

Viscoelastic phenomena in the fracture of thermosetting resins

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Comparisons of stress–strain and fracture behaviour of thermosetting resins have shown viscoelastic non-linearity to be compatible with the complex fracture behaviour of thermosets. Fracture on a load controlled test machine has shown additional evidence that non-linearity is present in the material. This phenomenon is linked to previous studies of the fracture surface that have shown evidence of viscoelasticity in the formation of the surface texture. The proposed mechanism is consistent with a crack tip blunting model of stick–slip behaviour. Parallels are shown to exist between known thermoset fracture behaviour and phenomena observed in composite delamination studies.

1. Introduction

The fracture of thermosetting resins is of special interest to the fracture behaviour of composite materials. This is due to the matrix material's dual role of facilitating load transfer between fibres as well as that of an adhesive between laminar layers. For these reasons the fracture behaviour of thermosets has been closely studied for some 20 years or more.

It is well known that the fracture behaviour of thermosets presents difficulties in discretely characterizing fracture toughness. Three distinct modes of crack growth can occur known as stable or continuous, catastrophic and stick–slip. Factors that are known to determine the mode of crack growth include strain rate and temperature as well as the material, curing conditions and environment.

It has been found that crack instability is caused by blunting of the crack tip due to yield [1]. The blunted crack retards crack growth and results in more strain energy being stored in the surrounding material. The excess strain energy allows the crack to grow at an accelerated rate, which cannot be sustained by the crosshead. This excess energy is absorbed during the creation of new fracture surfaces and when all excess energy is absorbed the crack will arrest again. Further support for this mechanism can be found from analytical studies that suggest a variation in R , the fracture resistance, during crack growth [2]. It can be shown that a variation in R with crosshead speed and crack velocity must occur. An explanation based upon yield is particularly attractive as it can account for the variation in R , as well as the prominent surface markings found down the fracture surface. These markings are known to correspond to a crack arrest event.

The blunting of the crack tip can cause problems with the initiation of cracks into test specimens. This is particularly so if the starter notch has a blunt finish.

A high degree of blunting before the crack initiates may result in catastrophic crack growth.

A recent study [3] of the fracture surface has found the periodicity of the surface texture to be dependent on the material and on the rate of fracture. The variation in the surface texture can be seen clearly in Fig. 1 [4]. The material properties found to be linked to the surface texture were the glass transition temperature and the rubbery modulus, but not the compressive Young's modulus.

From this experimental evidence it has been proposed that the crack propagates due to the formation of a liquid zone at the crack tip. This result is in disagreement with the blunting due to plastic yield mechanism.

The experiments presented here have been performed with the purpose of describing the crack growth behaviour in a variety of common thermosetting matrix materials. The fracture behaviour has been compared with the stress–strain behaviour and the response to different testing machines. A rationale for the behavioural variation is presented that proposes viscoelasticity to be the controlling factor.

2. Experimental procedure

2.1. Test materials

Five different thermosetting resins were used in this study. All were chosen due to their commercial use as matrix materials in structural composites. Three of the resins were from the epoxy family and these were Araldite K142, aramine ADR30 with ADR25 hardener) and secomin. To complement the epoxies, polyester 61–361 and phenolic were also used to give a broad range of common thermoset materials. All resins were cured to the manufacturers' recommendations and no variation in curing schedule or modifiers

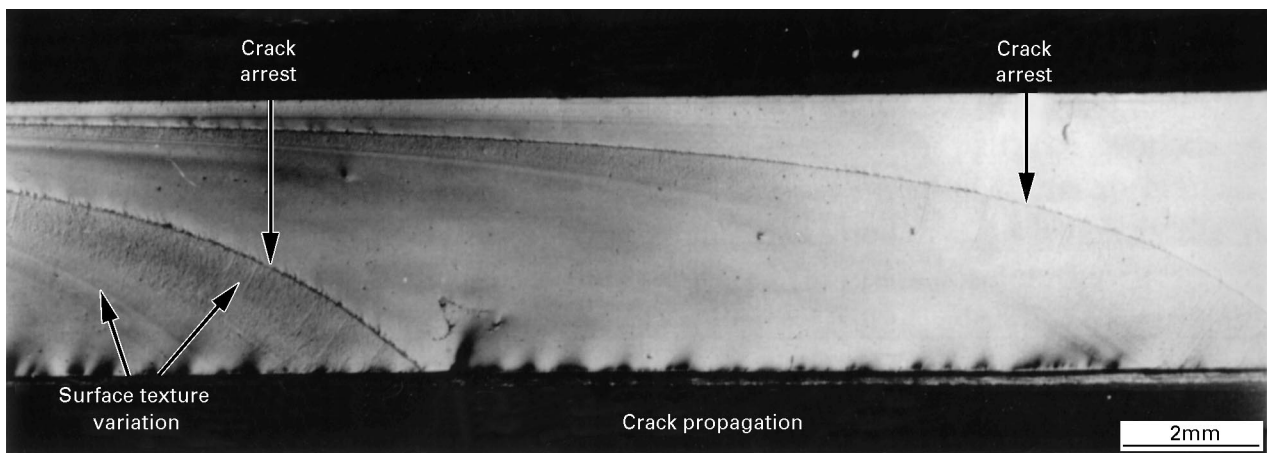


Figure 1 Tide lines and fracture surface texture in the DT specimen.

were used in this study. The resins were cast into slabs between a glass and perspex mould and later trimmed down to size.

2.2. Crack growth-experiments

All fracture studies were performed using the double torsion test geometry. This test specimen was selected due to its high geometric stability factor. Any variations in crack growth behaviour should therefore be as a result of material phenomena. A moderate aspect ratio was used to give a reasonably sized constant stress intensity region. The slabs were cut down to measure approximately $180 \times 60 \times 6$ mm. A starter notch was machined into one end of the specimen and this was sharpened by drawing a razor blade down the notch. The majority of fracture tests were performed on an Instron 1185 crosshead-driven testing machine with the rate of crosshead travel used as a control parameter.

Because a straight crack path was difficult to achieve in the specimen a number of tests were needed to be performed for all materials at each strain rate. The observed stress intensities of the curved crack front samples were similar to the straight cracks. However, the results from these specimens were of limited value due to the smaller constant stress intensity region, and for this reason were not included in Tables I–III. A total of 75 test specimens were used and from this a typically reliable set of data was obtained. Despite the small sample size the observed variation between materials is large and sufficient to

TABLE I Notch sensitivities of thermosetting resins^a

Material	Crosshead speed (mm min^{-1})					Average
	10	5	2	0.5	0.2	
Araldite	3.50	1.65	1.25	4.32	2.05	2.55
Aramine	0.94	1.12	1.01	1.12	0.66	0.97
Phenolic	0.27	0.30	0.26	0.31	0.33	0.29
Polyester	0.27	0.51	0.46	0.57	0.18	0.40
Secomin	0.59	0.63	0.36	0.72	0.32	0.52

^a Phenolic has the lowest notch sensitivity with Araldite the highest.

TABLE II Maximum stress intensities for thermosets^a

Material	Crosshead speed (mm min^{-1})					difference
	10	5	2	0.5	0.2	
Araldite	0	0.75	0.82	1.50	0.20	1.50
Aramine	0.82	0.82	0.84	0.84	0.72	0.12
Phenolic	0.31	0.35	0.31	0.38	0.35	0.07
Polyester	0.64	0.68	0.74	0.72	0.54	0.20
Secomin	0.86	0.44	0.42	0.45	0	0.86

^a Phenolic shows the least sensitivity to crosshead speed and Araldite the highest.

TABLE III Crack jump behaviour for thermosets^{a,b}

Material	Crosshead speed (mm min^{-1})					Average
	10	5	2	0.5	0.2	
Araldite	–	0.07	0.09	0.07	0.00	0.05
Aramine	0.07	0.12	0.12	0.19	0.10	0.12
Phenolic	0.10	0.29	0.17	0.26	0.29	0.22
Polyester	0.05	0.06	0.05	0.06	0.04	0.05
Secomin	0.05	0.07	0.00	0.00	–	0.03

^a No entry for failure in one crack jump event.

^b Zero energy for stable propagation.

lie outside any reasonable experimental deviation. This does not hold true within each material. Therefore no comment is offered for the observed sensitivity to crosshead speed of each individual material.

2.3. Stress–strain experiments

Due to the materials' low fracture toughnesses special consideration is needed to obtain the stress–strain behaviour at larger strains. The materials were tested in torsion to take advantage of the reduced principal stresses. Rectangular specimens were cut and prepared from the unstressed edge regions of the discarded fracture specimens. The machined edges were carefully polished to reduce the presence of cracks that might cause fracture. In this manner more of the elastic behaviour could be obtained than would be observed

through conventional tensile testing. The specimens were loaded by hand and, while the strain rate was not measured, all effort was made to ensure that the rate of loading was consistent from material to material. The loading was stopped when either fracture occurred or when the material showed signs of gross yielding.

3. Results

3.1. Notch sensitivity

The behaviour of the initial crack growth is often described as jump-in. The load required to begin propagation from an initiation notch is usually higher than that required for subsequent propagation. Hence, this behaviour is also known as notch sensitivity. This was found to vary greatly between the resins tested. Table I shows the maximum recorded stress intensity at various crosshead rates for all the resins tested. These results show phenolic and Araldite have extremes in variation with crosshead speed and in magnitude of sensitivity. Phenolic has a lower notch sensitivity than the other materials and this would make it easier to initiate a crack in the material. Conversely, Araldite has the highest notch sensitivity that would imply the highest fracture toughness.

3.2. Fracture toughness

Fracture toughness after jump-in is an important parameter as this is related to the rate of crack propagation in any real component. Readings were taken from the constant stress intensity region of the specimen, once jump-in had occurred, and are shown in Table II. These values highlight the variation in fracture toughness that occurs due to changes in crosshead speed. Araldite has the highest variation and phenolic the lowest. The behaviour of all materials can be further narrowed down to those displaying marked sensitivity to crosshead speed, such as Araldite and secomin, and those with little sensitivity, such as aramine, phenolic and polyester.

3.3. Stress–strain behaviour

Of special interest are the stress–strain curves for these materials that are shown in Figs 2a–e. The shear modulus was evaluated first by using modifying factors [5] for the rectangular section and then converting to elastic modulus by using a factor of $3^{1/2}$ for pure shear. The stress–strain behaviour showed a great deal of variation between materials with some failing by gross yielding while others failing by classical brittle fracture. The graphs show Araldite and secomin to have a marked non-linear variation; while phenolic, aramine and polyester show the most linear, classically brittle behaviour. This indicates that Araldite and secomin have a higher degree of non-linear behaviour. These two materials also showed quite noticeable load relaxation during the testing. Because of the non-linearity, the known tensile variation with time and temperature, and the load relaxation, these materials can be thought of as showing viscoelastic-like behaviour.

Of special interest is the comparison of this behaviour with the generalized stress–strain behaviour of polymeric materials shown in Fig. 2f [6]. If these materials were to display the full range of behaviour then it can be assumed that Araldite and secomin would lie in the more non-linear regions; while phenolic, polyester and aramine would lie in the linear regions. The materials were only tested close to one particular strain rate; however, it is reasonable to assume that these materials would display a wider range of viscoelastic behaviour if testing was conducted across a range of strain rates and temperatures. It is also possible that the materials would exhibit a complete viscoelastic response.

3.4. Crack jump behaviour

Table III shows the difference between stress intensities at initiation, K_{IC} , and arrest, K_{IA} , as a fraction of the critical stress intensity, K_{IC} . As such it is a measure of the stress intensity associated with the crack jumps. By considering a Griffith energy approach it can be shown that the figures in Table III are also proportional to the energy absorbed during the crack jumps. From basic Griffith theory it would be expected that higher values of crack jump energy would result in the formation of a larger fracture surface, a . This is confirmed in practice by phenolic and polyester resins. Phenolic was found to propagate in large crack jumps, with only a few required to cleave the entire specimen. Polyester on the other hand propagates through the specimen with a large number of small crack jumps.

3.5. Fracture on MTS testing machine

In an attempt to attain more stable crack growth some of the resins were also tested in an MTS electro-hydraulic testing machine. The entire testing rig used in the Instron was transferred into the crosshead of the MTS. To approximate “dead weight” conditions the specimens were loaded manually by using the load control. This was done to avoid the rate effects inherent in crosshead machines.

When comparing the same mode of propagation, the fracture toughness for all resins was found to be exactly the same as for the screw driven machine tests. In addition, all the resins tested showed their most stable mode of propagation when tested in this way.

It is interesting to consider the theoretical stability for the testing machine used. The mathematical expression for stability in a “soft” testing machine is [7]

$$\frac{1}{R} \frac{dR}{da} - \frac{[d^2(u/P)/da^2]}{[d(u/P)/da]} > 0 \quad (1)$$

where u is the displacement associated with the applied force, P .

When inserting the compliance for the DT (double torsion) specimen

$$C = \frac{u}{P} = \frac{3a_m^2}{Gw_mt^3} \quad (2)$$

where C is the compliance of the specimen; a_m is the crack length; t is the thickness of the specimen; w_m is the width of the ligament. G is the clear modulus.

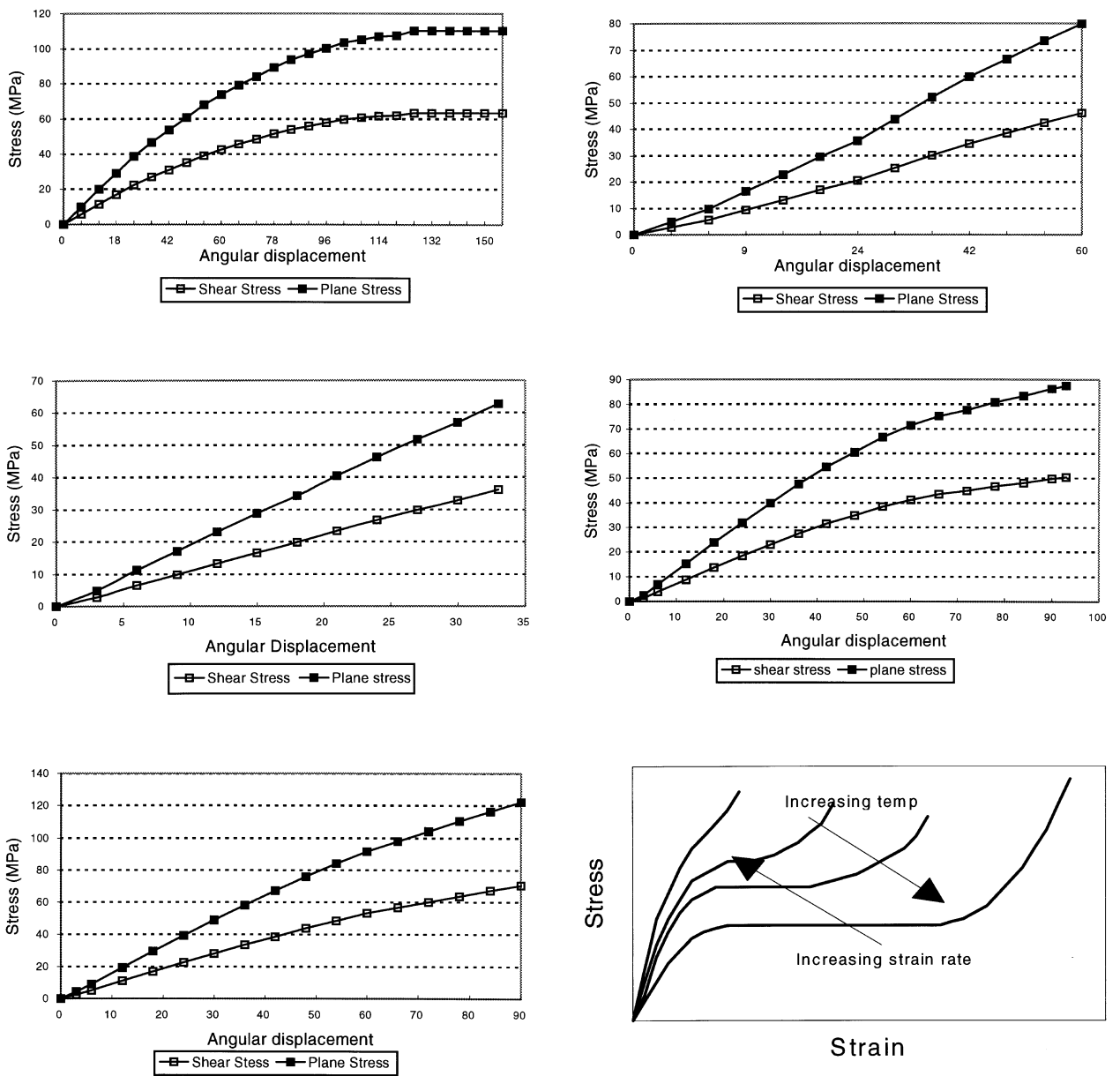


Figure 2 Stress–strain behaviour for: (a) secomin, failure by yield; (b) phenolic, failure by fracture; (c) polyester, failure by fracture; (d) Araldite, failure by yield; (e) aramine, failure by fracture; and (f) generalized behaviour for polymeric material. (□) shear stress, (■) plane stress.

This expression conveniently reduces to

$$\frac{1}{R} \frac{dR}{da} > 0 \quad (3)$$

The relation is to be expected because the high stability of the DT specimen will result in high dependence on the crosshead for crack growth rate. In a load controlled machine, such as the MTS, the controller will automatically move the crosshead to hold the applied load. If $dR/da \leq 0$ then the crack resistance would be reducing, or marginally stable, as the crack grows. Hence, the crosshead will accelerate. This would cause the crack to accelerate and result in an unstable system. For this reason the materials tested must have had a positive “*R*-curve” for the stable growth to have occurred. This in turn implies that the materials are not perfectly brittle and some degree of non-linearity is present.

4. Discussion

The observed stress–strain behaviour shows a high correlation with the sensitivity to crosshead speed

during normal crack propagation. The materials showing highest sensitivity, Araldite and secomin, are also the materials showing the most non-linear behaviour. Comparison of the stress–strain curves to the generalized behaviour, Fig. 2f, shows that more non-linear behaviour is favoured by low strain rates and high temperatures. These are the same conditions that have been noted by various authors [1, 4] to be more favourable for unstable (or catastrophic) crack growth. In contrast, high strain rate, low temperature conditions favour linear behaviour and result in stable propagation. This correlation of both strain rate sensitivity and propagation behaviour strongly suggests that non-linear, viscoelastic phenomena are the controlling factors in the crack stability of thermosetting resins.

The observations of notch sensitivity are apparently at odds with a crack tip blunting mechanism. It would be expected that materials that show the most non-linearity would be able to store more strain energy and have the largest crack jumps. On that basis Araldite, which displays the most marked non-linearity,

should have the largest jumps. However, phenolic has the most energy absorption during crack growth. The explanation for this lies in the critical fracture toughness values themselves. Because phenolic has a noticeably lower toughness than the other materials it is much easier for cracks to grow once any minor crack tip blunting effect has been overcome. The size of the crack jumps is therefore a balance between the non-linearity of the material and the fracture toughness. It is suggested here that phenolic has the highest ratio of stress yield, σ_{yield} , to K_{IC} . It is also noteworthy that Araldite has not been shown to be any tougher than polyester or phenolic. However, the epoxy family is normally considered the “strongest” thermoset for use as an adhesive or matrix. Possibly the most useful property possessed by Araldite is its very high notch sensitivity. This will result in extremely high durability in service due to a low sensitivity to flaws or inclusions.

It has been proposed [3] that the propagation of the crack is through the formation of a liquid zone at the crack tip. A heating effect is present due to the high thermal capacitance of the material combined with inefficiencies in the fracture phenomena occurring at the crack tip. These inefficiencies were part of Griffith’s original formulation of fracture behaviour and usually take the more familiar form of stress or acoustic waves. Studies of similar materials have shown [8] that this mechanism can result in localized high temperatures around the crack tip. Despite the evidence for a liquid crack tip the variation in the surface texture that would be expected to occur with environmental temperature does not appear to take place. It has been noted [3] that the surface texture is likely to be created by similar mechanisms as the crazing and fingering in thermoplastics. However, in thermoplastics the fingering and crazing is usually regarded to be a result of viscous flow occurring at the crack tip and not specifically due to temperature effects themselves.

Viscoelasticity is generally considered to be a consequence of the long continuous polymer chains that make up the atomic structure, as shown schematically in Fig. 3. The accepted mechanism for viscous flow is that the weak bonds between the chains can detach and the long polymers are free to twist and straighten. This mechanism is especially attractive as deformation of bonds is known to be easier at higher temperatures, and is therefore consistent with viscous flow phenomena. In the case of thermosets, shorter polymer chains are joined in an exothermic reaction. The resulting structure is usually thought of as being fully bonded with all chains interconnected. In a fully bonded structure, fracture can only occur by the large scale breaking of the polymeric chains in a brittle-like manner. The fully bonded ideal is only possible if perfect mixing, correct amounts of catalyst, monomer and correct curing conditions are all achieved. Because this is extremely unlikely some polymer chains must remain free and the structure will not be perfectly interlocked. This is shown in Fig. 3. These chains will be free to undergo deformation according to the viscous model and hence some viscous-like phenomena are possible. It is proposed here that the high stress gradients at the crack tip cause some amount of

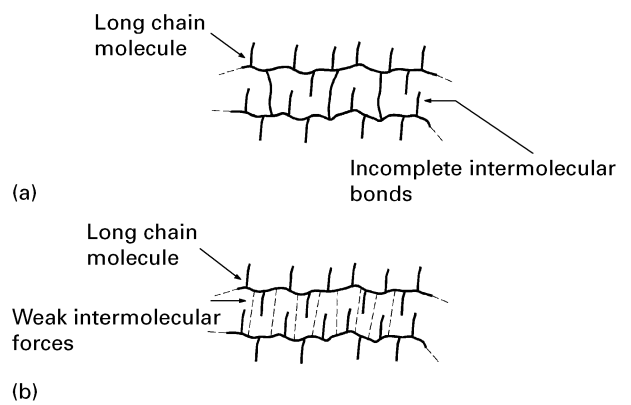


Figure 3 Schematic of the bonding in (a) thermoset and (b) thermoplastic polymers.

viscous flow to occur that is not generally observed in the bulk material. While this does not effect the majority of the material properties it can effect crack propagation due to the blunting effect. Further evidence for this idea comes from earlier studies [1, 3, 7] where control of stick–slip behaviour can be achieved by altering the curing schedule. This technique is normally used as the controlling parameter in most of the studies into stick–slip.

The fracture mechanism in thermosets is likely to be the same as that occurring in thermoplastics, with differences in scale being responsible for their apparent disparities. The mechanics of stick–slip propagation can be seen to be a result of blunting effects and the generalized stress–strain behaviour. During a crack arrest event low strain rates occur and viscous flow is favoured. In the high stress gradients at the crack tip it is entirely feasible that viscous flow could occur and continue to the point where the material’s elasticity increases again before failure. The prominent markings on the fracture surface, known to occur at crack arrest sites, can be seen to be the physical evidence of this flow. These sorts of markings are shown in Fig. 1 [4]. Once failure has occurred strain rates will be extremely high due to catastrophic-like crack growth according to the crack tip blunting mechanism. The general stress–strain curve at high strain rate would be applicable and less viscous flow would occur. The apparent fracture toughness will be lower, increasing the size of the crack jump further. This sort of variation in fracture toughness during crack propagation is consistent with the expected variation from analytical studies [2].

It is noteworthy that the varying surface textures so prominent on the fracture surfaces of these specimens can also be observed in real components. Often when fractured composite components are inspected variations in the tone or surface texture can be seen quite clearly on delamination surfaces. A number of authors [9–12] have noted that delamination often occurs in a stick–slip manner and have also observed surface texture variations. Authors have even gone so far as to evaluate an “*R*-curve” for this delamination growth [13, 14]. The explanation for the existence of an “*R*-curve” has often been put down to interactions between the fibres of adjacent laminae and the advancing

crack. This study has shown that an “*R*-curve” for the neat matrix must also exist. The evidence strongly suggests that delamination is through the resin-rich regions between adjacent laminae, and the importance of the matrix material has previously been shown [15]. The growth of cracks in this manner is of special importance as it is known that cracks will grow through these regions in preference to the laminae themselves [16–19]. A number of other authors have noted rate and temperature effects to be of significance in delamination [20–22].

From this information it would therefore be expected that the search for higher delamination resistant composites should concentrate on the fracture toughness of the matrix material in the interlaminar regions. It can also be argued that studies of the neat matrix material without fibres present should give sufficient evidence of superior matrix materials. Some success in delamination resistance has been achieved by a porous mat (interleave) being placed between adjacent laminae to create a more tortuous fracture path [23]. In addition, observations have been made that impactive delamination of soft core laminates is reduced when a core mat is used [24]. As well as the inclusion of an interlaminar constituent there would appear to be greater scope for the use of rubber modified or toughened matrix materials to increase delamination toughness of composites.

The presence of stick–slip propagation may be seen as an unwelcome complication to the studies of thermoset fracture. However, the links presented here between stick–slip propagation and composite fracture phenomena suggests that this behaviour is also present in these materials. Therefore studies of the parameters influencing stick–slip are important and due consideration of its significance in composites fracture is warranted.

5. Conclusions

The complex fracture behaviour of thermosetting resins shows high correlation to viscoelastic phenomena. The proposed mechanism for this is localized viscous flow occurring within the crack tip region, the presence of which controls further propagation due to crack blunting effect. This type of viscous flow is generic to polymeric materials; however, it is not usually attributed to thermosets due to their low fracture toughness. The rate and temperature behaviour of the viscous material are the cause of the variation in crack growth behaviour that is often encountered. This mechanism is consistent with the crack blunting mechanism and the observations of fracture surface texture. Changes in the appearance of the fracture

surface at crack arrest sites are a result of differences in the scale of non-linear flow that occur at the varying strain rates. The complex fracture occurring in the neat resins can also be seen to manifest itself in the delamination growth of composite materials.

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