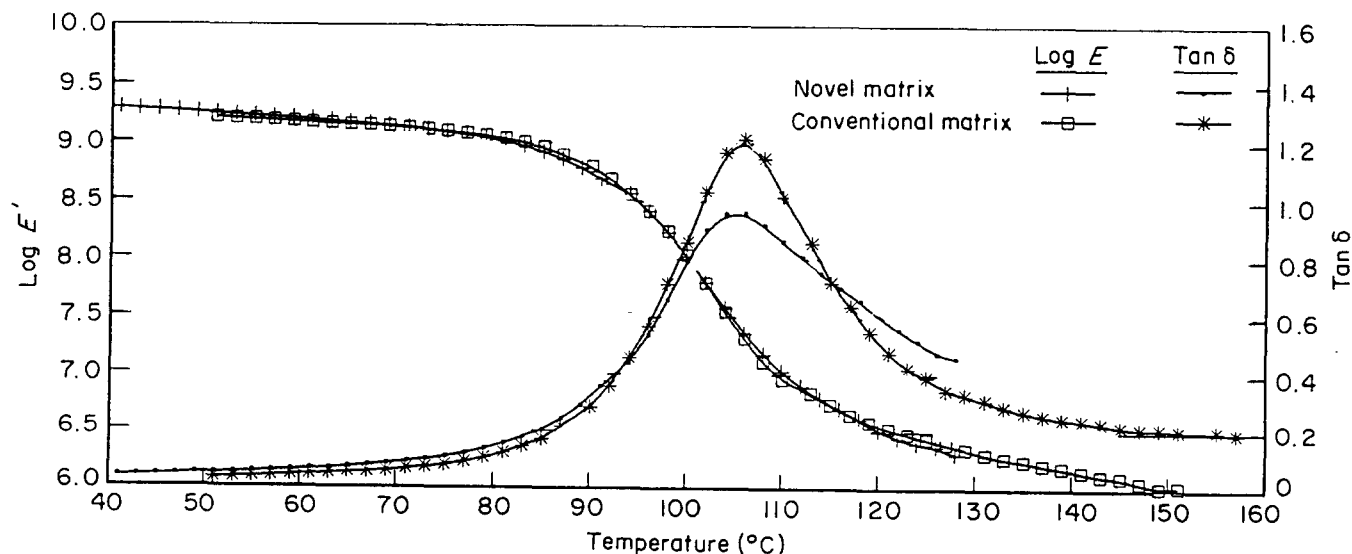


Fig. 8 Dynamic mechanical thermal analysis (frequency = 1 Hz, strain = $\times 4$, scanned at 2°C min^{-1})

Table 1. Comparison of conventionally and novel-toughened structural adhesives

Test	Epoxy/CTBN toughened	Epoxy/PUR/CTBN toughened
Lap shear strength (MPa) at:		
-55°C	46.5	45.0
+22°C	42.5	43.7
+80°C	22.1	28.0
+100°C	12.9	10.2
Floating roller peel strength (N mm ⁻¹) at:		
-55°C	5.4	7.9
+22°C	11.9	13.0
+80°C		11.7
Honeycomb climbing-drum peel strength (N mm ⁻¹) at:		
+22°C	10.0	13.1

Table 2. Mechanical properties of a novel-toughened prepreg*

Test	Strength value
Ultimate tensile strength at 22°C	1720 MPa
Interlaminar shear strength at 22°C	63 MPa
0° tensile modulus at 22°C	54 GPa
Lap shear strength at 22°C	26 MPa
Lap shear strength at 82°C	20 MPa
Floating roller peel strength at 22°C	6.1 N mm ⁻¹

*Prepreg was Fibredux 925G-RA 9041-5-25% cured for 1 hour at 120 ± 5°C

20–30% weight savings are confidently predicted¹¹ for aircraft structures (e.g., fuselages) utilizing such materials. Typical 'laminated' properties are given in Table 3 for two versions of GLARE; they compare favourably with monolithic aluminium.

It is in the specific strength properties (tensile, blunt notch and sharp notch) as well as the fatigue and impact performance where the benefits of this type of structure can be observed. The specific strength properties can be seen in Table 3, as can the impact values. Fig. 9 shows the orders of magnitude improvement in arresting crack growth under fatigue conditions.

The effect of the use of the novel toughener on this structure is difficult to quantify as this particular combination is essentially unique. However, Table 4 does show two results with experimental laminates where the matrix system was a conventional toughened epoxy; a considerable improvement is to be noted. It is believed that the enhanced toughening mechanism in the matrix resin formulation, producing 'tough' laminates even though the volume fraction of the reinforcement is very high, is the prime explanation for such composite structures being so resistant to fatigue loading and induced crack growth.

The toughened adhesive characteristics of the

Table 3. Comparison of GLARE laminates with monolithic aluminium

Test		GLARE-2	GLARE-3	2024-T3
Ultimate tensile strength (MPa)	L*	1230.0	755.0	440.0
	T*	320.0	755.0	435.0
Tensile yield strength (MPa)	L	400.0	320.0	324.0
	T	230.0	320.0	290.0
Elastic tensile modulus (GPa)	L	65.6	57.5	72.4
	T	50.2	57.5	72.4
Ultimate strain (%)	L	5.1	5.1	8.0
	T	13.6	5.1	8.0
Ultimate bearing strength (MPa)	L	704.0	690.0	1076.0
Blunt notch strength (MPa)	L	775.0	501.0	550.0
	T	290.0	501.0	550.0
Sharp notch strength (MPa)	L	650.0	409.0	350.0
	T	230.0	409.0	350.0
Energy to initiate damage† (J)		15.0	17.3	15.1

GLARE-2: 2024-T3/UD prepreg; 3/2 lay-up; 1.4 mm thick

GLARE-3: 2024-T3/50-50 cross-ply prepreg; 3/2 lay-up; 1.4 mm thick

*L — longitudinal direction; T — transverse direction

† Sheet thickness = 1.4 mm

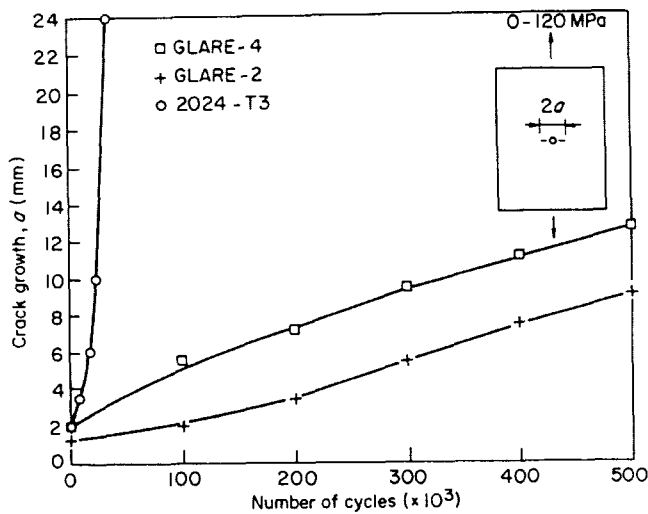


Fig. 9 Fatigue crack growth in GLARE-2 (2024-T3/UD prepreg) and GLARE-4 (2024-T3/70-30 cross-ply prepreg)

Table 4. Comparison of conventional and novel tougheners in a GLARE configuration

System	Blunt notch strength (MPa)	Floating roller peel strength (N mm^{-1})
Conventional toughener	703.3	6.5
Conventional toughener	706.9	4.9
Novel toughener	752.7	8.1

matrix, whilst ensuring both good adhesion to the aluminium substrate and no delamination under load, after the initiation of a crack in the aluminium substrate, enable a necessary but highly controlled degree of delamination to take place to the weaker interface (the surface of the glass reinforcing fibres) without catastrophic failure occurring. This controlled delamination is vital to the attainment of the fatigue properties as it blunts the tip of the crack, dissipates the crack energy and allows the load to transfer to the unbroken glass fibres, thereby bridging the crack and preventing any further growth. This process is represented schematically in Fig. 10. With a matrix system any less tough, unstable delamination between fibre and matrix — or, worse, between matrix and aluminium substrate — will take place, leading to an unchecked crack growth and a considerably lower fatigue life.

Conclusions

By careful attention to the system chemistry, it is possible to formulate matrices containing blends of liquid polyurethanes and epoxy resin/reactive liquid rubber adducts which by some form of blend synergy can impart enhanced toughness to both adhesive and prepreg materials, particularly as far as dynamic (impact) and fatigue loading are concerned, but not at the expense of the system's thermal properties.

Initial examination of the chemistry of such matrices leads to the belief that so-called spinodal decomposition takes place during cure which could

Fatigue crack closure in aerospace ARALL

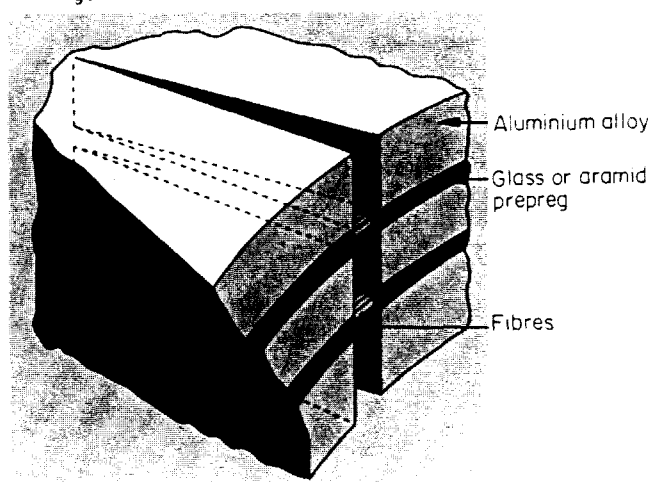


Fig. 10 Schematic representation of glass fibre 'bridging' to arrest crack growth in glass/epoxy reinforced aluminium laminates

produce co-continuous phases of polymeric material with particle sizes at the nanometre rather than the micrometre level. This would mean a more immediate and efficient response to a propagating crack leading to enhanced toughness.

Should the above initial observations be fully confirmed as a result of the numerous adhesive and composite test programmes already under way, then a new generation of tough, matrix systems for both structural adhesive and composite applications will become available.

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