The Strength of Alumina Trihydrate Filled Epoxy Resins

Mark Anthony Phipps

A thesis submitted in partial fulfilment of the requirements of Kingston University for the degree of Doctor of Philosophy

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ABSTRACT

The tensile and fracture properties of alumina trihydrate (ATH) filled epoxy resins have been determined up to a maximum volume fraction of 0.33 with a cold setting curing agent (Epikure T) and up to $V_r=0.54$ with a hot curing agent (piperidine). The effect of a reactive rubber on these properties, on its own and in ATH-filled composites have also been considered.

All filled compositions showed a lower tensile strength than the unfilled resin. The largest effect occurred at low volume fractions, up to $V_f = 0.1$, loadings higher than this did not reduce the strength any further. The addition of a rubber toughener (ATBN), to the ATH-filled composite, reduced the strength still further. The elongation to failure was also reduced. Young's modulus was increased and was in agreement with other studies and predictions of theoretical models. The Lewis and Nielsen equation was found to give a satisfactory approximation for both the ATH-filled and ATH-rubber compositions.

The fracture energy (G_{lc}) exhibited a maximum at a volume fraction of 0.1. The fracture toughness (K_{lc}) increased linearly with increasing volume fraction of filler. Addition of ATBN rubber to ATH-filled composites increased G_{lc} and K_{lc} further. The results correlated well with the crack-pinning prediction of Green at high volume fractions but showed some deviation at low loadings. The theory of Green gave a break-away value, r, of 0.75 (compared to r=1.8-2.0 for alumina). Fracture toughness results are discussed in terms of crack-pinning and crack-blunting mechanisms.

Experiments using model specimens suggested that failure in composites containing weak particles, such as ATH, was initiated by failure of the particle itself. These experiments showed that a polymer coating around the particles could improve the tensile strength by delaying fracture and then blunting any subsequent crack.

Various methods for applying a polymer coating to the filler were investigated. These included: Spray drying, solvent deposition, mechanical mixing and insitu polymerisation. The in-situ polymerisation route showed the most potential, but this needs further optimisation. Dedicated to my late Mother

JANET

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SUPPLEMENTAL LECTURES

As part of the course of study the following conferences, lectures and seminars were attended:

Title/Venue/Date	Hours
Particulate-Filled Composites	
Kingston Polytechnic, May 1990	4.75
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Manchester, British Plastics Federation. October 1990	13.25
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UMIST, Manchester. March 1991	19.0
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Kingston Polytechnic. April 1991	4.75
Polymer Blends and Mixtures	
SCI, London. December 1991	4.75
Particulate Technology	
SERC, Surrey University. July 1992	22.0
IBM/BP Seminars in Polymer Technology	
Imperial College, London.	24.0
Internal/External Research Colloquia	
Kingston University / Surrey University.	18.0
TOTAL	110.5

DECLARATION

I declare that while registered as a candidate for the higher degree of Doctor of Philosophy, I have not been registered or enrolled for another award of any other academic or professional institution. I also declare that no material contained in this thesis has been used in any other submission for an academic award. The work contained herein is solely the work of the candidate and a true and accurate description of that work carried out.

> > Mark A. Phipps

GLOSSARY OF SYMBOLS

SYMBOL	TERM
а	Crack length
В	Thickness
С	Compliance
d	Particle diameter
d _p	Interparticle spacing
ė	Strain rate
€ _{c,m,y}	Elongation (composite, matrix and yield respectively)
E _{c,m,f}	Young's modulus (composite, matrix and filler respectively)
G _{c,m,f}	Shear modulus (composite, matrix and filler respectively)
G _{Ic}	Critical strain energy release rate (Mode 1)
к	Bulk modulus
K _{lc}	Critical stress intensity factor (Mode 1)
l	Particle length
m _p	Plastic constraint factor
m	Modular ratio (E _f /E _m)
P _c	Load at failure
P _f	Maximum packing fraction
r	Break-away position (crack-pinning theory)
r _y	Irwin plastic zone radius
ry'	Von mise plastic zone radius (plane strain)
r,"	Von mise plastic zone radius (plane stress)
R	Universal gas constant
R	Dugdale plastic zone length
S	Stress concentration
S	Specific surface area
т	Temperature (Kelvin)
Τ _L	Line energy per unit length of crack
T _g	Glass transition temperature
U	Cross sectional area of a polymer chain

V _f	Volume fraction
V _f '	Apparent volume fraction
W	Width
Y	Geometric factor
α _m	Linear thermal expansion coefficient (matrix)
α _f	Linear thermal expansion coefficient (filler)
δ _t	Crack opening displacement
Δ	Displacement
θ	Angular coordinate
ν _(m,f)	Poisson's ratio (matrix and filler)
V*	Activation energy
ρ _α	Frictional force
ρ	Density
σ _{c.i.m.y}	Ultimate strength (composite, interface, matrix and yield
	respectively)
σ₀	Stress on bulk material
σ _p	Line zone internal stresses
σ _{r,t}	Radial and tangential stresses
τ _m	Shear strength of the matrix

GLOSSARY OF ABBREVIATIONS

ABBREVIATION TERM

A1100	Aminosilane
ATBN	Amine terminated elastomer
ATH	Alumina trihydrate (Aluminium hydroxide)
CTBN	Carboxyl terminated elastomer
CTOD	Crack tip opening displacement
CCl₄	Carbon tetrachloride
DCM	Dichloromethane
DMSO	Dimethylsulphoxane
ETBN	Epoxy terminated elastomer
FEA	Finite elemental analysis
HIPS	High impact poly(styrene)
HGB	Hollow glass beads
HTBN	Hydroxyl terminated elastomer
IPN	Interpenetrating polymer network
Latex	poly(vinylacetate) latex polymer
LEFM	Linear elastic fracture mechanics
MEK	Methylethylketone
MNDA	p-methan-diamine
mps	Mean particle size
ntf	Normal to force
Р	Piperidine curing agent
PEI	Poly(etherimide)
PMMA	Poly(methylmethacrylate)
psi	Pounds per square inch
ptf	Parallel to force
PTFE	poly(tetrafluoroethylene)
PVAc	Poly(vinylacetate)
SEM	Scanning electron microscope/microscopy
SENT	Single edge notch (tension) fracture specimen

SGB	Solid glass beads
SLGB	Split glass bead
SQGB	Square glass beads
Т	Epikure® T curing agent
TDCB	Tapered double cantilever beam fracture specimen
TGA	Thermogravimetric analysis

DEFINITIONS

Aspect ratio	Particle length / particle diameter
Fracture energy	The critical strain energy release rate (G_{lc})
Toughness	The critical stress intensity factor (K_c or K_{ic})
Fracture toughness	See "Toughness"
Particulate	A filler with an aspect ratio of approximately one
Composite	A cured resin containing ATH and/or a reactive rubber
	modifier
Glass bubbles	Hollow glass beads
phr	Parts per hundred 'resin' (where 'resin' = epoxy resin +
	hardener)
Volume fraction of filler	= volume of filler / total volume
Hybrid	A composite containing a filler and a rubber modifier
Laminate	A composite that contains glass fibre

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INTRODUCTION

Polymeric materials are used extensively in the developed world today. Thermoplastic polymers have achieved wide-scale acceptance but their applications have traditionally been in low-tech mass produced products, although this is not quite the case today. Thermosetting polymers, although they are not as widespread, are specialised polymers in niche areas where for example high thermal stability is required. Epoxy resins are one important class of thermosetting polymers.

These were commercialised in the late 1940s and its main applications have been in surface coatings, adhesives and structural composites^[1]. The growth area for these resins has been as the matrix in glass and carbon reinforced polymers (GRP and CRP) for the aerospace industry where its combination of high strength and low weight have allowed it to displace the traditional metallic materials. Epoxy resins are probably the most studied thermosetting resin, if not the most studied polymer. The level of interest belies the fact that it is not a high volume polymer in terms of its sales^[1]. The large wealth of academic interest stems from the resins versatility.

A major issue facing polymer based materials today is fire and fire resistance. Polymers, being organic, burn readily. Public awareness of this hazard has been heightened by recent fire disasters. The traditional methods of imparting fire retardancy to polymers are based on chlorine, bromine, phosphorus, antimony and boron. These could be easily added using functionalised curing agents^[2]. Studies have shown^[3,4] that smoke and toxic gases are a major cause of death in fires. The traditional additives do nothing to suppress the smoke generation and, in addition, they produce toxic gases themselves^[4]. These toxic gases can be comprised of strong acids which are not only harmful to humans but they cause considerable damage to any equipment that contains steel.

Alternative fire retarding materials include magnesium hydroxide^[5], tin oxide^[5] and alumina trihydrate^[7]. Alumina trihydrate (ATH) is the most widely used of these alternatives. It improves the fire resistance and reduces the smoke evolution, but there are several drawbacks: (1) A high loading is required and the increase in fire resistance is not as efficient as a halogen additive and (2) the mechanical properties of the host polymer suffers^[8]. The tensile strength and elongation are reduced but

the modulus is improved^[8]. For a material that is used in a structural application this could be a major problem. If the tensile strength could be improved, the applications and usefulness of this class of filler could be extended. They are already finding increasing use as a third phase in glass reinforced laminates^[7,9,10].

The ability of ATH to impart fire resistance to a polymer is not its only feature. It can improve the electrical properties of epoxies^[1], reduce shrinkage and because it is relatively inexpensive, it considerably reduces the cost of end products by reducing the expensive polymer content.

The properties of ATH filled systems has been investigated previously, but the number of investigations of ATH-filled epoxy resin is very small compared to the ones that consider other fillers, specifically, glass beads. Lange and Radford^[11,12] and Wainwright^[8] studied the tensile strength and fracture properties of ATH-filled epoxy resin. In addition, Wainwright^[8] looked at the viscosity, sedimentation and flammability. These studies looked at filler loadings up to a volume fraction of approximately 0.3 for fine particle sizes.

These studies were contradictory in their conclusions for the tensile strength response and the fracture toughening mechanisms. Radford^[11] concluded that the tensile strength reduction was caused by the inherent weakness of the ATH particles and that the fracture toughening mechanism was crack-pinning^[12]. Wainwright^[8], on the other hand, concluded that stress concentrations caused the reduction in strength and crack-blunting was responsible for the improved fracture properties.

The aim of this project was to investigate how ATH embrittles, and therefore weakens, the epoxy matrix and how this undesirable effect could best be moderated.

CHAPTER 1

LITERATURE SURVEY

1.1 INTRODUCTION

This literature survey covers published literature on specific topics relevant to this study. It details the fundamental theories and key discoveries which are the basis of the arguments in this thesis.

The literature survey covers the tensile properties of particulate-filled, rubberfilled and hybrid composites. The fracture properties and toughening mechanisms for particulate filled thermosetting polymers are also reviewed. The application of a polymer coating to the filler and its effect on the composite's physical properties are discussed.

1.2 MECHANICAL PROPERTIES

1.2.1 Modulus

The modulus of a material is defined as its resistance to deformation when a force is exerted. The deformation can cause stretching of primary bonds and bond angle widening (both are small); chain uncoiling (rubbers) or irreversible chain slippage. Three different moduli can be used to describe isotropic material's. These are the bulk (K), shear (G) and Young's modulus (E). These moduli are related to each other by the equation:

$$E = 2G(1+\nu) = 3K(1-\nu)$$
 (1)

where: v = Poisson's ratio

The addition of a high-modulus filler to a low-modulus matrix invariably leads to an increase in the modulus of the matrix (so long as the interfacial strength is high enough) and the increase is strongly dependent on the volume fraction of the filler. One of two states can be assumed, equal strain or equal stress. The Voigt model (Equation 2) assumes equal strain and relates Young's modulus to the volume fraction of filler using the 'rule of mixtures'.

$$E_{c} = E_{f}V_{f} + E_{m}(1 - V_{f})$$
(2)

where: E = Young's modulus

V = Volume fraction

f, c and m relate to filler, composite and matrix respectively. The Reuss model (Equation 3) assumes equal stress.

$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{(1 - V_f)}{E_m}$$
(3)

Equal stress models predict a higher modulus than equal strain ones. The bounds these two models predict are too widely separated to be of practical use.

Hashin and Shtrikman^[13] used the theory of elasticity to derive the upper and lower (Equation 4) bounds for rigid spheres embedded in an infinite plate.

$$G_{c} = G_{m} + \frac{(G_{f} - G_{m}) V_{m}}{1 + V_{m} \frac{6 (G_{f} - G_{m}) (K_{m} + 2G_{m})}{5G_{m} (3K_{m} + 4G_{m})}}$$
(4)

The upper bound is found by interchanging m and f in each term. The bounds these two equations produce are still too wide to be of practical use but they do serve as limits. Predictions outside of these bounds can be considered invalid.

Guth^[14] (Equation 5) and Smallwood^[15] were amongst the first workers to attempt to relate the modulus to the volume fraction of the filler. Their equations were based on Einstein's viscosity equation and can be applied at high and low volume fractions respectively to filled-rubber composites.

$$E_c/E_m = 1 + (2.5V_f) + (14.1V_f^2)$$
 (5)

Kerner^[16] proposed Equation 6. He assumed that the filler particles were spherical and that the interfacial adhesion was strong.

$$\frac{G_c}{G_m} = \left[\frac{G_f V_f}{AG_m + BG_f} + C\right] / \left[\frac{G_m V_f}{AG_m + BG_f} + C\right]$$
(6)

where: $A = (7-5\nu)$, $B = (8-10\nu)$, $C = (1-V_f)/15(1-\nu)$

Lewis and Nielsen^[17] modified Kerner's equation. By introducing the maximum packing fraction (P_f) they accounted for particle size and particle size distribution effects. Their equation is:

$$\frac{E_c}{E_m} = \frac{1 + ABV_f}{1 - B\Phi'}$$
(7)

where:

$$A = (7-5\nu) / (8-10\nu) B = (G_f/G_m) - \frac{1}{(G_f/G_m)} + A \quad \Phi' = \left[1 + \left(\frac{1-P_f}{P_f^2}\right) v_f\right] v_f$$

Narkis^[18,19] proposed the semi-empirical equation shown in Equation 8. This relates specifically to spherical fillers and is applicable over a volume fraction range of 0.1 - 0.5.

$$\frac{E_c}{E_m} = \frac{1}{S(1 - V_f^{1/3})}$$
(8)

S is an empirical parameter approximately related to the stress concentration factor and it has values in the range of 1.4 - 1.7.

A cubic model (Figure 1) was used by Paul^[20] and later Ishai^[21,22] to model the modulus of a filled system. The assumption was, that a system consisting of discretely dispersed particles, could be represented by a single continuous phase confined within a homogeneous matrix. This representation is suitable for compression and tensile modulus predictions.



The cubic model of Paul and Ishai

Paul^[20] assumed a uniform stress state to approximate the upper bound (equation 9) whereas Ishai^[21,22] assumed uniform strain (equation 10) to formulate the lower bound.

$$\frac{E_c}{E_m} = \frac{1 + (m-1) V_f^{2/3}}{1 + (m-1) (V_f^{2/3} - V_f)}$$
(9)

$$E_{c} = E_{m} \left[1 + \frac{V_{f}}{(m/m-1) - V_{f}^{1/3}} \right]$$
(10)

where *m* is the is the modular ratio between the filler and matrix (E_r/E_m) .

Numerous other equations^[23-27] have been used to relate the filler volume fraction to the modulus increase.

The volume fraction, although a major factor, is not the only one that can influence the modulus. Filler/matrix adhesion can have a large effect^[28]. Within the matrix, the filler particle acts as a nodal point for the polymer chain, in effect the site of a crosslink. If the adhesion is strong, the motion of the polymer will be constrained by the particle's surface and therefore at a minimum. If there is no adhesion then the polymer will have a maximum potential for movement because it will only be in biaxial constraint (as in plane stress).

Bueche^[29] proposed the following equation based on the assumption that the filler particle increases the effective crosslink density of the polymer:

$$E_c = E_m + \left(\frac{3 s R T X}{u}\right)$$
(11)

where: s = Specific surface area of the filler

R = Universal gas constant

T = Absolute temperature

 $X = V_f / (1 - V_f)$

u = Cross sectional area of the polymer chain

Sato and Furukawa^[30,31] proposed the equation shown below (Equation 12). If certain surface effects are ignored^[32] the equation becomes:

$$\frac{E_{c}}{E_{m}} = \left[\left(\left(1 + \frac{1}{2} - \frac{\psi^{2}}{1 - \psi} \right) \left(1 - \frac{\psi^{3} T}{3} - \frac{1 + \psi^{2} - \psi^{2}}{1 - \psi + \psi^{2}} \right) \right) - \frac{\psi^{2} T}{3 (1 - \psi)} \left(\frac{1 + \psi^{2} - \psi^{2}}{1 - \psi + \psi^{2}} \right) \right]$$
(12)

where $\psi = V_f^{1/3}$. T takes the value of one for no adhesion and zero for perfect adhesion.

The shape of the filler particles can also affect the modulus of the composite. In general, most equations assume that the filler particles are spherical but in reality most are not. There are some equations that consider the effect of the particle's shape.

Halpin^[33] used a geometric fitting parameter in his empirically based expression, the general form of which is identical to the Lewis and Nielsen equation (Equation 7) except that the constants, A and B, are now defined as:

$$B = (m-1) / (m+A)$$

A=2xAspectratio=2 (1/d) (13)

A more recent relationship was proposed by Chow^[34]. This equation takes shape into account by using the ratio of the major to the minor axis of the filler particle. The increase in modulus is given by:

$$\frac{E_c}{E_m} = 1 + \left[\frac{\left(K_f / K_m - 1 \right) G_1 + 2 \left(G_f / G_m - 1 \right) K_1}{\left(2 K_1 G_3 + G_1 K_3 \right)} \right] V_f$$
(14)

8

where
$$K_i = 1 + (K_f/K_m - 1) (1 - V_f) \alpha_i$$

 $G_i = 1 + (G_f/G_m - 1) (1 - V_f) \beta_i$
 $i = 1 \text{ or } 3$

 α and β are parameters which depend on the filler's aspect ratio and the Poisson's ratio of the matrix.

One final consideration is the effect of particle agglomeration. Agglomerations have been shown to affect the modulus^[32]. The effect will depend on the load bearing capacity of the agglomeration^[35]. If the agglomerate is reasonably strong, with good interfacial adhesion, the modulus will be increased. Ahmed and Jones^[35,36] studied the effect of agglomerations of sand and glass beads without chemical bonding (i.e. only frictional forces). They found that the moduli were higher when a hot cure was used. They postulated that the agglomerations altered the mechanism by which the stress was transferred and the thermally induced compressive stresses increased the interfacial strength of the agglomerates, and hence their load bearing capacity. They concluded that under these conditions the composite with the higher incidence of agglomerations would have the higher modulus and the proportion of agglomerates was more influential than the particle size of the filler.

1.2.1.1 Previous studies

There have been numerous studies of the effect of a particulate filler on the modulus^[37-41]. Moloney^[42] showed that the modulus of the composite increased as the modulus of the filler increased. Tod^[41] showed that hollow glass beads, with a low modulus, did not affect the modulus much. Spanoudakis and Young^[28,38] investigated a glass bead-filled epoxy with mean particle sizes of 4.5 and 62µm. They found that the particle size had no effect on the modulus. Moloney^[42], used a silica-filled epoxy resin with particle sizes of 60 and 300µm, and also found that the modulus was unaffected by particle size. Ahmed and Jones^[35,36] showed that the residual stress state could affect the modulus as well. They suggest that, when there is poor interfacial adhesion between the phases, the residual compressive stress could increase the interfacial strength and enhance the modulus.

1.2.2 Tensile strength

The tensile strength of a particulate filled polymer will depend on many factors. The work of Griffith^[43] showed that the strength of a glass fibre was very sensitive to defects in the material. These 'flaws' could be internal defects or merely surface scratches. In the early part of this century Inglis showed^[44] theoretically that the stress in the vicinity of a flaw was higher than in the bulk of the material. Therefore flaws reduce the strength of the material. It is impossible to make materials perfect; the actual strength will never attain the theoretical strength (calculated from bond strengths).



Figure 2 The upper and lower bounds of tensile strength responses

The physical properties of fillers affecting the strength are: (1) particle size and shape (2) volume fraction, and (3) interfacial adhesion between polymer and filler. Landon *et al*^[45] and Bigg^[46] showed that there are two general limits to the tensile strength of filled polymers. The upper bound assumes perfect adhesion between filler and matrix, the lower bound assumes no adhesion (Figure 2). All observed strength values of filler/matrix compositions fall somewhere between the two bounds.

The lower bound response was described mathematically by Nicolais and coworkers^[47,48] in equation 16. They assumed that the load was only carried by the polymer matrix and therefore, the reduction in strength is a result of the reduction in cross sectional area.

$$\sigma_c = \sigma_m \left(1 - b V_f^a\right) \tag{16}$$

where: σ_c = Tensile strength of the composite

 σ_m = Tensile strength of the polymer matrix

b = a constant related to stress concentrations

a = a constant related to the shape of the filler

The value of b varies with the arrangement of the filler particles. It takes a maximum value of 1.21, and is reduced if the filler aspect ratio is increased (because the stress concentrations reduce). The interfacial strength will also affect this value. The constant, a, has been reported to be between 0.66 and 1^[47] but the former is most commonly used. Earlier Nielsen^[32] proposed a similar equation, again based on the reduction in CSA, that included the stress concentration effect (S) as a variable:

$$\sigma_{c} = \sigma_{m} \left(1 - V_{f}^{2/3} \right) S$$
(17)

where S is the stress concentration factor, which can have a maximum value of one when there are no stress concentrations. Generally S would be expected to have a value of approximately 0.5.

The value of the upper bound is more difficult to describe mathematically. This type of response implies that the filler reinforces the polymer. Fillers that show this response have a high aspect ratio, fillers such as talc, wollastonite or short glass fibres.

Leidner *et al*^(49,50) proposed Equations 18 and 19, which apply to spherical fillers.

$$\sigma_c = (\sigma_i + C \tau_m) V_f + \sigma_i S (1 - V_f)$$
(18)

$$\sigma_{c} = C \rho_{\alpha} V_{f} + \kappa \sigma_{i} (1 - V_{f})$$
(19)

11

where σ_i = polymer/filler interfacial strength

 τ_m = Shear strength of the matrix

 ρ_{α} = frictional force

 κ = relative change in strength of the matrix due to the filler

= a + bd^{-1/2} (d = particle diameter)

S = Stress concentration factor

C = a constant

The constant C was determined to be 0.83 by Leidner et al^[49,50].

The equations assume that the strength is the sum of the stress carried by the filler (the first term) and that carried by the matrix (second term, allowing for the stress concentration caused by the filler). Equations 18 and 19 assume good and poor adhesion respectively. Their study concluded that smaller particles weaken the composite to a lesser extent, and the strength was inversely proportional to the particle diameter (confirming the work of Hojo *et al*⁽⁵¹⁾ and Alter⁽⁵²⁾).

Schrager^[53] proposed that there is a volume of matrix (V_m) associated with each filler particle, a 'polymer shell', which increases the apparent volume fraction of filler. He proposed:

$$\sigma_{c} = \sigma_{m} EXP \left(-r V_{f}\right) \tag{20}$$

where: $r = (V_f + V_m') / V_f$

By fitting experimental data for glass bead-filled epoxy composites, Schrager determined r to be 2.66. However, this model is only valid over a limited range of volume fractions. A similar model was proposed previously by Passmore^[54] for porous systems.

Kelly^[55] proposed equation 21 to relate the strength of a polymer filled with a particulate filler with an aspect ratio greater than 1. He related the strength of these systems to the strength of the analogous glass bead composite and to their shape, using a fitting parameter.

$$\sigma_{c} = \frac{1}{2} \frac{1}{d} \tau_{m} V_{f} + \sigma'_{m} (1 - V_{f})$$
(21)

12

where: I = particle length

- d = particle diameter
- σ'_m = the strength of the glass bead filled composites at the same volume fraction
- τ_m = shear strength of the matrix (taken as $\sigma_v/\sqrt{3}$)

1.2.2.1 Previous studies

Tensile strengths vary considerably from one system to another. Figure 3 shows the behaviour of different fillers. Bigg^[46] found that some forms of talc increased the tensile strength of thermoplastics with an increase in filler loading. Moloney *et al*^[56] showed that a silica filled epoxy resin declined in strength initially but as the filler loading increased to 50% (by volume) the strength recovered.

Polymers filled with alumina trihydrate have been studied by Wainwright and co-workers^[8,9] and earlier by Radford^[11]. Wainwright^[8,9] found that the tensile strength fell dramatically at low filler levels (<0.1 volume fraction) and then levelled off. His study was conducted at constant particle size distribution. Radford found that the strength was affected by particle size. Both authors found that coupling agents did not significantly affect the composite strength. Radford concluded that the inherent weakness of the ATH particle was the cause of the poor tensile strength. Hojo *et al*^[61] found that increasing the particle size of silica in epoxy from 25µm to 175µm reduced the strength by half.



○ Ramsteiner and Theysohn[37], □ Landon *et al*[45], ● Srivastava *et al*[57], ■ Moloney *et al*[56]

Ramsteiner and Theysohn^[37] studied the tensile properties of polypropylene filled with glass beads, talcum and wollastonite at different temperatures. They found that the model of Kelly^[55] predicted the strength of the wollastonite system but not the talcum. They concluded that the additional stress concentrations were responsible for the deviation.

1.2.3 Elongation

There is very little literature on the elongation at break of particulate filled polymers. Equations^[32,5], such as that of Nielsen^[32] (Equation 22), consider elongation in its simplest fashion. He assumed that the elongation is only due to the polymer matrix and that the matrix breaks at the same strain with the filler as without and there is perfect adhesion. As the matrix content is reduced the elongation will reduce in relation to the volume, i.e. to a cube root function.

$$\mathfrak{E}_{c} = \mathfrak{E}_{m} \left[1 - V_{f}^{1/3} \right]$$
(22)

If there is minimal adhesion between filler and polymer the elongation will be higher, than for perfect adhesion, because of the voiding formed by particle-matrix debonding.

The prediction of Equation 22 for perfect adhesion, proposed by Nielsen^[32], are compared with the results of Wainwright and Pritchard^[58] for alumina trihydrate (Figure 4). For these results the equation predicts the correct trend but under-estimates the reduction in elongation.



The elongation of ATH-filled epoxy resin compared to Nielsen's equation

1.2.4 Yield stress

Although thermosetting polymers are brittle materials, they can undergo yielding (i.e plastic deformation). Testing in tension has two major disadvantages for measuring the yield stress, (1) often specimens fracture before yielding is observed, and (2) an extrinsic yield point is measured and not an intrinsic one (Figure 34, Page 62). Particulate-filled epoxies fracture before yielding in uniaxial tensile tests. For this reason a uniaxial compression test is preferred for yield stress determinations.

The yield stress is dependent on temperature and strain rate because of a
polymer's viscoelastic nature. It increases as the temperature is reduced or the strain rate is increased^[59]. This behaviour has been modelled using the Eyring theory^[59]. This assumes that yielding is an activated-rate process.

$$\frac{\sigma_y}{T} = \frac{\Delta E^*}{\nu^* T} + \left(\frac{R}{\nu^*}\right) \ln\left(\dot{e} / A_E\right)$$
(24)

where:

- $\Delta E^* = height of the potential energy barrier$
 - R = universal gas constant
 - σ_v = yield stress
 - v* = activation energy
 - $A_E = constant$
 - ė = strain rate
 - T = temperature

Bauwens-Crowet^[60] et al showed there was good agreement to experimental data for PMMA.

Argon and co-workers^[61,62] proposed that yielding was thermally-activated production of local molecular kinks. The activation energy is obtained by modelling the intermolecular energy change as the displacement field of two equal and opposite wedge disclination loops. They related the shear modulus to the yield stress by the equation:

$$\left(\frac{\tau}{G}\right)^{5/6} = A - B\left(\frac{T}{G}\right)$$
(25)

where: τ = yield stress

G = shear modulus

T = absolute temperature

A and B are constants

This theory can predict the yield stress at absolute zero and it is capable of describing the temperature, pressure and strain rate dependence of the yield stress.

Bowden *et al*^[63,64] proposed an alternative mechanism. They suggested that yielding was the thermally-activated nucleation of small sheared regions. Young *et al*^[65] applied the theories of Argon^[61,62] and Bowden^[63,64] to an epoxy resin filled with glass beads and a rubber toughener. They found that both theories explained the behaviour, but Argon's theory was most satisfactory.

The addition of a strong particulate filler to a resin has been shown to increase the yield stress^[65-67]. The particulates effect on the yield stress is related to the volume fraction of particulate, the interfacial adhesion and the particle strength. Brown^[66] pointed out that the ratio of the yield stress to the modulus was in the range of 1/60 to 1/30. Therefore, any filler that increases the modulus will increase the yield stress as well.

There have been several equations proposed to model the relationship between volume fraction and yield stress. Ishai and Cohen^[66] proposed:

$$\sigma_{yc} = \sigma_{ym} \left(\frac{1}{1 - 1 \cdot 2 V_f^{2/3}} \right)$$
(26)

where:

 σ_{ym} = Yield stress of the pure matrix

 σ_{vc} = Yield stress of the composites

Turcsanyi *et al*⁽⁶⁹⁾ proposed a more complicated solution (Equation 27). They used a hyperbolic function to describe the change in cross sectional area (CSA) of the matrix as a function of the filler content. They considered the particle size, particle shape and particle size distribution by using the maximum packing fraction.

$$\sigma_{yc} = \frac{1 - V_f}{1 + A V_f} \sigma_{ym} EXP[BV_f]$$
(27)

A is related to the maximum packing fraction (P_f) so that when $P_f = 0.74$ (equating to hexagonal close packing) A takes a value of 2.427 and when $P_f = 0.524$ (face centred cubic packing), A = 2.318. B is a fitting parameter. The authors do not attach any significance to B, but it would be anticipated that this would relate to factors like

the interfacial adhesion and particle shape/strength. The effect of B on the predicted yield stress is shown in Figure 5.



The effect of parameter B in Turcsanyi's^[69] model on the predicted yield stress

1.3 FRACTURE SURFACE TOPOGRAPHY

The fracture surface topography of tensile specimens was fairly well studied by Cantwell^[70] and co-workers. They correlated the fracture surface morphology with the thermal and mechanical history of the specimen. They described the four distinct regions on the tensile specimen surface previously identified by Wronski^[71]. Figure 6 shows these regions schematically for a silica filled epoxy. The areas are: (1) the initiation site - this may be a defect, but is not always evident; (2) the debonded/mirror zone - a region of very smooth and glassy material; (3) the smooth zone - in unfilled epoxies this is usually evident as an array of parabolic markings; (4) rough zone. In particulate filled specimens the mirror zone is replaced with a debonded region. In filled and unfilled specimens the size of the mirror and the smooth zones increase with an increase in temperature. The size of the mirror zone has been correlated with the stress at fracture by the Jarras equation^[72]

The surface morphology^[73] correlated well with the stored elastic energy at the onset of fracture. When the specimen fractures, the stored energy must be consumed. In the mirror zone/smooth zones the energy is used to accelerate the

crack through the specimen. As the crack reaches a limiting velocity the energy must now be expended in another way. Cantwell *et al*^[70] proposed that this energy supply criterion explains crack bifurcation. The bifurcation of the crack results in the rough region on the surface as the crack propagates on different planes.



Schematic representation of the tensile fracture surface of a particulatefilled matrix

(reproduced from reference 70)

The post-mortem examination of fracture mechanics specimens can yield a great deal of information about the crack propagation mechanisms at work during the test, but care must be exercised because information can be misleading.

There are several important features on the fracture surface. In unmodified epoxy resins one of the major features is the "striations". These are a group of lines on the surface, (Figure 7). These structures have been reported in materials such as: epoxies^[74], polyimides^[76], polyesters^[76], and phenol formaldehyde resins^[77]. Atsuta and Turner^[78] proposed that these lines were caused by a change in the orientation of the tensile stress to the crack front. It has been shown^[79] that the crack deviates out of the main fracture plane in the crack arrest region. Moloney *et al*^[80] proposed that these lines were caused by the zone of microcracks in the crack tip region. Their evidence stems from direct observation in an SEM with subsequent post mortem observation of the fracture surface. Their work would seem to suggest

that similar mechanisms operate in the core of the specimen to those at the surface, and to validate the use of the direct SEM observation technique.



Figure 7 An SEM micrograph of the striations on the surface of an LEFM specimen

A feature seen on filled and unfilled resins are "river lines". These are steps on the surface that lie parallel with the direction of crack propagation. A possible reason for their formation could be defects or local inhomogeneities in the polymer causing the crack to propagate on two planes parallel with each other. Melin^[81] has shown theoretically that two cracks in a brittle material cannot meet because of the stress state in the proximity. A similar feature is the "tail" seen behind filler particles, which is proposed as evidence of crack-pinning; Melin's theoretical work has been proposed as the reason for the occurrence of these tails.

In a filled thermosetting resin the fracture surface can be examined to obtain information on the path of the crack during propagation. The amount of debonding, matrix failure or trans-particle fracture will give information on the interfacial strength between the particle and the matrix. The adhesion is a key factor in the strength and toughness of the final composite and in crack propagation mechanisms. The amount of debonding will depend on the strain rate to which the fracture surface relates. Several reports^[82-84] have demonstrated the dependence of the amount of debonding on the velocity of the crack. A comprehensive study was conducted by Cantwell *et al*^[84] and their results are shown graphically in Figure 8.



The effect of crack velocity and temperature on particle-matrix debonding (Reproduced from reference 84)

1.4 FRACTURE PROPERTIES

1.4.1 Small Scale Yielding

The stress at the crack tip has been shown to be larger than in the bulk material. Therefore, it is reasonable to expect that the yield stress of the material may be exceeded at the tip area because of the stress concentration effect. If the yielded zone is very small compared with the overall dimensions, the disturbance in the elastic stress field is negligible. Under these conditions the assumptions of LEFM will still hold true.

Inwin^[85] suggested that if the material was elastic up to the tensile yield stress, σ_{y} , and then becomes plastic, the extent of the plasticity (called the plastic zone or more correctly the deformation zone), is shown to a first approximation in Figure 9.



where: δ_t = crack-tip opening displacement r_y = Plastic zone radius a = Crack length

a+ry = Effective crack length

The plastic zone will be circular around the crack tip, therefore effectively the crack tip is at the centre of the zone. This means the value of a, should be a + r_y . In practice this approximates to a because $a \gg r_y$. The size of the plastic zone radius is given by:

$$r_{y} = \frac{1}{2\pi} \left(\frac{K_{Ic}}{m_{p} \sigma_{y}} \right)^{2}$$
(28)

The quantity m_p , the plastic constraint factor, has been shown^[86] to be unity for plane stress and $1/\sqrt{3}$ for plane strain conditions

The crack tip displacement (δ_t) is the width of the crack just behind the radius portion of the crack tip. In plane strain the displacement is:

$$\delta_t = \frac{K_{Ic}^2}{E\sigma_y} (1 - v^2)$$
(29)

The plastic zone, in plane stress, can also be modelled using the Dugdale^[87] line zone procedure (Figure 10). It is assumed that yielding of the material at the crack tip makes the crack longer by the length of the plastic zone, *R*. The stress singularity at the crack tip is exactly cancelled out by a series of internal stresses of magnitude σ_p which act on the boundary of the plastic zone.



where:

 σ_p = Plastic zone surface stress σ_y = Yield stress δ_t = Crack opening displacement

R = Plastic zone length

The value of σ_p is usually taken to be equal to σ_y , the yield stress. The length of the plastic zone ahead of the crack is related to K_{lc} , (for $\sigma_0 \ll \sigma_p$) by^[88,89]

$$R = \frac{\Pi}{8} \left(\frac{K_{Ic}}{\sigma_p} \right)^2$$
(30)

If $\sigma_p = \sigma_y$, then the crack opening displacement is that given in Equation 29.

The Dugdale line zone model is more suitable to very thin specimens and blunt cracks^[90]. But it has been found^[21] that the sub critical crack growth region in rubber toughened epoxies approximates to the Dugdale plastic zone length, *R*.

The Tresca^[91] and Von Mises^[92] yield criteria give alternative shapes of the plastic zone in a specimen. These yield criteria were both developed for metals, but have been modified and applied to polymers^[93.97]. The basic equations do not adequately describe the pressure sensitive nature of the yield stress of polymers. Modifications to the Von Mises equation have been proposed by Raghava^[93,94] and others^[95-97]. Their theories have modified the yield stress term to account for the hydrostatic pressure. The pressure dependence was taken to be linear by Sternstein^[95] and Bauwens^[96] and non-linear by Raghava^[94]. Figure 11 shows the

plastic zone predicted by the Von Mises equations (31 and 32) as a function of thickness.

$$r_y'' = \frac{K_{Ic}^2}{4\pi\sigma_v^2} \left(1 + \frac{3}{2}\sin^2\theta + \cos\theta\right)$$
(31)

$$r'_{y} = \frac{K_{Ic}}{4\pi\sigma_{y}^{2}} \left(\frac{3}{2}\sin^{2}\theta + (1-2\nu)(1+\cos\theta) \right)$$
(32)



The plastic zone in an elastic-plastic material was modelled by Bascom^[98]. The shape was determined to be oval and akin to the shape of a rugby ball. Figure 12 depicts schematically the shape of the plastic zone.



Figure 12

The proposed^[98] shape of the plastic zone in an elastic-plastic material

It is interesting to note that in plane stress, along the $\theta = 0^{\circ}$ axis the Irwin, Von Mises and Dugdale models predict the same value of r''_y, but they differ in plane strain. These differences are caused by the varying values of the plastic constraint factor, m_p.

The plastic zone is much smaller in the central region (plane strain) than at the edges. This is due to triaxial constraint imposed by the bulk of the polymer. At the edges there is only biaxial constraint, so the yield stress is higher in the plane strain region of the thickness. The Dugdale model predicts a larger plastic zone size than either the Irwin or Von Mises models under plane strain conditions. The actual shape of the plastic zone is still the subject of conjecture. The plastic zone in epoxy resins has been variously reported to be a Dugdale line zone^[90,99], or an Irwin/Von Mises zone shape^[100]. Moloney and Kausch^[81] found that Bascom's model was the most appropriate. In a recent paper, Ni *et al*^{(101]} showed that the shape of the rubber cavitation zone in ABS was consistent with the Irwin theory, and demonstrated visually that the plastic zone reduced in size through the thickness towards the centre of the specimen. Pearson and Yee^[102] studied a rubber modified epoxy and found that the plastic zone changed shaped with composition, but were generally consistent with Bascom's model.

The size of the plastic zone is a little easier to define than the shape because it can be determined by direct observation or indirectly by calculation. The plastic zone is more difficult to observe directly in plane strain than in plane stress. There have been few attempts to compare the theoretical plastic zone with experimental results.

Shaw and Tod^[103] studied G_{lc} of a rubber modified epoxy resin in an adhesive joint. They varied the thickness of the joint and found that a thickness of about 0.5-

1.0 mm gave a maximum in G_{lc} . They attributed this to the bond thickness equalling the plastic zone size (2 r_y). Further increases in thickness reduced G_{lc} because of an increase in constraint (a shift from plane stress towards plane strain). Janamami^[104] showed that the Irwin model gives the most reasonable estimate of the plastic zone size in UPVC tube.

1.4.2 Crack propagation stability

The incorporation of a filler will affect the propagation of the crack through the material. Three modes of crack propagation have been identified in thermosetting resins^[59]: A) stable brittle, B) unstable brittle and C) stable ductile. These are shown schematically in Figure 13. The stability of crack propagation can be affected by many different variables.

The temperature and strain rate can affect the stability of crack propagation. Type A is normally observed at low temperature or high strain rates and in highly filled polymers; type B is seen at ambient temperatures in unfilled thermosets or very low strain rates and type C is observed at elevated temperatures where excessive crack blunting causes stable tearing. The yield strength of the composite will be important; a high yield strength will again favour stable propagation^[59].

The particle size has been shown to affect the stability of propagation^[38]. Spanoudakis *et al*^[38] found that at a constant volume fraction of 0.46, particles of 4.6µm and 62µm exhibited stable and stick/slip behaviour respectively. An increase in the volume fraction of the filler will also promote stable propagation^[67]. The interfacial strength can play a part in the propagation. It has been shown by Sahu and Broutman^[106] that a reduction in interfacial strength favours unstable propagation.



Figure 13 A schematic diagram of the load - displacement responses in a fracture test

1.4.3 Fracture Toughening Mechanisms

1.4.3.1 Introduction

The addition of a reactive liquid elastomer is a well known method of improving the crack resistance of an epoxy resin. This technology is widely applied in structural adhesives. Numerous rubbers have been studied in epoxy resins alone. The most notable of these is carboxy-terminated butadiene-acrylonitrile rubber (Hycar[®] CTBN), but other functional end groups have been used with similar results. The alternative terminating groups (on the butadiene-acrylonitrile copolymer chain) include: amine^[106,107] (ATBN); hydroxyl^[108,109] (HTBN); epoxide^[110] (ETBN). Alternatively thermoplastics such as poly(etherimide) (PEI) have also been shown to be effective tougheners^[111,112].

The toughening effect of a particulate filler has not been studied as much as that of the rubber toughening agent. The parameters that control the fracture characteristics in these systems include particle size and shape, interfacial adhesion and particle strength. These major factors and those for the rubber tougheners will be discussed in the following sections.

1.4.3.2 Particulate-filled composites

Lange and Radford^[12] were amongst the first workers to study the effect of a filler, in this case alumina trihydrate, on the fracture behaviour of an epoxy resin.

Their study showed that the fracture energy of the system was improved by the incorporation of the filler. The proposed mechanism for the improved fracture energy was crack pinning. This mechanism was first proposed by Lange^[113]. He suggested that when the crack meets an inhomogeneity, such as a filler particle, it will be momentarily pinned by that obstacle. The crack front will then bow out between the particles, before finally breaking away. The energy required will not only be for the creation of the new surfaces but, by analogy with the theory of dislocations, the newly formed length of crack front because it is assumed to possess a line energy. Figure 14 shows a schematic diagram of this process. Using this model Lange derived the expression:

$$G_{IC(C)} = G_{IC(m)} + 2 \frac{T_L}{d_p}$$
 (33)

where: T_L = the line energy per unit length of crack front d_n = interparticle spacing

This concept was taken further by $Evans^{[114]}$ who calculated the line energy contribution (T_L) in terms of the particle diameter to the interparticle spacing. His analysis also showed that the line energy contribution depended on the filler's particle size. Green *et al*^[115,116] subsequently recalculated the figures of Evans to estimate the increase for spherical and cubic particles.

Kinloch *et al*⁽¹¹⁸⁾ have observed the bowing of the crack front between glass particles. The formation of characteristic "tails" behind the particles has been cited as evidence of the crack pinning mechanism. This mechanism will depend on several different factors: the filler's inherent strength; the interfacial adhesion, and the shape of the bowed crack at break-away.

The interfacial adhesion of the particle is paramount. It has been shown^[116] that if the interfacial adhesion is weak, then the crack will prematurely break-away before it has reached its full potential and therefore for energy absorption. The strength of the particle is as important as the interfacial adhesion. If it is weak and fails it will prematurely release the crack from the pinning site. Again, this will not absorb the maximum possible amount of energy. This type of behaviour has been reported for fillers such as hollow glass microspheres^[41] and dolomite^[119].



The fracture energy depends on the volume fraction and is found to exhibit a maximum^[117,120]. The position of this maximum depends on the particle size^[121]. This is because the critical parameter is the ratio of the particle diameter to the interparticle spacing and not just the particle size. The fracture toughness tends to rise linearly with volume fraction up to the highest volume fractions reasonably attainable, but this behaviour is not universal. Moloney *et al*^[19] showed that if a weak particle is used then K_{lc} can actually level off. This behaviour has been attributed to the onset of trans-particle fracture and so the pinning process is curtailed. The crack pinning mechanism is widely thought to be a major toughening mechanism in strong particle filled epoxies.

It has been shown^[59] that in glassy polymers (PMMA etc) the propagation is governed by a constant crack opening displacement criterion when the crack propagation is stable brittle (Type C). The criterion in plane stress (plane strain is shown in Equation 29, page 22) is defined by the equation:

$$\delta_t = \frac{K_{Ic}^2}{\sigma_y E}$$
(34)

29

To a first approximation it has been found^[122,123] that thermosetting polymers also obey this propagation criterion. A plot of K_{tc} versus the modulus should yield a straight line for increasing volume fraction, if the criterion is obeyed. In these cases the principal toughening mechanism is crack pinning, but the break-away will occur at a critical crack opening displacement.

Later in 1980 the phenomenon of stick/slip (s/s) behaviour in fracture tests was reasonably explained by Kinloch and Williams^[122] and by Yamini and Young^[79]. They proposed that the behaviour could be explained by the blunting of the crack by plastic deformation. It was known previously^[123] that a high yield stress, σ_v , favoured continuous propagation and a low yield stress favoured stick/slip. In essence this means that less shear yielding leaves sharp cracks whereas more yielding produces blunt cracks. This criterion was treated mathematically by the proposers. Put simply the criterion means that in stick-slip fracture a certain level of stress must be attained at a distance (c) in front of the crack before propagation will occur. The criterion can be applied and checked by measuring the variation of K_c with crack tip radius. Crack tip blunting is an important toughening mechanism. The adhesion and strength of the particle play an important role in this mechanism as well as the one described previously. Spanoudakis and Young^[28] found that particles with no adhesion showed an increase in G_{lc} over the well bonded analogue, and weak interfaces also promoted unstable crack propagation, in agreement with other workers^[105]. They showed that K_x was unaffected by surface adhesion. The reduction in adhesion for the filled polymer will reduce the yield stress^[73] of the composite and increase crackblunting at low volume fractions. The stick-slip to stable crack propagation transition was shifted to higher volume fractions.

Faber and Evans^[124,125] proposed an alternative toughening mechanism for particulate filled polymers. The fracture energy (G_{lc}) is directly related to the new surface area created during fracture. Therefore, particulate-filled polymers can be toughened by a simple increase in the surface roughness. Faber and Evans studied the surface roughness in short fibre-filled epoxy. Their study considered the mathematical aspects as well as the practical. The theory uses the tilt of the filler at the surface to calculate the increase in overall area. The angle will be directly related to the volume fraction of filler and its aspect ratio.

A different mechanism was proposed more recently by Low^[126]. He proposed

that toughening could occur through the thermal mismatch between the filler and matrix (obviously there will be stresses due to shrinkage and these will be greater if the resin is cured at high temperatures). The basic idea is that if the filler's thermal expansion is greater than that of the matrix, (i.e. $\Delta \alpha = \alpha_m - \alpha_f < 0$), after curing the resulting compressive stresses can cause toughening. This is achieved because the applied force will need to be greater to overcome the compressive stresses on the matrix. The effect will be more efficient if the matrix-filler adhesion is strong enough to cope with the radial forces. Conversely if the thermal expansion of the filler is less than that of the matrix then weakening occurs. In addition, if the resulting tensile stresses are large enough, microcracks can be initiated in the matrix before a force is applied. Low estimated the magnitude of these forces using the equation:

$$-\sigma_{r} = 2\sigma_{t} = \frac{\Delta\alpha\Delta T}{(1+\nu_{m}/2E_{m}) + (1-2\nu_{f}/E_{f})}$$

$$\simeq \Delta\alpha\Delta TE_{m}$$
(35)

where:

 α = Thermal expansion coefficient

 σ = Stress (r=radial, t=tangential)

The usefulness of this mechanism is difficult to ascertain. A few studies have considered the effect of residual stresses on the properties of epoxy resins^[127,128]. Kinloch^[129] examined the effect of residual stress on fracture and Cornwall and Krstic^[130] also used thermal mismatch to quantify toughening. At first sight this mechanism may be relevant but its contribution is difficult to quantify.

1.4.3.3 Rubber-Modified Composites

The increase in fracture toughness (K_{kc}) of a rubber modified polymer has been attributed to several different mechanisms: crazing^[131-133]; shear flow and crazing^[134,135]; rubber tearing^[136,137]; rubber cavitation and shear yielding^[122,138-142]. Figure 15 illustrates these mechanisms.

A craze is formed by the nucleation of microvoids under a tensile stress. The microvoids develop in concentrated bands perpendicular to the applied stress. They do not coalesce to form true cracks because they become stabilised by fibrils of deformed polymer. The resulting localised yielded area of microvoids and fibrils is

called a craze. The major difference between a craze and a true crack is the craze's ability to transmit stress across its faces. When a crack finally initiates it is via the breakdown of the fibrils within the craze. Crazing has only been reported in epoxies when the specimen was very thin^[143] (of the order of a few microns). It is not a significant toughening mechanism in bulk epoxy resins, but is very important in certain thermoplastics.

Tearing is the ultimate cause of failure of rubber particles when they have bridged the crack. This mechanism, although not a major contributor to the toughness enhancement, does play a part. Yee *et al*^[102] showed that if rubber cavitation does not occur, then toughening is via rubber particle bridging, but bridging is not as efficient a mechanism as cavitation.

Cavitation occurs when the particle is subjected to triaxial stresses (hydrostatic tension). A cavity opens up in the centre of the particle, eventually causing failure. This relieves the local stresses and absorbs energy. As will be discussed later this is an important mechanism in epoxies.

Shear yielding (also called shear flow), is the plastic flow of the polymer under an applied tensile stress. Shear deformation consists of a change in shape without a significant change in volume i.e. the cross sectional area reduces in accordance with Poisson's ratio. Again this is an important toughening mechanism.



Figure 15 A schematic diagram of the damage growth in a toughened polymer (Reproduced form reference 14)

1) shear band formation near rubber particles, 2) fracture of rubber particle after cavitation, 3) stretching, 4) debonding, 5) tearing of rubber particle, 6) trans-particle fracture, 7) crack deviation by hard particle, 8) debonding of hard particle, 9) diffuse shear yielding, 10) crazing / cavitation / voiding, 11) plastic zone at crack tip, 12) shear band/craze interaction

Sultan and McGarry^[132,133] were amongst the first workers to demonstrate that an epoxy resin could be toughened by the incorporation of a reactive elastomer. Their study found that the particle size of the rubber domains affected the increase in toughness. Small particles (<0.1µm) were not as effective as larger (1-5µm) ones. The vield behaviour of the epoxy system they used could be described by a pressure modified Von Mises criterion. On the basis of the yield behaviour of the polymer they concluded that the toughening mechanism was crazing. This mechanism has also been cited by other workers^[131,134] to explain toughness increases in rubber modified epoxies. Some time later Bucknall and Yoshii^[134] studied the volume dilatation during tensile creep of a rubber toughened epoxy. They found that there was toughening and a volume change. With the assistance of direct observation of a craze in the polymer from TEM, they concluded that toughening was via shear flow and crazing. It was later pointed out^[139] that their mechanism did not explain the stress whitening which occurs and that they had neglected the fact that a volume change also accompanies voiding of the rubber. Lilley and Holloway^[145] have also reported direct observation of crazing in epoxy polymers, but many workers doubt this mechanism.

An alternative mechanism was advanced by Kunz and Beaumont^[136,137] in the early eighties. This model attributed the increase in toughness to the energy absorbed when the rubber particles stretch and finally tear. This model was not new and was an adaptation of the model of Buchdahl *et al*^[146] and Merz^[147] which was first proposed to describe HIPS. Kunz and Beaumont^[136,137] described their model mathematically, relating the fracture toughness to the failure energy of the rubber. Their model adequately described the observed two fold increase in toughness but did not explain the ten fold increase found by other workers. The particle bridging model proved fairly popular even though Newman and Strella^[148] had earlier shown that this mechanism could, at best, only account for 10% of the observed increase in toughness.

Around the same time Bascom and co-workers^[139,149,150] found that the toughness of a rubber modified epoxy was directly related to the size of the plastic zone. They proposed that the toughness was derived from the cavitation of the rubber particles caused by the triaxial stress field in front of the crack. This would increase the size of the plastic zone and elongation of the rubber. Plastic flow of the matrix also contributed. Kinloch et al^[151] showed micrographs of cavitated rubber particles that supported this mechanism. They concluded that the cavities on the surface were caused by the shear bands. Pearson and Yee^[152] conducted a comprehensive study on the deformation mechanisms in rubber modified epoxy. They showed fairly conclusively that the toughening mechanism was as follows: As the load increases the rubber particles in the vicinity of the crack-tip cavitate, relieving the triaxial tension; on further loading, the cavities increase in size. The largest ones will then initiate shear bands on account of the stress concentrations caused by the rubber particles. It is generally accepted that the main toughening mechanism is shear yielding of the polymer, which effectively blunts the crack. The cavitation of the rubber particles reduces the constraint on the polymer and hence the yield strength; this aids the shear yielding process.

1.4.4 Rubber phase effects

1.4.4.1 Morphology

The compatibility between the rubber and the resin and the way it changes during vitrification will directly affect the final morphology of the system. Two morphologies can result: a single continuous phase (the resultant polymer will be clear) or a two phase system (a "cloudy" polymer). It has been clearly demonstrated^[153] that the two phase system exhibits higher toughness than the single phase system.

The morphology of the system is governed by the compatibility between the rubber and the resin. For the desired two phase system to result, the rubber must phase separate *in situ* during cure. This is achieved by using a rubber with polar end groups, examples of which are given above. The typical structure of such a rubber is represented by CTBN below:



Figure 16 Carboxyl terminated butadiene-acrylonitrile rubber (CTBN)

The ratio of the acrylonitrile to the butadiene will determine the overall polarity of the rubber and hence the final morphology.

1.4.4.2 Particle Size, Volume Fraction and Interfacial Adhesion

Other attributes of the rubber have been investigated with respect to their effect on toughening. These include the particle size and particle size distribution, the volume fraction, the interfacial adhesion and the glass transition temperature (T_{α}).

In a recent paper Pearson and Yee^[102] investigated the influence of the rubber particle size on the toughening mechanisms. Apart from reaffirming the cavitation/yielding mechanism, they found that a bimodal particle size did not have any synergistic effect and the crack bridging mechanism was affected by particle size; very large particles were not as effective as smaller ones. They showed by microscopy that the large particles toughened by crack bridging whereas smaller particles toughened by the cavitation mechanism. Pearson and Yee^[102] concluded that absolute particle size was not important but that the ratio of the particle size to the plastic zone size was. Cavitation of the rubber is required for maximum toughness and if the rubber particle is larger than the plastic zone there is no triaxial stress to cause cavitation.

The fracture energy will be directly related to the volume fraction of the rubber added. Bucknall and Yoshii^[134] studied this relationship and found it to be linear. They also found that the toughness was related to the volume fraction of rubber actually precipitated. Unreactive curing agents like piperidine give almost 100% of the added rubber as precipitated rubber domains and this was found to give a higher fracture toughness.

The interfacial adhesion of the rubber to the matrix has been studied. In the cavitation/shear yielding mechanism the cavitation of the rubber particle is crucial. If the interfacial adhesion is reduced there comes a point where the particle will debond and not cavitate which results in reduced toughness. This was found to be the case. Chan *et al*⁽¹⁵⁴⁾ showed that debonding of the rubber particles produced virtually no toughening effect.

1.4.5 Hybrid Composites

The toughening of epoxy resins using reactive rubber is efficient but tends to substantially lower the modulus. Conversely, the addition of a particulate filler increases the modulus but tends to impair the tensile strength of the final composite. The combination of the two methods has been proposed to obtain a balance between the modulus and strength.

Maxwell and co-workers^[65,118,165] made a comprehensive study of the properties of hybrid systems containing glass beads and CTBN rubber in an epoxy matrix. They found that the addition of rubber toughening agent to the glass bead/epoxy composition did indeed increase the fracture toughness and this is supported by several other groups^[8,119,166]. The main difference between the rubber modified and unmodified systems was that the maximum in G_{lc} was shifted from 0.12 to 0.3 V_f respectively (Figure 17). The maximum in G_{lc} has been reported by Lange and Radford^[12] and Phipps *et al*^[156] for ATH filled epoxy systems.



The toughness of a hybrid system compared to an unmodified resin.

The major energy absorbing mechanisms at work in the hybrid composite are pinning and blunting of the crack (cavitation and debonding can also occur but are not as important). Maxwell^[65,118] concluded that crack-pinning was the major toughening mechanism at low temperatures while crack-blunting was the major toughness contributor at high temperatures. It was quite clear that the mechanisms of the glass beads and the rubber worked independently of each other to contribute to the overall toughness of the composite.

Tod and Wolf^[41] concluded that the compressive strength of the filler has a bearing on the toughness of the composite. The lower the compressive strength the lower K_c becomes. In their study the lowest compressive strength used was 2000 psi (14 MPa). The composites used were fabricated at high temperature. If the residual stresses due to thermal mismatch are taken into account then the strength of the particle may well be exceeded.

The deformation of a hybrid system was investigated by Young *et al*^[65]. They measured the yield stress of various combinations of glass/rubber/epoxy and compared the experimental results with some theoretical equations. Their results were modelled well by the theories of Argon^[61,62] and Bowden and co-workers^[63,64] but Argon's theory was found to give the best fit to the data. They also concluded that Young's modulus was predicted very well by the equations of Ishai and Cohen^[22].

1.5 COATED FILLERS

1.5.1 Introduction

Previous sections covered the properties of thermosetting resins containing rigid and elastomeric particles respectively. This section will cover the situation where the two are combined. There are two cases to be considered: (1) simple mixing of the elastomer and particulate phases with the resin; (2) situating the elastomeric phase as a coating around the rigid filler particle. The idea of coating the filler is not new and was proposed in 1968 by Matonis and Small^[157], but the physical method of applying the elastomer has not been developed adequately.

1.5.2 Theoretical Studies

There have been a few theoretical studies on the mechanical properties of coated filler-resin composites, generally using Finite Elemental Analysis (FEA). The most extensive of these studies was concluded by Broutman and Agarwal^[158]. In this analysis they assumed that the rubbery layer had a modulus of 1000 psi (7 MPa). They evaluated the stress distribution around the interface, when stressed in the z direction, for volume fractions of 3.04 and 24.3 % (r_2/r_1 of 0.357 and 0.714 respectively Figure 18), this equates to a rubber content of 0.48 and 3.02% respectively. They found that the rubbery layer altered the stress distribution around the around the particle quite dramatically. Figure 19 shows the stresses around the particle with and without a rubbery layer.



A schematic diagram of the analysis of Broutman and Agarwal



The stresses on a spherical particle with and without a rubbery layer (Reproduced from reference 158, $r_2/r_1 = 0.714$)

The stress distribution was shown to be similar to the stress distribution around a cavity^[159] or around a particle that has debonded from the matrix. The reason proposed for this was that the rubber's low modulus did not transfer the stresses to the particle, and so the rubber effectively eliminates them. This may have advantages for irregular particles as it would reduce their stress concentrating effect, although if it equates to a cavity (void) this would not be better if the particle was spherical or not angular. They also showed that the modulus was reduced by the rubbery layer. Table 1 shows their predicted modulus as a function of filler loading.

Filler loading (%)	Composite modulus, psi (GPa)		
	Without interface x10 ⁶	with interface x10 ⁶	
3.04	12.3 (85)	11.05 (76)	
24.30	16.7 (115)	6.97 (48)	
43.83	22.4 (154)	3.84 (26)	
Notes:	Reproduced from Ref. 158. Ceramic (416 GPa) in a glass matrix (81 GPa)		

Table 1The prediction of modulus from the analysis of Broutman and Agarwal

In conclusion, they determined that an elastomer with a modulus of 10⁴ psi (69 MPa) would give a reasonable combination of tensile strength and toughness with maximum strain energy absorbtion during impact.

Matonis and Small^[167] analysed a similar case. They showed that if the elastomer layer was very thin (of the order of 0.999, expressed as the ratio of particle radius, R_0 to rubber layer ratio, R_1) compared to the filler's particle size, the stress distribution around the particle will not be significantly affected, and that the stress field will also fairly insensitive to the coating modulus. They concluded that there would only be a slight increase in the toughness of the composite for thin layers but a significant improvement for thicker layers. This shows that the properties of the rubbery layer will govern the composite properties; thick layers would reduce the modulus significantly, but thin layers would put more emphasis on the interfacial strength between filler and elastomer. They pointed out that the shape of the filler will certainly affect the results.

Several theoretical studies have been carried out on how a polymer interphase would affect the properties of a fibre reinforced polymer. Daadbin *et al*⁽¹⁶⁰⁾ studied the effect on load transfer while Nassehi *et al*⁽¹⁶¹⁾ and Gardner *et al*⁽¹⁶²⁾ analysed the stress distributions.

1.5.3 Practical Studies

There have been only a few studies of elastomer coated filler systems in the open literature compared with rubber toughened systems.

There are four main application methods cited in the literature for producing a polymer coated filler. Peiffer and Nielsen^[163] used a method developed by Iler^[164]. This method produces thick coatings (glass fibres in the case of Peiffer and Nielsen) by the alternating deposition of positively and negatively charged species on to the surface. Goodman^[165] and Jeffs^[166] show that it is possible to coat an inorganic filler with a water based polymer using a spray dryer. Others^[167] have shown that the same method could be used with water curing polymers in an organic solvent. By far the majority of coatings are applied by solvent deposition. In most cases these are applied to fibres^[167,168] but glass beads have also been used^[169-172]. The coating of particulates is quite difficult if agglomerations are to be avoided. Popov and coworkers^[173,174] and Oyama *et al*^[175] used an in-situ polymerisation method. They pretreated the filler to make it receptive prior to carrying out the polymerisation of vinyl chloride monomer. Popov^[172,173] used chalk that was pretreated with peroxy succinic acid or acrylic acid while Oyama *et al*^[175] used a vinyl silane as the pretreatment for their silica particulate.

The physical property most improved by the use of the elastomer layer is the impact resistance^[163,176]. These studies were conducted using continuous^[176] or chopped^[163] fibres and the coatings were applied by solvent deposition. The thickness of the coating has a large influence on the final properties of the composite. Peiffer and Nielsen^[163] used an acrylic latex as the coating. They found that the thickness of the coating was approximately the same as the diameter of the latex micelles and that a layer of 0.2µm gave the best impact properties. Amdouni *et al*^[170] and Gerard *et al*^[176] studied glass beads in an epoxy resin. They found that K_{lc} showed a maximum when the ratio of layer thickness to particle radius was around 3% (i.e. about 0.2µm on a 15µm particle). The improvement was explained in terms of shear yielding in the matrix, enhanced by the elastomeric layer. The compression strength of the composite is not affected by the thickness of the layer.

The adhesion of the layer to the filler and the matrix can have a large influence on the composite properties. The elastomeric layer can improve the interfacial adhesion^[163] and the resin can swell and penetrate the layer forming an interpenetrating network (IPN) and thus improving the adhesion. Popov^[173,174] and Boven *et al*^[177] coated polymers on to their particulates by in-situ polymerisation to improve the adhesion of the filler to thermoplastic matrices. Glass bead filled polystyrene was studied by Dekkers *et al*^[172]. They concluded that there was no toughening effect of the coated beads because the elastomer debonded at the poles before any benefit was attained.

The introduction of the elastomeric layer has an effect on the modulus of the composite. This is not unexpected, but the modulus is not significantly lower than that of the dispersed rubber hybrid systems. The reduction in the modulus is less substantial if the difference in moduli between the matrix and the elastomer is less.

The effect of a coating on the mechanical properties has not been widely investigated. Wainwright and Pritchard^[178] found that an ATBN/epoxy coating on ATH did not affect the tensile strength of the composite but the elongation at break was increased at the expense of the modulus. The extent of the coating's coverage of the filler particles was not determined by Wainwright, but it is highly likely that the coverage was not complete; the coating method involved milling to obtain the powder and the ATH would probably cleave in this process because of its inherently weak structure, destroying the complete coating.

CHAPTER 2

EXPERIMENTAL

2.1 RESIN SYSTEM

2.1.1 Epoxy resin

The epoxy resin system used throughout this study was a bisphenol-Aepichlorhydrin resin (Figure 20). This resin consists of Epikote[®] 828 (Shell Chemicals UK) modified by the addition of 15% Cardura[®] E10 (Figure 21), a reactive diluent. This resin is sold under the trade name Epikote[®] 816 and an equivalent resin (330) was supplied by Stag Polymers and Sealants. Before using the resin, it was conditioned over phosphorus pentoxide for one week.



Schematic structure of the epoxy resin molecule (n=0 to 1)



Figure 21 The structure of Cardura E10 Cardura[®] E10 is a mixture of highly branched saturated C₁₀ isomers. Branches R¹, R² and R³ are alkyl groups, of which at least one is a methyl group.

2.1.2 Curing agents

Two different curing agents were used: (1) a room temperature agent, Epikure[®] T (Figure 22); this is a mixed primary, secondary and tertiary aliphatic amine and (2) a high temperature curing agent, piperidine (Figure 23). These curing agents have radically different curing rates. Piperidine is very much slower than Epikure[®] T. The use of these two curing agents enabled the effect of curing temperature to be introduced. They were used at a resin-to-curing agent ratio of 100:18 and 100:5 w/w respectively in all compositions. Epikure[®] T was obtained from Shell Chemicals UK Ltd. and the piperidine from Aldrich Chemicals. Curing schedules were as follows:

Epikure Troom temperature for twenty-four hours followed by three hours
post-cure at 80°CPiperidinesixteen hours at 120°C followed by slow cooling over 4-5 hours.



Figure 22 Epikure T



Figure 23 Piperidine

2.2 PARTICULATE FILLERS

Two grades of alumina trihydrate^a (ATH) fillers were used FRF20 and FRF5 (BA Chemicals Ltd). These were dried over silica gel at 50°C for one week before use. The glass bead filler was supplied by Croxton and Garry UK Ltd but is a Potters-Ballotini "Spheriglass" product. The beads had a surface treatment of CP03 (this is epoxy compatible, and is believed to be an amino-silane). Hollow glass beads (HGB, termed "glass bubbles") were supplied by Potters-Ballotini directly under the trade name Sphericel. Particle sizes were determined^b using a Malvern Mastersizer E and are shown in Table 2.

Filler	Product code	Particle size (µm)	
		Malvern	Manufacturer
ATH	FRF20	16	15-20*
ATH	FRF5	86	60-90*
Glass beads	CP3000	9	12-26§
Glass bubbles	110P8	11	8+
Notes:	Determined by * Coulter Counter § Sieving + Unknown		

Table 2The particle sizes of the fillers

- a Appendix 1 contains additional information
- b In co-operation with Alcan Chemicals UK Ltd

2.3 CASTINGS

Specimens were prepared by casting flat sheets (200mm x 250mm x 300mm) or casting into silicone moulds of the required specimen shape. Silicone moulds were manufactured from machined master templates. Cast sheets were subsequently machined to the required shape. The filler was dispersed into the resin by vigorous mechanical stirring and the mixture was then degassed under vacuum before the slow addition of the curing agent. After thorough mixing, the slurry was poured into the moulds and cured. Epikure® T castings were degassed for the second time after addition of the curing agent. The thickness of the sheets was controlled before gelation and was dependent on the intended use. A dispersing agent (Hypermer FP4, ex ICI) was added to ATH filled castings at a level of 0.5% (found experimentally) on weight of ATH. The dispersant was dissolved in the resin before any other additions. This aided dispersion of the filler and reduced the viscosity of the slurry.

2.4 RUBBER ADDITION

The rubber tougheners used were ATBN (1300x16) and CTBN (1300x8). They are random copolymers of butadiene and acrylonitrile, terminated with a selectable functional group. Figure 24 shows the ATBN structure schematically (CTBN differs only in the carboxylic acid end group). These were supplied by BF Goodrich (UK) Ltd.



(x=5, y=2 and n=1)

Rubber addition was of two kinds: (1) simple mixing with the epoxy resin matrix (2) rubber coating of the ATH particles. Simple mixing was used unless otherwise stated. The coating materials and methods are detailed in a later section. If rubber was to be incorporated then this was stirred into the resin at 50°C before the ATH (if required). The amount of rubber added was normally constant at 10 phr; curing

then proceeded in the usual way.

2.5 POLYMER COATING

Five different kinds of polymers were used in the coating experiments. These were: poly(vinyl acetate), poly(etherimide), a carboxyl terminated butadiene-acrylonitrile copolymer/epoxy resin adduct (CTBN adduct), polyamide and poly(methyl methacrylate).

2.5.1 Poly(vinyl acetate)

This polymer was supplied, and used, as an emulsion latex dispersion. The emulsion was stabilised by anionic/non-ionic surfactants and had a low viscosity. The latex was supplied by Vinamul Ltd. The glass transition temperature (Tg) is quoted as 22°C by the supplier. The latex contains approximately 60% polymer by weight.

2.5.2 Poly(etherimide)

The poly(etherimide) was supplied by European General Electric under the trade name ULTEM 1000. The structure is represented in Figure 25. ULTEM 1000 is soluble in DCM (dichloromethane) and the epoxy resin.



Figure 25 The structure of ULTEM 1000 Poly(etherimide)

2.5.3 CTBN adduct

The CTBN adduct was produced using the method outlined by Lin *et al*^[179]. Some modifications to this procedure were made according to literature from BF Goodrich^[180]. The reaction sequence was as follows:

300g of CTBN (1300x8) and 64.8g of epoxy resin (Epikote 828) were measured in to a 1 litre reaction kettle (1:2 stoichiometric ratio). 0.55g of

triphenylphosphine was added as the curing agent. Triphenylphosphine was used because of the differing reactivities of its primary and secondary amines at room temperature. Polymerisation was carried out at 85°C under a nitrogen atmosphere. This temperature was maintained until the measured acid value was below 0.005. This required approximately seventeen hours. After cooling the adduct was dissolved in methyl ethyl ketone (MEK) and 14.9g of MNDA (p-methan-diamine, a second curing agent) was added. The structure of MNDA is shown in Figure 26. The product was left at room temperature for a further four days to finish the reaction. The adduct was ready to use.

The acid value was determined as follows: 1-2g of material was withdrawn from the reaction kettle and dissolved in a 3:2 v/v solution of toluene: propan-2-ol. This was titrated to an end point using phenolphthalein indicator and 0.1N alcoholic KOH. The equivalent acid value was calculated from equation:

Acid value =
$$\frac{\text{volume KOH x normality}}{\text{sample weight x 10}}$$
 (36)

2.5.4 Polyamide

Two sources of polyamide were used. The polymer used in coating by a solution in DMSO was Nylon 6 from Aldrich Chemicals. For the *in-situ* polymerisation experiments the polymer was produced by interfacial condensation of sebacoyl chloride and hexamethylene diamine. They were dissolved in dichloromethane and water respectively.

2.5.5 Poly(methyl methacrylate)

Poly(methyl methacrylate) was used for in-situ polymerisation experiments. The

polymer was produced by suspension polymerisation. The preparation is described in section 2.12.7 (page 57)

2.6 SILANE APPLICATION

Two silane coupling agents were used in the coating and model experiments. They were an amino-silane, γ-aminopropyltriethoxy silane (A1100), supplied by Union Carbide and a vinyl silane, Vinyltrimethoxy silane, obtained from Aldrich Chemicals.

$$P_{2}N - CH_{2}CH_{2}CH_{2} - Si - O - C_{2}H_{5}$$

 $O - C_{2}H_{5}$

Figure 27 γ-Aminopropyltriethoxy silane

$$H_2C = CH - SI - O - CH_3$$
$$O - CH_3$$

Figure 28 Vinyltrimethoxy silane

The silanes were applied to the filler by mechanical mixing with a coffee grinder. The filler and 5% w/w silane were weighed in to the grinding cup and mixed for approximately two minutes. Because of the cohesive nature of the amino-silane it was diluted (50%) with methanol; the vinyl silane was used neat. The sides and base of the cup were then cleaned and the filler/silane was mixed for a further three minutes. The silanated filler was "cured" in an oven for one hour at 110°C to ensure good adhesion. Glass inserts for the model experiments were treated for forty-five minutes in a 5% solution of amino-silane in a methanol/water mix (90/10). The beads were cleaned in dichloromethane before coating.

2.7 TENSILE TESTS

Specimens for tensile tests conformed to ISO method R 527 (E) Type 1. They were cast in silicone moulds. Figure 29 shows the specimen schematically, with

dimensions. They were tested in tension using a Zwick 1484 semi-computerised materials testing machine at a crosshead speed of 5 mm/min. The jaw separation was constant at 120mm for all determinations. Modulus figures were calculated by the machine between 0.2 - 0.6 % strain for loadings up to 100 phr, and 0.1 - 0.3 % above this loading.



2.8 FLEXURAL TESTS

Specimens for flexural testing were machined from a single cast sheet with dimensions of 120mm x 13mm x 6mm. The loading pins had a diameter of 6.4mm. The lower pins were set a distance of 96mm apart with a single top pin, centrally positioned. The specimens were tested according to ASTM D790 (method A), using a Zwick 1484 at a speed of 2.5 mm/min.

2.9 FRACTURE TESTS

For all specimens the "sharpness" of the starter crack is very important, more so for SENT than TDCB. A sharp crack was introduced at the base of a precut notch using a razor blade chilled in liquid nitrogen. A single sharp blow was generally enough to produce a natural starter crack. The measurements were made using an INSTRON 1114 machine at a constant crosshead speed of 0.5 mm/min.

2.9.1 Tapered double cantilever beam

The critical strain energy release rate of various compositions was determined using the tapered double cantilever beam geometry (TDCB) as devised by Mostovoy and Ripling^[1817]. Figure 30 shows the specimen schematically with dimensions. The advantage with this specimen is that the change in compliance with respect to crack length is a constant (where the compliance is a dimensionless geometrical factor). The mode 1 fracture energy is calculated from the equation:

$$G_{Ic} = \frac{4P_c^2}{B \cdot T_n \cdot E} \left[\frac{a^2}{h^3} + \frac{1}{h} \right]$$
(37)

where: P_c = the fracture load, B = specimen thickness, T_n = groove thickness and E = Young's modulus. The section in large brackets is the compliance ($\delta a/\delta C$), which for the specimen used was 1550 m⁻¹.



The tapered double cantilever beam specimen

The specimens were manufactured by casting into silicone moulds.

2.9.2 Single edge notch

The critical stress intensity factors of the composites were determined using the single edge notch geometry (SENT) and broken in tension. Figure 31 shows a diagram of the specimen with dimensions. Specimens were machined from cast sheets. The design and testing of the specimen conformed to the recommendations in the ASTM's publication - STP 410^[182]. The distance between loading points was at least three times the width, to ensure uniform stress at the crack-tip. The fracture toughness was calculated from the fracture load by the equation:
$$K_{Ic} = Y. \quad \frac{P_c a^{\frac{3}{2}}}{BW} \tag{38}$$

$$Y = \left[1.99 - 0.41\left(\frac{a}{w}\right) + 18.70\left(\frac{a}{w}\right)^2 - 38.48\left(\frac{a}{w}\right)^3 + 53.85\left(\frac{a}{w}\right)^4\right]$$
(39)

The geometric factor, Y, was determined by Brown and Srawley^[182] using a boundary collocation method. They showed that their calculation (shown in equation 4) was accurate to within 1% of experimentally determined compliance for a/w values up to 0.5.



2.10 COMPRESSION TESTS

The compression strength of certain composites was determined according to ASTM D695. Cylindrical specimens of 12.7mm (diameter) x 25.4mm (height) were used. They were tested on a Zwick 1484 materials test machine at a constant crosshead speed of 1.0 mm min^{-1.} The platens of the jig were greased to reduce the "barrelling" effect.

2.11 MODEL EXPERIMENTS

Specimens used for these experiments had dimensions of 300mm x 70mm x 6mm. They were tested on a Zwick 1484 materials test machine at a crosshead speed of 0.5mm min⁻¹ with a jaw separation of 120mm. The castings had various beads inserted before gelation. These inserts had a diameter of 10.0 - 11.0mm. All

glass beads were pretreated with an amino-silane coupling agent as described above. Table 3 gives the various inserts used with their abbreviations:

Insert	Designation	Silane (A1100)	Coating
Solid glass	SGB-0	1	
bead	SGB-LX	1	PVAc latex
Square glass bead	SQGB-0	1	
PTFE bead	PTFE-0		
Split glass bead	SLGB-0	1	
	SLGB-LX	1	PVAc latex
	HGB-0	1	
Hollow glass bead	HGB-A	1	CTBN Adduct
	HGB-LX	1	PVAc latex

Table 3Details of specimens for the model experiments

2.12 COATING METHODS

The experiments discussed in this section were only pilot trials. None of them have been exhaustively tested.

2.12.1 Fluidised bed

Figure 32 shows the apparatus assembled. The gas supply was compressed air and was provided from a small compressor. The flow rate of the air was not measured, it was sufficient for agitation of the particle bed but not enough to cause excessive losses of fine particles. The main glass tube had a glass sinter set in as an integral part; this supported the bed at rest. FRF20 was used as the bed medium. An injection system was made from a small gravity feed paint spraying gun that was specifically modified for the task. The main tank was pressurised to 40 psi and the carrier line was set to 20 psi. This pressure differential between tank and carrier air line ensured a constant flow of the coating solution into the bed.



Figure 32 A photograph of the fluidised bed apparatus

2.12.2 Solvent/polymer washing

Four methods were attempted using a polymer dissolved in an appropriate solvent. These methods rely on the fact that some polymer will be left on the surface after filtration or that there is some polymer/filler attraction.

- The polymer (polyetherimide 10g) is dissolved in to 50 cm³ of dichloromethane. To this 100g of FRF20 was added and the dispersion stirred for fifteen minutes. The slurry was vacuum filtered in a Buchner funnel. The ATH was allowed to dry before analysis for the extent of coating and agglomeration.
- 2) The polymer is dissolved in the solvent as above. ATH was mixed with the solvent/polymer and stirred for fifteen minutes. The slurry was spread on to a flat surface to dry. The dried cake was then ground in a coffee grinder before analysis.
- 3) An adduct of CTBN was prepared (details given above). The adduct (5g) was dissolved in MEK (300ml) and ATH was added (50g). This was stirred for twenty minutes. The solvent was stripped under vacuum at 120°C. Analysis

was as previously described.

4) Nylon 6 (10g) was dissolved in dimethylsulphoxide (DMSO - 100cm³) at 150°C. ATH (50g) was added and stirred for a further sixty minutes. The slurry was vacuum filtered hot and washed with water to remove remaining DMSO. Similar preparations to this one were tried except: a non-solvent was added, the mixture was cooled slowly, and the mixture was poured into water for rapid cooling.

2.12.3 Precipitation

The latex (8g) was added to a slurry consisting of 100g of FRF20 and 100g of water. The mixture was stirred for fifteen minutes. The precipitation was accomplished by adjusting the pH to above 9 using sodium hydroxide and adding 2g of aluminium sulphate to act as a coagulant. The solids were vacuum filtered. Drying was accomplished by two methods:

- A freeze drying process. This involved smearing a thin layer of the paste on to a glass cylinder and freezing it using liquid nitrogen. This was placed in a chamber and a high vacuum applied. Under these conditions the water was removed by sublimation. Results were assessed by SEM.
- 2) Conventional drying in an oven at 80°C under vacuum for twenty-four hours. The dried cake was ground using a coffee grinder. The powder was sieved over a 45µm gauze before SEM inspection.

2.12.4 Casting

ATBN, being an amine, will cure an epoxy resin if present in sufficient quantity. This reaction could be used to form a highly filled elastomer sheet.

- ATBN and epoxy are mixed (400 phr ATBN). After thorough mixing the ATH was added (250 phr) and mixing in. Curing was accomplished in an oven at 120°C for sixteen hours. The cake was broken up using a coffee grinder.
- 2) There is a similar reaction between ATBN and bismaleimide. Preparation was as given above.

2.12.5 Spray drying

The latex and filler were stirred into water so that the total solids were approximately 50%. The latex content was varied between 1% and 10% by weight of filler. An example composition is given below. For these experiments, the inlet temperature was 300°C and outlet 150°C. The slurry was added at a rate that maintained these conditions. The additions lasted approximately two hours. The reservoir tank was stirred the whole time.

Typical composition for 10% polymer:

Water	10Kg
ATH	5Kg
Latex	833g (10% polymer)
Dispex	~5g (anti-foaming agent)

Dispex was added to reduce the foaming caused by stirring. The resulting powder is analysed in the SEM to determine the extent of coating and agglomeration.

2.12.6 Mechanical mixing

The filler is placed in a 'Moritz' mixer. A Moritz is a high shear mechanical mixer. Figure 33 shows the equipment schematically. The latex is added and mixed until the internal temperature reaches 110°C, this ensures drying of the coated filler. Varying amounts of latex (nominally 0.5 - 5% latex on weight of filler) were used for different coating thicknesses. The effect of additional water was also investigated by doubling the water content of the latex at 5% loading. Thicker layers were investigated by multiple application of polymer latex.



Figure 33 Schematic of the 'Moritz' high shear mixer

2.12.7 In-situ polymerisation

In-situ polymerisation of the polymer onto the filler surface was attempted by two methods.

1) Poly(methyl methacrylate) was used for method 1 because of the ease of preparation. Modifications to this general method included the following: no stabilizer and pretreatment of the filler with vinyl silane. Separation of pure PMMA and coated filler/filler was achieved by using the differences in density (PMMA = 1.19 g/cm³, ATH = 2.42 g/cm³). Carbon tetrachloride was used as the separating medium because its density is in the right region (1.5 g/cm³) and it is a non-solvent for PMMA. Analysis was via SEM and TGA. The general preparation was as follows:

100g ATH, 10g suspending agent (di-sodium hydrogen phosphate dodecahydrate), 1g stabilizer (hydroxyethyl cellulose) and 220cm³ of water were placed in a stirred reaction vessel to which a condenser, thermometer and nitrogen feed were added. The vessel was warmed before 1.5g of initiator (azo-bis-isobutyro nitrile) was added. The monomer was added over thirty minutes from a compensated dropping funnel. Reflux was maintained between 82-93°C. This temperature was maintained for sixty minutes after the end of

the monomer addition. At the end of the hold period the reaction was cooled, irrigated with water and the filler/polymer dried in an oven at 80°C.

2) Polyamide was also used in an interfacial condensation reaction. The polymer coating was built-up in a multiple stage process. An amino-silane coupling agent (section 2.6) treated filler was mixed with hexamethylene diamine in water for ten minutes, filtered and dried in a vacuum oven. The filler was then treated with sebacoyl chloride in DCM and again filtered and dried. This sequence was repeated five times. Analysis was by SEM and TGA.

2.13 CHARACTERISATION

2.13.1 Electron microscopy

The coverage of the coating material was evaluated by SEM. Filler was fixed to an electron microscope stub using double sided tape. Specimens were gold coated using a Polaron sputter coater (1KV and 10mA discharge current) before observation in the microscope. Fourteen coats were applied, half with the specimen at an angle of 45° to ensure a continuous gold layer and reduce charging. Relevant images were recorded on to photographic film. Transmission electron microscopy was carried out when necessary using a Philips EM301 machine. Again relevant information was recorded on photographic film.

2.13.2 Thermogravimetric analysis

Thermogravimetric analysis was carried out on a Perkin-Elmer TGA 7 machine. Thermograms were recorded over a temperature range of 50°C - 800°C at 10°C per minute under an air atmosphere. Differential traces were recorded peak temperatures and peak areas were calculated from them.

2.13.3 Contact angle

ATH tablets were made in a stainless steel mould and compressed in a press. These were loaded with approximately 100g of ATH with the appropriate surface treatment and then subjected to a force of 22 Kgf/m² for ten minutes. Four drops of the resin were placed on to the ATH tablet. After curing they were cut in half and each end was polished before SEM examination. Measurements of the contact angle were taken from the SEM micrographs.

2.14 QUALITY CONTROL

The true volume fraction of filler in castings was measured by burning off the volatiles in a furnace. Approximately 10g of material was weighed (to four decimal places) into a ceramic crucible of known weight. It was then placed in a furnace at 600°C for twenty hours. Samples were allowed to cool before reweighing. Burn-off was done on ATH containing castings only and on ATH powder itself. The density of ATH filled specimens was measured by using a Micrometrics helium pycnometer. Each measurement was repeated five times and an average computed. This equipment gave density values that were accurate to the 4th decimal place. From the precise volume fraction of filler and the density of the specimens, the void content could be calculated. Void contents are expressed as a percent of the true volume fraction. The void content showed the effectiveness of the degassing process.

2.15 STATISTICAL METHODS

Data from tensile tests, fracture toughness and fracture energy were analysed statistically to obtain the mean, standard deviation and standard error. Analysis between means of two sets of data was carried out using the t-test or the Mann-Whitney U test to decide if the means were significantly different. The choice of test depended on the variance of the two data sets. Normally the variances were approximately equivalent; the t-test was applied. Data within a set were analysed in two ways. 1) visually, for tensile specimens, for abnormal flaws and 2) using the Q-test if one result was suspected of being non-representative.

CHAPTER 3

RESULTS AND DISCUSSION

SECTION 1 GENERAL PROPERTIES

3.1.1 Void content

The void content of a casting is an important quantity in relation to its tensile strength, a poor quality casting will give abnormally low strength results. The true volume fraction of filler of a representative selection of castings was measured by ashing in a furnace at 600°C. The true density of the specimen was measured using a helium pycnometer. The void content is expressed as the volume fraction of air required to lower the density, calculated from the true ATH content, to the true density. Sample calculations are shown in Appendix 2.

Numinal		Furnace ashing		Helium pycnometer		
ATH Content (phr)	Curing agent	True ATH content (phr)	Calculated density (g/cm ³)	Apparent ATH content (phr)	True density (g/cm ³)	Void content§
0		0	-	0	1.1713	0
5		5.2	1.203	4.9	1.2000	0.002
20	Epikure T	20.0	1.282	19.3	1.2780	0.003
70		70.5	1.419	68.8	1.4832	0.005
100		99.6	1.578	94.6	1.5634	0.012
0		0	-	0	1.1593	0
50		49.8	1.403	49.3	1.4008	0.002
100	Dimentations	100.4	1.580	100.4	1.5798	0.001
150	Piperidine	151.7	1.700	151.1	1.6989	0.001
200		202.7	1.781	199.6	1.7761	0.004
250		253.2	1.851	241.5	1.8360	0.012
Notes: $\S = Volume \text{ fraction of air necessary to reduce density}$						

Table 4The void content of selected compositions

Densities and filler volume fractions are given in Table 4. The results show that the castings contained approximately the volume of filler intended and void contents for all, but the very highest volume fractions, were low. Piperidine cured castings gave lower void volumes than the equivalent Epikure[®] T ones. This is because the

higher curing temperature reduces the viscosity which makes air removal easier.

3.1.2 Compression strength

The compression strength results are shown in Table 5. All compositions showed yielding in the uniaxial compression test. Two different load-displacement responses were observed and the type of response depended on the composition. Figure 34 shows these responses schematically.



Figure 34 Schematic examples of the load-displacement curves observed in the uniaxial compression tests

The yield stresses quoted, unless otherwise stated, are for an intrinsic yield point. If the composition did not show an intrinsic yield point, the yield stress was found by extrapolation (Figure 34).

Adding ATH increased the compression yield stress at all loadings. Figure 35 compares the yield stress of ATH/epoxy with other filled epoxy systems. The yield stress is related to the effective load bearing cross sectional area (1-Vf') and this is equivalent to the minimum area of matrix perpendicular to the principal load.

ATH content (phr)	ATBN content (phr)	Curing agent	Yield stress (MPa)	Yield strain (%)	Modulus (GPa)
0	0		87.6 (1.9)	11.8 (5.1)	1.18
50	0	Epikure T	100.4 (1.9§	7.9 (2.4)	1.39
100	0		10 5.8 (0.4)§	6.7 (0.4)	1.60
0	0		94.6 (1.6)	12.2 (0.4)	0.94
100	0		107.8 (6.0)	10.6 (0.8)	1.59
150	0	D' II.	112.9 (1.9)	7.5 (0.4)	1.77
200	0	Piperidine	119.5 (2.2)	7.5 (0.4)	1.95
0	10	1	78.4 (0.6)	7.1 (0.4)	0.97
100	10		91.0 (1.6)§	5.5 (1.6)	1.42
1.1 density g	glass bubbles		88.7 (1.2)	10.2 (0.4)	0.96
0.2 density §	0.2 density glass bubbles	Epikure T	47.2 (1.3)	6.7 (0.4)	0.72
glass	glass flakes		116.3 (0.9)	1.74	
Notes: § = No intrinsic yield point shown. Standard deviations in brackets.					

Table 5The compressive properties of various compositions

The absolute value of Vf' can only be found in probability terms. Nicolais and Narkis^[69] proposed equation 40 to model the yield stress response of filled polymers. They assumed that there was no adhesion and only the matrix transfers the stress (ignoring frictional and shear forces).

$$\sigma_{yc} = \sigma_{ym} \left(1 - 1.21 V_f^{2/3} \right)$$
 (40)

Clearly, this model is inadequate to predict the behaviour of many systems because it does not account for the filler being able to contribute to load bearing. The upper limit could only be $\sigma yc = \sigma ym$ whereas it has been shown that many fillers increase the yield strength in compression (Figure 35).



Turcsanyi *et al*⁽⁶⁹⁾ recently proposed an alternative relationship. In contrast to the previous model, Turcsanyi assumed that the strength reduces to near zero when the CSA of the filler equals one and not when the maximum packing fraction (Pf) is reached. They calculated the effective load bearing area to be:

$$(1-V_f) = \frac{1-V_f}{1+AV_f}$$
 (41)

where A is related to the packing arrangement of the filler particles. Values of A can range from 2.318 for a face centred cubic array to 2.427 for hexagonal close packed. These equate to maximum packing fractions (Pf) of 0.740 and 0.524 respectively. For the filler used in this study the maximum packing fraction was measured at 0.60 (using the rubbing and compaction method^[5]), which suggests a loose hexagonal packed arrangement giving a value for A of 2.358. Turcsanyi's^[69] *et al* full equation is:

$$\sigma_{yc} = \frac{1 - V_f}{1 + A V_f} \sigma_{ym} EXP[BV_f]$$
(42)

where σ_{yc} and σ_{ym} are the composite and matrix yield stresses respectively. The exponential term in the equation is the effect of volume fraction upon the yield stress. The authors did not suggest any material significance for the parameter B, although it would be envisaged to include the particle and interfacial strength in the epoxy system investigated here. The effect of B on the relative composite strength is shown in Figure 5 (Page 18).

This model was shown^[69] to give good agreement with experimental results for filled thermoplastic materials. Agreement with filled thermosets is not as good but is reasonable given the relative simplicity of the model. Figure 36 shows the prediction of the equation for the results of this study and those of Moloney^[119]. The values of B for the curves are 3.73, 3.123 and 3.37 for silica^[119], dolomite^[119] and ATH respectively.



The yield strength of some filled epoxy resins compared to the model of Turcsanyi^[69] et al (open symbol data taken from reference 119)

3.1.3 Maximum packing fraction

The maximum packing fraction (Pf) of the ATH fillers were determined using the rubbing and compaction method^[5] and these are shown in Table 6. The maximum packing fraction affects the viscosity of the filled resin and the modulus. The higher the maximum packing fraction the more filler can be incorporated without the risk of voids.

The agreement between the maximum packing fraction measured by the rubbing and compaction method and that calculated from manufacturers data is random. It seems that the two methods cannot be reliably compared.

<u></u>				
ATH grade	Pf measured	Pf Calculated*		
FRF20	0.60 (±0.1)	0.61		
FRF5	0.63 (±0.1)	0.72		
Notes:	* = Calculated from manufacturers oilNotes:absorption data (d-oil = 0.94).Pf = Maximum packing fraction			

Table 6The maximum packing fraction of the ATH grades

The magnitude of Pf suggests a hexagonal close packed arrangement of the particles^[69].

3.1.4 Summary

Void contents of the specimens used in this study have been shown to be low. From the low void contents, it can be concluded that the manufacturing methods used gave high quality specimens up to the highest filler loadings used for each curing agent.

For certain compositions the yield stress, compressive modulus and yield strain have been calculated for ATH filled epoxy resin. The compressive yield stress increased with increasing volume fraction of filler although, the increase was less than for silica and alumina but greater than dolomite and glass bubbles. The models of Nicolais^[69] and Turcsanyi^[69] were compared to the results from this study and those of Moloney^[119] for silica and dolomite. It is shown that the Nicolais model was inadequate but the model of Turcsanyi *et al* provides a better estimate.

The maximum packing fraction for each of the fillers has been measured and compared to the manufacturers oil absorption data.

SECTION 2 MODELLING EXPERIMENTS

3.2.1 Introduction

The behaviour of filled thermosetting polymers has been modelled using large scale specimens with glass and PTFE particles incorporated. Two different polymer coatings were used; one hard and one soft (Tg's of approximately 30 and -55°C respectively). The aim was to gain insight into the mechanisms leading to failure in ATH-filled epoxy resins. In addition the potential of a polymer-coating on the filler could be assessed. It should be noted that these experiments do not take in to account any particle-particle interactions and it would be expected that these could be significant.



Figure 37 An example of the specimens used in the modelling experiments

The insert materials/geometries were PTFE, round glass beads, square glass beads, hollow tube and a glass bead with an introduced line of weakness (Figure 38). The volume fraction of filler the insert represents was calculated (by equivalent cross sectional areas) to be approximately 0.15 (=37phr). An example of one of these specimens is shown in Figure 37. Two polymers were coated on to the beads, a poly(vinyl acetate) and a reactive rubber adduct. The use of the adduct was limited because the high temperatures caused 'sagging' of the polymer but this was

minimised by curing the inserts in a tunnel oven while being constantly rotated.



Figure 38

The geometries of the inserts used in the modelling experiment

The PTFE insert was used to simulate deformable particles which cause minimal constraint on the surrounding polymer matrix, as in rubber modified thermosetting polymers. Round glass inserts were used as the basic modelling particle. These were silane coated to ensure good adhesion (ATH has good adhesive properties to epoxy resins). Shape effects were modelled by using a square glass bead. Weak fillers were investigated using solid glass beads with a split through the centre and a thin walled glass tube. Split-beads were tested with the weak plane in the 0° and 90° directions to simulate the anisotropy of ATH. The two halves of these inserts were held together with high melting point vacuum grease. This "adhesive" served two purposes; to loosely hold the two halves of the insert together but still transmit some stress and to keep the resin out.

3.2.2 Uncoated inserts

The strength results followed a predictable trend (Table 7). They reduced in the order: no insert> PTFE > solid glass bead > square bead > split-beads > hollow bead.

The PTFE inserts debonded under the applied load and the hole was visibly elongated. The strength reduction was the least of all the inserts, at 27%. The PTFE insert does not model the intended particles very well. A composite containing debonded particles would be expected to have a lower strength than one with well-bonded particles^[121] and adding ATBN rubber reduced the strength (see section 3 - tensile properties) of the polymer by 27% at a volume fraction of ≈0.06 (5 phr). There are probably two reasons for the insert not accurately modelling the intended particles; 1) particle-particle interactions are not accounted for and 2) the models

only relate deformations in two dimensions (x,y) and not the three (x,y,z) that occur in reality.

Insert	No. of specimens	Strength (MPa)	Strain (%)	
None	3	61.8 (4)	5.7	
PTFE	3	45.0 (3.5)	4.4	
SGB	4	11.2 (0.6)	1.8	
SQGB	4	9.9 (2.8)	1.5	
SLGB (ntf)	4	8.25 (0.9)	1.3	
HGB	4	6.6 (0.9)	1.1	
SLGB (ptf)	2	11.9 (3.0)	1.7	
SGB-LX	2	18.7 (3.4)	2.3	
SLGB-LX (ntf)	3	16.4 (2.5)	1.3	
HGB-LX	3	7.8 (0.2)	1.2	
HGB-Add	3	7.8 (0.1)	1.2	
Notes:	S/HGB = Solid/Hollow glass bead, SQGB = Square glass bead, SLGB = Split glass bead, LX = Poly(vinyl acetate) latex, Add = CTBN adduct, p/ntf = parallel/normal to force respectively, Standard errors in brackets.			

Table 7Results of the model tensile specimen experiments

All the other inserts showed a large reduction in strength. For all the glass inserts the strength reduced more than would be expected in real composites. Even so, when ranked in order of strength, they follow a logical trend. This suggests that these experiments are reliable for drawing general conclusions.

Orientation effects

Orientation effects can be seen in the two results for the split-beads. The bead with the weakness normal to the applied load showed a significant reduction in strength compared to the parallel orientation. This indicates that in an anisotropic filler, like ATH, the particle orientation can be a significant factor.

The tensile strength of ATH, in either direction, is not known. Its

crystallographic planes are held together by Van der Waals forces so would not be expected to be very great. If particle fracture is a significant factor affecting the tensile strength of the composite, then it could be postulated that a coating that strengthens the particle, could improve the composite strength.

Stress distributions

Stress patterns around the inserts were observed using polarising lenses. These patterns can be used to explain the strength results. The stresses around deformable/debonded and strong particles were analysed using finite element techniques by Guild and Young^[183-184]. They showed that the maximum stress would occur at the equator for a debonded/deformable particle and at the poles for a well-bonded particle. Photoelastic stress patterns are shown for a glass bead and a PTFE bead in Figures 39 and 41 respectively, corresponding photographs of the fractured specimens are shown in Figures 40 and 42. A glass bead treated with a release agent failed as if it was a hole. This agrees with the prediction of Guild and Young^[183-184].



Figure 39 The photoelastic stress pattern around a well bonded glass bead

The split (ntf) and hollow beads failed at their equators which reflects the reduction in stress bearing capacity of these particles. The split-bead, that had its weak plane parallel to the load, again failed along the line of weakness (Figure 43),

but the strength was higher. These failure modes are seen in ATH composites. Figure 44 shows an SEM micrograph of a typical ATH composite fracture surface. ATH particles have predominantly fractured along their crystallographic planes for all orientations. There is some instance of debonding, but this seen as a minor failure mode.



Figure 40 The failure of a specimen that contained a well bonded glass bead



Figure 41 The photoelastic stress pattern around a cavity



Figure 42 The failure of a specimen containing a PTFE insert



Figure 43 The failure of a split bead specimen that has the split parallel to the force



Figure 44 The typical fracture surface topography for an ATH-filled epoxy

3.2.3 Coated inserts

The addition of a polymer coating on the inserts provided some interesting results. Two polymers were used, a poly(vinylacetate), this was supplied as a water based latex, and a CTBN adduct. The adduct is essentially CTBN end-capped with an epoxy resin (Epikote[®] 828 here). These represent a soft coating (CTBN adduct Tg \approx -50°C) and a more rigid one (PVAc Tg \approx 30°C).

In all cases the coated inserts showed improved strength compared to their uncoated analogues (Figure 45). For solid round beads the increase was 65%. Other beads did not show such a dramatic increase but improvements were statistically significant (t-test).

There are two possible mechanisms by which the coating increased the strength; 1) the coating reduces the stress on the particle and therefore delays particle fracture and 2) once particle failure has occurred, the coating can delay propagation of the crack (crack-blunting).

A clue to the mechanisms are provided by the photoelastic stress patterns. Figures 46 shows the photoelastic stress pattern around an uncoated hollow bead. The particle has failed and the stress concentrations around the cracks can be clearly seen. For the coated hollow beads the particle fracture before ultimate failure occurred and it was the coating's ability to blunt the crack that was responsible for the improvement.



Figure 45

A comparison of the strength of coated and uncoated beads (error bars represent standard deviations)



Figure 46 The photoelastic stress pattern around a hollow glass bead

Coated solid glass beads showed large increases in strength. The photoelastic stress field around this particle is shown in Figure 47. The distribution is totally different from that for the uncoated bead (Figure 39, page 71). The stress field is similar to the hole (Figure 41). This agrees with the theoretical study of Broutman and Agarwal^[158]. Using finite element analysis, they showed that a thin coating, of a soft material, would alter the stress distribution around the particle to be similar to

a cavity. It shows that the coating has reduced the stress transferred across the particle. The proportion of stress transferred to the particle depends on the modulus of the coating^[158], the softer the coating, the less stress will be transferred. The impact of this on the tensile strength of real composites will depend on the relative strength of the particle. For weak particles where crack initiation is caused by particle fracture, it could be prevented or delayed.



Figure 47 The photoelastic stress pattern around a latex coated glass bead

3.2.4 Summary

The strength and failure modes of ATH-filled composites have been modelled using large scale specimens. The results suggest that particle fracture could initiate failure in ATH-filled composites. Polymer coating is suggested as a possible solution.

Using the modelling specimens, the potential for a polymer coated filler has been evaluated. These experiments showed that a polymer coating could enhance the strength of a composite containing a weak filler. Crack-blunting is identified as a possible toughening mechanism.

SECTION 3 TENSILE PROPERTIES

3.3.1 Results

ATH content (phr)	Curing agent	Strength (MPa)	Elongation (%)	Modulus (GPa)
0		77.1 (2.0)	4.4 (0.1)	3.16 (0.11)
5		64.7 (0.3)	4.0 (0.1)	3.04 (0.07)
10	To have T	59.8 (0.6)	3.4 (0.3)	3.17 (0.09)
20	Epikure 1	52.6 (2.3)	1.8 (0.1)	3.61 (0.05)
50		52.3 (0.7)	1.4 (0.1)	4.98 (0.06)
100		49.3 (1.8)	0.8 (0.1)	7.18 (0.14)
0		79.5 (1.8)	3.8 (0.3)	3.15 (0.06)
100		56.3 (0.6)	0.8 (0.0)	6.9 (0.06)
150	Piperidine	52.0 (0.6)	0.6 (0.1)	9.46 (0.11)
200		51.3 (1.0)	0.5 (0.0)	12.2§
250		44.7 (1.0)	0.3 (0.0)	15.1, 19.1*
Notes: phr = parts per hundred resin. § = Value from only one specimen. * = Values of the two valid results				

Table 8The tensile properties of ATH-filled epoxy resins

The tensile properties of ATH/ATBN hybrid composites					
ATH content (phr)	Curing agent	Strength (MPa)	Elongation (%)	Modulus (GPa)	
0	Epikure T	61.6 (0.3)	5.0 (0.3)	2.49 (0.05)	
5		57.6 (0.3)	3.7 (0.2)	2.59 (0.4)	
10		51.1 (0.9)	2.6 (0.2)	2.67 (0.05)	
20		47.6 (5.8)	1.9 (0.1)	2.84 (0.08)	
50		39.2 (0.6)	1.1 (0.1)	3.84 (0.05)	
100		35.2 (0.9)	0.7 (0.1)	4.60 (0.04)	
100	Piperidine	49.4 (0.4)	1.1 (0.1)	5.29 (0.05)	
phr = parts per hundred resin. Standard errors given in brackets (Std deviations are approx double). All specimens contained 10phr ATBN					

Table 9 The tensile properties of ATH/ATBN hybrid composites

Table 10The tensile properties of ATBN modified epoxy resins

ATBN content (phr)	Curing agent	Strength (MPa)	Elongation (%)	Modulus (GPa)
0		77.1 (2.0)	4.4 (0.1)	3.16 (0.11)
5		70.9 (0.5)	4.8 (0.2)	2.86 (0.05)
10		61.6 (0.3)	5.0 (0.3)	2.49 (0.05)
15	Epikure T	40.7 (0.8)	6.5 (0.7)	1.58 (0.04)
20		30.3 (0.7)	8.1 (1.2)	1.17 (0.05)
25		27.7 (0.6)	10.1 (0.8)	0.73 (0.03)
30		23.5 (0.8)	17.6 (1.1)	0.37 (0.03)
0		79.5 (1.8)	3.8 (0.3)	3.15 (0.06)
5		63.1 (0.2)	4.2 (0.1)	2.89 (0.07)
10	D'autition	57.8 (0.8)	5.6 (0.3)	2.32 (0.05)
15	Piperiaine	45.0 (0.6)	8.7 (0.8)	2.06 (0.01)
20		33.9 (0.7)	13.7 (1.2)	1.62 (0.05)
25		27.9 (0.6)	22.4 (3.1)	1.33 (0.05)
Notes: phr = parts per hundred resin. Standard error in brackets				

3.3.2 Young's modulus

The modulus is defined as the material's resistance to deformation by an applied stress. In its simplest form the modulus is related to the stress by Hooke's law:

$$Youngs Modulus (E) = \frac{Stress(\sigma)}{Strain(e)}$$
(43)

Polymers do not strictly follow this relationship because of their visco-elastic properties. Rubbers exhibit the greatest deviation whereas thermosets show the least, although over small strains, thermosets can be approximated to Hooke's law.

The unfilled resin showed some deviation from Hookean behaviour, but only just before failure. Composites containing ATH showed only slight deviations, but at high filler loadings, no deviation was observed. Example stress-strain plots of filled and unfilled composites are shown in Figures 48 and 49. Rubber-modified composites showed greater deviation than their unmodified analogues. All modulus measurements were taken at low strain levels and over a small range (typically 0.2-0.6% strain), over these small strains, Hooke's law was applicable for all materials tested in this study.



The stress-strain responses of ATH-filled epoxy resin



The modulus of filled polymers has been modelled by many people. The simplest approach (Guth^[14] and Smallwood^[15]) only relates the volume fraction of filler to the modulus. Kerner's^[16] equation provides an elaborate but versatile predictive tool. Lewis and Nielsen^[17] modified Kerner's equation. They introduced the maximum packing fraction (Pf) to account for particle size effects. The equations of Ishai and Cohen^[22] were shown to be appropriate for glass bead-filled epoxies by Spanoudakis^[28,38]. Other studies have covered the shape^[33,34], the adhesion^[30,31] and the effect of agglomerations^[35,36]. Figure 50 shows the predictions of some of the models mentioned.

Results for various formulations are given in Tables 8 and 9. All the models predict that the filler will increase the modulus and this was the case with ATH. Comparing the results for the ATH/epoxy system with the models shows that the equations of Mooney^[185], Eilers^[186] and Guth^[14] over-estimate the composite's modulus and those of Ishai and Cohen^[22] and Kerner^[16] under-estimate it at high volume fractions (Figure 51). The Lewis and Nielsen^[17] model provides the best estimate for both ATH-and ATH/rubber-filled composites (Figures 51 and 52). There is some deviation from the model at high volume fractions but this is probably caused by a higher incidence of voids in the specimens. At low volume fractions there is some positive deviation. Ahmed and Jones^[35,36] suggested that, at low

volume fractions, particle agglomerations trap resin between the particles and this leads to an apparent increase in volume fraction of filler and therefore increases the modulus. It is difficult to say if these agglomeration effects are significant because the differences could equally arise from normal experimental scatter.



Young's modulus predictions from various models



Young's modulus of ATH-filled composites from this study and Wainwright's study compared to the models of Nielsen and Lewis^[17], Kerner^[16] and Ishai and Cohen^[22]



The tensile modulus of hybrid composites compared to the equation of Lewis and Nielsen^[17]

3.3.3 Elongation

The elongation is not a central property to this study but will be covered for completeness.

The elongation of all the ATH-filled composites reduced as the filler content increased. Results are presented in Tables 8 and 9. Adding a reactive rubber increased the ultimate elongation. The relationship between the filler loading and the elongation at failure is a property where the experimental results are reported but theoretical arguments are rare. The simplest model is that of Nielsen^[32] (equation 44). His equation treats the reduction in elongation as purely a volume effect. The strain at failure in the composite is assumed to be the same as in the unfilled state. A modification^[5] of Nielsen's equation is shown in equation 45. In the same manner as the modification of Kerner's modulus equation, the maximum packing fraction is used to introduce a particle size/distribution element. The results from this and Wainwright's^[8] studies are shown compared to both equations in Figure 53.

$$\boldsymbol{\varepsilon}_{c} = \boldsymbol{\varepsilon}_{m} \left[1 - V_{f}^{1/3} \right] \quad (44) \qquad \boldsymbol{\varepsilon}_{c} = \boldsymbol{\varepsilon}_{m} \left[1 - \left(\frac{V_{f}}{P_{f}} \right)^{1/3} \right] \quad (45)$$

where: ϵ = elongation, V_f = volume fraction, P_f = maximum packing fraction and subscripts c, f and m relate to composite, filler and matrix respectively.



The tensile elongation of ATH-filled composites from this study and Wainwright's^[8] study compared to some theoretical models

Considering the simplicity of the equations and the assumptions made, equation 45 predicts the results for ATH-filled composites with reasonable accuracy. For hybrid composites, the fit is not so good, the prediction is consistently higher than the results.

3.3.4 Tensile strength

3.3.4.1 Introduction

The tensile strength depends on three main factors; Young's modulus, E; critical strain energy release rate (fracture energy), G_{lc} and the flaw size, 2a. These factors can be related according to the modified Griffith equation:

$$\sigma_{c} = \sqrt{\frac{EG_{Ic}}{\Pi a}}$$
(46)

Adding a high modulus filler increases the fracture energy^[8,28,38,56] and the modulus, it is therefore conceivable that fillers like alumina, silica or glass bead could improve the tensile strength of a polymer. In reality, only fillers with a high aspect ratio (glass fibres^[187], flyash^[57], mica^[5], etc.), reinforce the matrix, most other fillers reduce the strength^[5,10,56,121] (Figure 54). This suggests that the critical flaw size (2a) is increasing faster than EG_{lc}. The tensile strength of a filled composite depends on the fillers size, shape, strength and the interfacial strength between the filler and the matrix.



(○ Ramsteiner *et al*^[37], □ Landon *et al*^[45], ● Srivastava *et al*^[57], ■ Moloney *et al*^[56])

3.3.4.2 ATH composites

All the composites that contained ATH showed a lower tensile strength than the unfilled resin (Table 8, page 77). The biggest effect occurred at low volume fractions (up to $V_f = 0.1$), above this the strength did not fall any further. This agrees with the results of Wainwright^[9] and, to a lesser extent, those of Radford^[11] (Figure 55). The fall in strength at very high volume fractions is caused by an increase in void content (section 3.1.1). The level at which the 'plateau' occurs depends on the particle size and size distribution of the ATH filler.

Several equations have been proposed to model the tensile strength of a filled polymer. Some simply consider the reduction in matrix CSA with the introduction of the filler^[47,48], others consider the interfacial strength and the stress concentration effect^[25,49,50]. Figure 56 shows the predictions of some of these models.



Wainwright^[8] (\Box **II**), Radford^[11] (Δ) and this study (\bigcirc **●**)

All the models predict the reduction in strength with increasing filler content but none of them predict a plateau except the analysis of Leidner and Woodhams^[49,50] (equations 47 and 48) which can allow for two response regimes.

$$\sigma_{c} = 0.83 \rho_{\alpha} V_{f} + K \sigma_{m} (1 - V_{f})$$
(47)

$$\sigma_{c} = (\sigma_{i} + 0.83\tau_{m})V_{f} + \sigma_{i}S(1 - V_{f})$$
(48)

where: ρ_{α} = frictional stress exerted on the filler by the resin,

K = relative change in the strength of the matrix due to the filler,

$$\tau_m$$
 = shear strength of the matrix,

S = stress concentration factor.



Tensile strength predictions of some theoretical models (Leidner and Woodhams^[49,50], Nielsen^[25], Nicodemo^[47,48] and Schrager^[53])

At low volume fractions equation 47 is appropriate and at higher volume fractions equation 48 is applicable. For each equation the intercept constants were determined (by extrapolation to V_f=1) as -112 MPa ($0.83\rho_{\alpha}$) and 52.5 MPa ($0.83\tau_{m}$). It is clear that this model does not describe this ATH system very well. The rapid fall in strength results in a negative interfacial friction value, which is not physically possible. The shear stress of the matrix is predicted to be 63 MPa, which is a reasonable estimate, the von Mises^[37] criterion predicts it to be approximately 50 MPa). Leidner and Woodhams' analysis suggests that these constants are independent of particle size but this was not the case in these materials. An analysis of the results of Wainwright^[58] for ON920v yields results of -120 and 41 MPa.

Sahu and Broutman^[188] used finite element modelling to analyse the tensile strength of glass bead-filled resin. They assumed that failure was caused by stress concentrations. Their results showed that the strength instantly reduced with the first addition of filler but then remained almost constant. This analysis was limited but it does illustrate that a plateau in strength is theoretically possible. From the analysis of Sahu and Broutman^[188] it would be possible to suggest that the tensile strength in this system is governed solely by the stress concentration effect of the filler although this is undoubtedly a major factor it cannot be the only one otherwise the smallest addition of filler would reduce the strength to the plateau level, and this was not seen. In addition, it would be expected that the strength response would be the same for all fillers of the same type and size. Silica has a similar irregular shape and would be expected to have a similar stress concentration effect, but, the tensile strength response is different (Figure 57). Clearly, there must be other significant factors, in addition to stress concentrations, affecting the strength.



The tensile strength responses of silica and ATH-filled epoxy resins (□ Wainwright^[8], ■ Nakamura et al^[189], ● Moloney et al^[119], ○ this study)

Moloney^[119,190] *et al* studied dolomite, a mineral that is similar to ATH. They showed that the fracture properties were dominated by trans-particle fracture and that the tensile strength of the filled resin suffered because the particles themselves would act as a source of flaws^[56]. Nakamura^[189] *et al* showed that in a silica-filled epoxy composite, failure was caused by particle fracture (when the particle size was greater than the inherent flaw size of the resin). Although silica is a strong filler, they observed that the larger particles contained flaws that were introduced during manufacture. These flaws weakened the particles and led to particle fracture under an applied load.

ATH would be expected to act similarly to dolomite and the weakened silica, although fracture toughness results (section 3.4.3) and compression strengths (section 3.1.2) suggest that ATH is not as weak as dolomite. Indeed, tensile fracture surfaces, from ATH-filled composites, are dominated by cleaved ATH particles
(Figure 58). In addition, as expected^c, large scale debonding was not observed and consequently stress whitening was not seen during tensile tests.



Figure 58 The failure initiation site of a composite containing 100phr of ATH

A particle cleavage mechanism would go some way in explaining the rapid drop in the strength at low volume fractions. A crack from a cleaved particle would produce a starter crack at least the size of the particle and it would be bigger than one started from cohesive matrix failure and sharper than one created by particle debonding. Post-mortem SEM examination of fracture surfaces was inconclusive. The fracture surface of a 20 phr ATH-filled specimen is shown in Figure 59. There are fractured particles (A) and debonded ones (B) but it is not possible to deduce what is cause and what is effect. Cantwell^[73,87] and Vekinis^[83] reported debonding of particles after crack initiation when the crack propagation speed was very low. If debonding was initiating fracture, the application of a silane coupling agent, to enhance interfacial strength, should improve the tensile strength. Wainwright^[8]

c Physical bonding would be expected between the resin and the hydroxyl rich surface of ATH

effect. Almost no debonding was seen in the materials in this study at high volume fractions, only fractured particles (Figure 58).

The initiation site is approximately 200µm in diameter for 20 phr of filler. This correlates well with the calculated flaw size from the Griffith equation (equation 46) which is 215µm. The same is true for 100 phr (Figure 58). The calculated flaw size is 338µm and the observed was approximately 400µm.



Figure 59 The fracture initiation site of a specimen containing 20phr of ATH

Griffith^[43] (Equation 46, Page 83) showed that the ultimate strength of a composite depends on two factors, crack initiation and crack propagation. One measure of the material's resistance to crack propagation is the fracture toughness (K_{ic}). The fracture toughness of ATH^[8,191], silica^[119], alumina^[119] and glass bead^[42,121] filled epoxy resins increased with filler volume fraction. Initially the introduction of flaws by the filler particles propagate easily: consequently, the tensile strength reduces. As the volume fraction increases, the resistance to crack propagation increases. Theoretically, if the fracture toughness rose rapidly enough, the tensile strength would recover. This behaviour has been reported for silica and alumina by Moloney^[42] *et al*, for silica by Nakamura^[189] *et al* (Figure 57) and for glass bead-filled epoxy by Spanoudakis and Young^[28]. Although ATH filled resins have a higher K_{ic} than the glass bead-filled epoxy its strength does not recover. It seems likely that the ATH particles' strength is the limiting factor on the tensile strength of the composite.

3.3.4.3 Rubber modified composites

Results are given in Tables 9 and 10 (page 78). Stress-strain plots for these materials are shown in Figure 60. As stated earlier, the tensile strength of a composite depends on initiation of a crack and the subsequent propagation of that flaw. The tensile strength of the composites could be improved if the propagation energy could be increased enough, if the initiation step is unaffected. Reactive rubbers such as CTBN and ATBN are well known toughening agents for epoxy resins (see literature survey). The addition of ATBN increases the fracture toughness quite substantially. The effect of this toughening agent on the tensile strength is considered here.



Figure 61 shows the tensile strengths of rubber-modified epoxies of this study compared to the results of Ting^[192], Bascom *et al*^[98], Meeks^[193] and Storey *et al*^[194]. Both the results of Meeks and Storey showed an improvement in strength with the addition of the reactive rubber although this was not seen in this and the other studies. The results of this study correlated well with those of Bascom. The rubber reduced the strength of the resin by approximately 20% (Figure 62). It is caused, in part, by the reduction of stress bearing area but is probably caused by the stress concentrations introduced by the rubber inclusions. The rubber increased the

elongation at failure.

Adding the rubber to an ATH-filled matrix reduced the strength still further. The reduction followed the model of Nicolais and co-workers^[47,48] well at low volume fractions (Figure 62) but at high volume fractions there is some evidence for the development of a plateau, similar to ATH-filled composites. The fracture toughness of the rubber-modified composite was greater than that of the non-modified analogue. The effect of this is seen at low volume fractions where the first additions of ATH have not produced such a rapid fall in the strength.



A comparison of the relative tensile strength of rubber modified epoxy resin from various studies



The tensile strength of ATH- and ATH-rubber filled composites compared to the model of Nicolais and Nicodemo^[47]

3.3.5 Summary

The addition of ATH to an unmodified and rubber-modified epoxy increased the tensile modulus of the composite. The relationship between volume fraction of filler and the modulus can be adequately described by the Lewis and Nielsen^[17] equation.

Results of this study are analysed in comparison to similar particulate fillers. The tensile strength of the epoxy matrix was reduced by the addition of the filler. The largest effect occurred at volume fractions up to 0.1 but above this further filler addition does not affect the tensile strength to any great extent.

Fracture surfaces are dominated by particle fracture. It is proposed that at high volume fractions, and to a lesser extent at low volume fractions, crack initiation is caused by particle fracture. The addition of a rubber toughener reduced the strength still further, although the rate of decline at low volume fractions was less.

SECTION 4 FRACTURE PROPERTIES

3.4.1 Introduction

The fracture properties of different fillers have been determined by various workers^[e.g.28,38,41,56,172]. These fillers fall into two main categories^[56]; strong fillers (alumina, silica etc. and glass beads); weak fillers (e.g. dolomite, alumina trihydrate and glass bubbles). The fracture of glass beads has been extensively studied over the last two decades^[e.g.28,38,41,172] but there has been only limited work carried out on other fillers and even less on these fillers in a rubber-modified matrix. In this study the fracture properties of epoxy composites containing ATH, with and without rubber modification, have been determined.



Fracture properties have been determined usina different two specimen geometries; tapered double cantilever beam (TDCB) and single edge notch (SENT). All compositions showed linear stress-strain curves (an example is shown in Figure 63) and therefore conformed to the criteria for linear fracture mechanics. The only doubts about the applicability of LEFM are with the rubber modified epoxy compositions of 20 phr and higher. The size of the plastic zone may be large enough to constitute а

significant error to the measured crack length, a. Stress whitening was evident in the rubber containing compositions but not the epoxy/ATH ones.

Fracture results are given in Table 11 (page 97) with a calculated error. Each result is the average of 5 specimens, (because of the notch sensitivity of the SENT shape the results are the lowest 5 specimens out of approximately 7 to 8 determinations). The value of G_{lc} was determined using a TDCB geometry and K_{lc} using the SENT specimen (the equations used to calculate these parameters are

given in Chapter 2), the alternate parameter for each shape was calculated using the equation:

$$K_{IC}^{2} = \frac{EG_{IC}}{(1-v)}$$
 (49)

For some calculations unknown variables were either estimated or assumed. The calculation of plastic zones requires the tensile yield stress but most of the compositions did not show an intrinsic yield point in the uniaxial tensile test. When a natural yield point was not seen, the tensile strength was used. Williams^[196] suggests that this is an acceptable approximation. Poisson's ratio (used in equation 49) for ATH is 0.3^[5]. For the polymer, Wainwright^[8] measured it to be 0.4 but this is a high value in comparison^[196] to PVC and polystyrene (0.36 and 0.34). Based on the comparisons, the value taken in this study was 0.33. The rubber was assumed to be an almost perfect elastomer, so Poisson's ratio was taken as 0.48. For all composites Poisson's ratio was calculated by the rule of mixtures.

3.4.2 Toughening mechanisms

There are several toughening mechanisms that are active in particulate filled and rubber modified epoxies. Although these mechanisms have been discussed in the literature survey (Chapter 1), it would be useful to summarise the five main mechanisms (increased surface roughness, toughening by thermal-mismatch, crackbridging, crack-pinning and crack-blunting) again at this point.

The fracture energy is related to the new surface area created by crack propagation. It therefore follows that an increase in the surface roughness will increase G_{kc} . Faber and Evans^[124,125] produced a mathematical argument to quantify this effect as the initial tilt and the twisting of the crack front around the particles. This mechanism is generally thought to be a minor contributor to the total increase in G_{kc} .

Toughening by thermal mismatch was proposed recently by Low^[126]. Essentially, he suggests that residual stresses (radial and tangential), inherent in any filled polymer, can cause constructive or destructive toughening. It depends on the curing temperature, size and direction of the differences in the thermal expansion coefficient, α . For a rigid filler like ATH, $\Delta \alpha$ is +ve ($\Delta \alpha = \alpha_m - \alpha_f$), so the

model predicts destructive toughening. This is not the case in practice, many rigid fillers have been shown to produce constructive toughening.

Crack-tip blunting is the major toughening mechanism^[e.g.132,133,140-142] in rubbermodified epoxy resins. The rubber modifier forms discrete domains that cavitate in the triaxial stress field in front of the crack-tip. The cavitation reduces the constraint on the surrounding polymer and produces a transition from plane strain to plane stress conditions, this enables extensive shear yielding to occur which blunts the crack. In rigid filled systems crack-blunting can also occur, by matrix debonding at the interface, this again reduces the constraint.

The crack-pinning mechanism is the one most often quoted as the major reason for toughening in filled thermosetting polymers^[12,41,42,117,190]. First proposed by Lange^[113] it was extended by Evans^[114] and then subsequently by Green^[116,116]. In essence the filler particles interact with the crack front causing it to bow out between the particles. Energy is expended in increasing the length of the crack front.

3.4.3 ATH filled composites

The addition of ATH to an epoxy resin has been shown to increase $G_{lc}^{[8,12,191]}$ and $K_{lc}^{[8,191]}$. In these studies the toughening mechanisms have been quoted as crack-pinning by Lange and Radford^[12] and crack-blunting by Wainwright^[8]. The results for this study are given in Table 11 (Page 97) and shown graphically in Figure 64. The results reported here agree with the previous studies, in fact there is reasonable agreement between all three studies.

The thermal mismatch model of Low^[126] is inadequate for this particulate-filled epoxy system because it predicts a negative toughening effect. Faber and Evans^[124,125] proposed a different explanation for the fracture energy increases. Figure 3 illustrates the prediction of their model compared to the results of this study (the aspect ratio of ATH is assumed to be 3). Again the model is not suitable, therefore, it can be concluded that the increase in surface area alone does not adequately describe the fracture energy trends in this system.



The fracture energy of ATH/Epoxy composites from different studies



The fracture energy results compared to the model of Faber and Evans^[124,125]

The maximum in the G_{kc} falls somewhere between a volume fraction of 0.10 and 0.19. Wainwright^[9] identified the transition between stick-slip and stable propagation (example traces are shown in Figures 66 and 76, pages 98 and 107) to occur at a volume fraction of approximately 0.16. The maximum seems to correspond to this

transition. It has been proposed^[62,123], and generally accepted, that stick-slip crack propagation is caused by a crack-blunting mechanism. It would be reasonable to assume that crack-blunting also occurs in this system where there is unstable crack propagation. Although a crack-blunting mechanism does not fully account for the observed behaviour over the whole volume fraction range, as will be discussed.

Fracture toughness results are given in Table 11 together with an estimate of precision. The fracture toughness of ATH is compared with the results of Moloney^[56] for alumina, silica, short glass fibre, glass bead and silicon carbide in Figure 67. It can be seen that ATH does not increase K_{ic} as much as the equivalent loading of silica or alumina but is greater than for glass beads. This trend is not predictable by a crack-blunting mechanism but is predicted by crack pinning. Green showed that cubic particles increase K_{ic} more than spherical particles and this has been confirmed experimentally by Moloney^[56] *et al.*

ATH content (phr)	ATBN content (phr)	Curing Agent	G _{1c} (Jm ⁻²)		K _{ic} (MNm ^{-3/2})	
			TDCB	SENT§	TDCB§	SENT
0	0		100 (8)	99.4 (6)	0.58 (0.02)	0.59 (0.02)
5	0		Ŧ	259 (23)	-	0.92 (0.05)
10	0		-	442 (29)	-	1.30 (0.04)
20	0	Ерікиге і	251 (11)	260 (19)	1.05 (0.01)	1.17 (0.06)
50	0		246 (10)	-	1.19 (0.03)	-
100	0		222 (13)	246 (11)	1.29 (0.04)	1.37 (0.03)
0	0		98.3 (6)	111 (10)	0.60 (0.02)	0.65 (0.04)
50	0		243 (20)	268 (18)	1.13 (0.06)	1.22 (0.05)
100	0		237 (10)	234 (28)	1.34 (0.03)	1.40 (0.08)
150	0	Рірегіате	199 (8)	201 (14)	1.42 (0.03)	1.62 (0.10)
200	0		171 (4)	286 (11)	1.61 (0.02)	2.05 (0.04)
250	0		•	210 (14)	-	2.04 (0.07)
Notes: phr = Parts per hundred resin. Standard errors in brackets, standard deviations are approximately double. §= Calculated values						

Table 11The fracture properties of ATH-filled composites



The load-displacement trace from a G_{ic} test of an ATH-filled composite



Alumina trihydrate is considered a weak filler because of its 'slate like' crystal structure (Figure 68). Despite this, the fracture toughness behaviour is different from that induced by other weak fillers. It has been shown that the fracture toughness of dolomite^[119] and hollow glass beads^[41] levels off at a particular volume fraction (Figure 69) which is believed to be caused by an increased frequency of trans-particle fracture. The limiting value of K_{tc} depends upon the strength of the

particle. Tod and Wolfe^[41] showed that the fracture toughness correlated with the compressive strength of the particle. The compression strength of the composite will therefore give a good indication as to the strength of the filler particle. It is found that dolomite does not affect the yield stress^[190], glass bubbles reduce it and ATH increases it (Table 5, Page 62 and Figure 70). These compression results suggest that ATH is stronger than either glass bubbles or dolomite but weaker than alumina or silica. Considering the crystal structure of ATH, it is only weak in one plane and it is this that accounts for the lower toughness compared to alumina. These trends are explainable by a crack-pinning mechanism because the weak plane reduces the efficiency of the toughening mechanism and it therefore follows that the orientation of an anisotropic filler like ATH will have a bearing on the efficiency of the mechanism.



Figure 68 The structure of an ATH particle

In his paper, Green^[116] gives the theoretical increase in toughness for spherical and cubic fillers. Figure 72 shows the predicted toughness increase for rectangular fillers at three possible breakaway positions compared with the results of this study and those of Moloney^[56] *et al.* The theoretical breakaway position (r, Figure 71) is a measure of the penetrability of the filler particle, in effect the particle strength. Strong fillers would be expected to give high value of r and weak fillers a low one.



The fracture toughness (Kic) of epoxy resins containing weak fillers (data taken from references 119[O] and 41[**I**])



The yield strength of epoxy resins containing various fillers (open symbol data taken from references 56 and 66)

The trends in K_{lc} for alumina, silica and ATH follow the theory well (above loadings of 0.195 Vf of ATH). The breakaway value, r, for alumina and silica is just below the theoretical maximum of 2. This accurately reflects the high strength of these particles. Alumina trihydrate was found to give an r value of approximately 0.75 but below 50 phr the results are higher than predicted by Green^[116] for crack-



Schematic diagram of Green's model showing the breakaway position, r

pinning (Figure 72 and 73). Earlier it was concluded that because stick-slip crack propagation was observed, that crack-blunting was occurring. It would be logical to assume that there will be interaction between the crack front and the particles at all volume fractions. It would follow therefore that crack-pinning should operate, at least to some extent, over the whole volume fraction range (except at ultra high volume fractions when the particles are virtually touching each other). Therefore, it is possible to suggest that there isn't a mechanistic transition but a combination of mechanisms. Crack-pinning is the major toughening mechanism at high volume fractions and crack-blunting is important at low volume fractions but in between there is a combination of the two.

Some evidence to support this proposal is seen in Figure 74. The micrograph shows that there are "tails" behind the filler particles and that there was only minimal debonding^d. The formation of "tails" is caused by the crack propagating around the particle on different planes. Melin^[B1] showed theoretically that the two crack fronts can not stay coplanar. The occurrence of these "tails" has been cited^[59] as evidence of the crack-pinning mechanism.

d



A comparison of the fracture toughness results of this study (●■) and those of Moloney et al^[56] (○□) to the predictions of Green^[116]



The crack-pinning prediction of Green^[116] compared to the fracture energy results from this study

In the crack-pinning mechanism, the particle bridges the fracture surfaces. As already shown, ATH is a weak filler (r = 0.75) and it would be unlikely that it could carry the high loads involved and would, as a result, fracture. The fracture mode (of the particle) will depend on the orientation but will most likely occur along the crystallographic planes, indeed trans-particle fracture is typical on the fracture

surfaces of tensile and fracture toughness specimens. The orientation effect can be seen in Figure 74 where the particles arrowed A, B and C show the three possible results of crack-bridging.

- Particle A The particle is perpendicular to the crack front. Debonding or cohesive failure of the matrix has occurred (a hole is left on the other fracture surface).
- Particle B The particle is again perpendicular to the crack front. Fracture along the crystal planes has occurred.
- Particle C The particle is coplanar to the crack front. Fracture of the particle has occurred again with one part on each fracture surface.



Figure 74 An SEM micrograph showing the "tails" behind the ATH particles (20 phr)

If the proposed combination of mechanisms are assumed to be correct, it follows that using the predicted and measured values of K_{lc} , the contributions of crack-pinning and crack-blunting can be calculated. The contributions from each are shown in Table 12. The introduction of the filler drastically inhibits the crack-blunting

mechanism because of increasing constraint (discussed in the next paragraph). A transition from stick-slip to stable propagation occurs at 0.16 Vf and at this point the estimated contribution of crack blunting is 4-5%.

The crack-tip opening displacement has been shown^[59] to increase when crack propagation is stick-slip. The CTOD's reflect the degree of crack-tip blunting. For ATH-filled composites the CTOD's, though not conclusive, increased up to 20-phr and then reduced with increasing volume fraction. This trend is consistent with the proposed mechanistic combination.

Crack-blunting reduces as the volume fraction of ATH increased. Because of the strong interfacial adhesion, each filler particle immobilises the matrix that is immediately next to its surface. This increases the constraint which, in turn, increases the yield stress (Table 5, page 62) and this makes crack-blunting less favourable.

ATH content (phr)	r/c	CTOD (µm)	% Contribution		Spanoudakis ^[38]	
			Pinning	Blunting	r/c	Blunting (%)
0	_	1.5	0	100	-	100
5	0.036	4.5	71	29	0.161	22
20	0.145	5.7	78	22	0.323	28
50	0.362	5.3	96	4	0.646	21
100	0.725	4.6	99.2	0.8	0.967	5
150	1.088	4.3	100	0	1.288	0
Notes	Notes Crack pinning contributions are calculated from values by Green, r=0.75 for this study and spherical interacting for Spanoudakis					

 Table 12

 The contributions of crack-pinning and blunting to the fracture toughness

The proposed fracture mechanisms for the ATH/epoxy system studied here are consistent with those proposed by Spanoudakis and Young^[38] in 1984 for glass bead-filled epoxy resin. They showed that the fracture toughness trends could be explained by the simultaneous action of crack-blunting and crack-pinning. Although they did not attempt to estimate the contributions of the two directly they did show that when corrected for the action of crack-blunting the toughness was consistent with the crack-pinning model of Green^[116]. Table 12 shows the estimated contribution

of crack-blunting for the results of Spanoudakis^[38] for 16µm particles. The contribution of crack-blunting, at the transition between stick-slip and stable, is approximately 4-5% and agrees with the ATH system. It is not possible to say if this figure is significant or if it translates to any other systems with the available published data. The results of Moloney^[56] *et al*, for rectangular particles (Figure 72, page 102), show good correlation to the crack-pinning model over the whole volume fraction range but the resin system they used gave stable propagation, even unfilled, so crack-blunting was not a factor for their composites.

3.4.4 Rubber modified composites

3.4.4.1 Rubber toughened composites

The use of reactive elastomers as a toughening agent in epoxy resins has been known since the late 1960's. Although these systems are not in themselves a central part of this study the results form a backdrop for the hybrid (ATH-rubber) composites to be discussed later.

ATH A content co (phr) (ATBN	Curing agent	G _{1c} (Jm ⁻²)		K _{tc} (Jm ⁻²)	
	content (phr)		TDCB	SENT+	TDCB†	SENT
0	0		100 (8)	99.4 (6)	0.58 (0.02)	0.59 (0.02)
0	5	i	573 (42)	-	1.36 (0.08)	-
0	10		695 (27)	-	1.40 (0.03)	-
0	15	Epikure T	4058 (474)	-	2.69 (0.16)	-
0	25		3492 (412)	-	1.68 (0.12)	-
0	30		3179 (282)	-	1.23 (0.09)	-
0	0		98.3 (6)	111 (10)	0.60 (0.02)	0.65 (0.04)
0	5		-	1262 (216)	-	2.00 (0.17)
0	10	Piperidine	1348 (45)	2145 (55)	1.90 (0.03)	2.32 (0.05)
0	15		-	2447 (112)	-	2.42 (0.06)
0	20		•	2390 (84)	-	2.11 (0.04)
Notes: phr = Parts per hundred resin. † = Denotes calculated values. Standard errors in brackets.						

Table 13The fracture properties of an ATBN modified epoxy

The fracture mechanisms operating in rubber modified epoxies are now well understood. It is generally accepted that the rubber particles cavitate in the triaxial stress field in front of the crack-tip. The rubber's cavitation relieves constraint on the surrounding polymer and this allows enhanced shear yielding to occur. The yielding blunts the crack and hence increases the material's fracture resistance.

The fracture properties of ATBN modified epoxy resin are shown in Table 13. There is a very large body of literature covering rubber modified epoxies and there is little this study could add. In spite of this, it is worth discussing some aspects of the present system in comparison to previous studies.



Figure 75 The morphology of the rubber modified resin (10phr)

Figure 75 shows the morphology of an Epikote 816-ATBN composite. Although not formally calculated, the particle size of the rubber phase can be estimated to be in the region of 0.5-3.0 microns and there is evidence of cavitation by some of the rubber domains (arrowed). From the particle size of the rubber it can be assumed that crack wake bridging was not significant. Pearson and Yee^[102] showed that if the particle size is small in comparison to the plastic zone size (3µm and 30-90µm respectively here) cavitation occurred but if the triaxial stress field was not large enough to cause cavitation then crack-bridging occurred.

Table 14 (page 108) lists plastic zone sizes and CTOD values for various compositions. Kinloch and Williams^[122] and Gledhill *et al*^[123] showed that the CTOD

increased when crack-tip blunting occurred. Calculated CTODs for the materials in this study also increased as the volume fraction of rubber increased. Specimens with rubber loadings of up to 15 phr for Epikure[®] T and 20 phr for piperidine exhibited stick-slip behaviour but higher loadings showed stable ductile propagation. An example of a load-displacement trace is shown in Figure 76 for an epoxy containing 10 parts of ATBN.

In previous studies^[79] the Dugdale line zone size has been correlated with markings on the fracture surface where a stick-slip event had occurred. These markings have been postulated to be slow crack growth regions and taken to be the extent of the plastic zone. In rubber modified thermosets the deformation zone size can be easily seen because of a stress-whitened area at the point of crack arrest. The whitening arises by diffraction of light by the holes left by cavitated rubber particles.



Figure 76 The crack propagation of a rubber modified epoxy (10phr ATBN)

ATBN content (phr)	Curing agent	CTOD (µm)	Plastic zo	Stress		
			Irwin	Dugdale	whitened zone length (µm)†	
0		1.3	3.1	23	-	
5		8	20	145	-	
10	1.1.7	11	28	299	440-500	
15	Ерікиге Г	98	232	1716	2060-4100	
25		121	195	1445	N/A	
30		150	145	1076	N/A	
0		1.5	3.3	26	-	
5		19	53	395	480-1400	
10	Piperidine	35	85	633	980-1240	
15		55	153	1136	1300-5000	
20		71	206	1522	-	
Notes:	Epikure T value from TDCB and piperidine values from SENT specimens. \dagger = error of approximately ± 50µm.					

 Table 14

 Further fracture properties of ATBN modified epoxy resin

As expected, the plastic zone size increases with increasing rubber content. Measurements of the plastic zone size were made using a travelling microscope and these are shown in Table 14 together with the calculated estimates of the Irwin^[85] and Dugdale^[87] equations. Clearly, the Irwin model under estimates the size of the deformation zone, the stress whitened zones on the specimens were approximately equal to - to double the Dugdale estimate. The specimens containing 25 and 30 phr ATBN did not stress whiten and they showed stable-ductile crack propagation.



A comparison of the fracture toughness of rubber modified epoxy from three studies

It is evident from the results in Table 13 that the fracture toughness and fracture energy both increase but peak at around 15 phr. This trend has been reported before in these systems. Bascom *et al*^[99] and Ting^[192] reported similar results^e for a CTBN-filled epoxy resin (Figure 77). It can be seen from the stress-strain curves that a change occurs above this loading, in fact for Epikure T at 15 phr, two different types of stress-strain curves were observed. Bascom^[99] suggested that the fracture resistance reduces because the rubber and epoxy form a blend. It has also been suggested^[197] that some systems phase invert at high loadings of CTBN. TEM analysis of a specimen that contained 30phr of ATBN was inconclusive because the specimen is extensively damaged by the microtome.

3.4.4.2 Hybrid Composites

The number of studies that have used both particulate filler and a rubber modifier is small compared to those that use them separately. By far the majority of these studies have involved CTBN and glass beads. In this study ATBN was used as the modifier and ATH as a filler, (unless otherwise indicated the rubber content was constant at 10 phr). The fracture toughness and fracture energy results are shown in Table 15.

e

Kic results were derived for Bascom and Ting by calculation from published literature

The rubber modifier altered the crack propagation of the ATH-filled composites. The transition point from stick-slip to stable propagation was increased to between 50 - 100 phr of filler from approximately 40 phr for the unmodified composites. If the theory for the fracture properties in ATH-filled epoxies postulated earlier is correct, an increase in the ductility of the matrix (by the addition of the rubber) would indeed be expected to raise the transition point from stick-slip to stable crack propagation because of the enhanced shear yielding (due to the reduction in yield stress) and therefore increased crack-blunting.

ATH content (phr)	ATBN content (phr)	Curing agent	G_{tc} (Jm ⁻²)		K _{Ic} (Jm ⁻²)	
			TDCB	SENT†	TDCB†	SENT
0			695 (27)	-	1.40 (0.03)	-
5			668 (22)	-	1.40 (0.02)	-
10	10	Enikure T	675 (59)	-	1.39 (0.03)	-
20	10	Epikure I	671 (82)	-	1.45 (0.09)	-
50			558 (47)	-	1.55 (0.06)	-
100			358 (32)	•	1.41 (0.01)	-
0	10	Piperidine	1348 (45)	2145 (55)	1.90 (0.03)	2.32 (0.05)
50			-	749 (37)	-	1.72 (0.04)
100			348 (8)	545 (33)	1.46 (0.02)	1.80 (0.06)
150			-	446 (21)	-	2.04 (0.09)
Notes: phr = Parts per hundred resin. + = Denotes calculated values. Standard errors in brackets.						

Table 15The fracture properties of hybrid composites



The effect of rubber modification on the fracture energy

The rubber's morphology was not affected by the filler's presence. Figure 79 shows the surface topography of a fracture specimen containing ATBN and ATH. Rubber particulates can still be seen and are identified by the arrows in the micrograph. This indicates that there wasn't an interaction between the filler's surface and ATBN and the particle size of the rubber does not seem to have been altered by the presence of the filler particles, which is still around 1µm.



Figure 79 The fracture surface topography of a hybrid composite (100phr ATH / 10phr ATBN)

The fracture energy and toughness trends of these hybrid composites are different than other particulate fillers. The fracture energy is substantially increased over the unmodified composites (Figure 78). The effect of the rubber reduced as the filler loading increased. It seems logical that the same fracture mechanisms that operated in the ATH-filled system (crack-pinning and crack-blunting) are operating in the rubber-modified analogue. It is likely that the introduction of the filler interferes with the cavitation of the rubber particles and therefore the extent of the plastic zone. By immobilising a shell of material, the filler would increase the constraint on the polymer which will reduce the localised shear yielding that the rubber enhances.

The fracture toughness shows the same general trend (Figure 80), the toughness reduces, but then recovers. The modified line does not seem to converge with, but continues almost parallel to the line for unmodified composites. Again, this suggests that the ATH interferes with the mechanisms of the rubber but even so the rubber is still able to contribute to the toughness.



It seems that the combination of filler shape and strength produces this unique behaviour. Tod and Wolfe^[41] studied hybrid systems that contained 10 parts by volume of CTBN and glass bead of various strengths (Figure 81). They found that the lower the strength of the filler (measured as compression strength), the lower the fracture toughness enhancement. They concluded that the reduction in fracture toughness, of the rubber modified composite containing the weak hollow beads, was caused by a change in the toughening mechanism from shear yielding to crack-pinning. For the weak particles, where almost no toughening was observed, particle fracture dominated. In ATH systems a similar trend was observed but, there is a recovery in the toughness at high volume fractions. The effect of the ATH of the fracture toughness is similar to the SSX hollow bead. Comparing the two suggests that the ATH particle has a similar strength to the 2000psi (compression strength)



The fracture toughness of an ATH-hybrid composites compared to glass bead hybrids

hollow-bead. Differences between the ATH and that of the SSX bead could be explained by easier void nucleation^[66] for the spherical beads.



There are three distinct response areas for the fracture toughness of these ATH systems (shown in Figure 80) and these are shown schematically in Figure 82. Areas A and B have already been discussed above, the main mechanisms for these regions are crack-blunting and crack-pinning respectively. In area C the rubber is still making a contribution to the overall toughness, but at a much lower level. Two mechanisms could be responsible of the toughening: crack-tip blunting and crack wake bridging. It is possible that crack-blunting is still occurring, although it is unlikely because the addition of such large quantities of filler increases the yield stress and it has been shown^[79] that above a compressive yield strength of 100MPa crack blunting becomes less favourable. For these materials the compressive vield strength is around this value for the hybrid composites and the ATH composites are well above it. The tearing of the rubber particles, as they bridge the crack wake, is the more likely mechanism in area C. Pearson and Yee^[102] showed that when cavitation of the rubber particle does not occur, leading to crack blunting, the particle will bridge the crack and fail by tearing. Vekinis et al^[83] have observed this type of failure during an in-situ SEM fracture test (under plane stress conditions).

3.4.5 Summary

The fracture toughness and fracture energies of composites containing both

ATH and ATBN rubber have been determined. The fracture toughness was increased by the addition of ATH and was greater than for comparable glass bead-filled composite but less than for silica or alumina ones. The fracture energy peaked at a volume fraction of approximately 0.1 of ATH. The results are compared to current models for the fracture mechanisms. The main toughening mechanism is crack-pinning at high volume fractions where there is stable propagation and crack-blunting at very low volume fractions. In the intermediate loadings (up to the transition between stick-slip and stable propagation) it is proposed that there is a combination of the two mechanisms

The addition of ATH to a rubber-modified matrix caused the fracture toughness to fall, but it recovered at high filler volume fraction. A similar combination of mechanisms is used to explain the trends for the hybrid materials as in the ATH-filled composites.

SECTION 5 POLYMER COATING

3.5.1 Coating methods

3.5.1.1 Introduction

The results of the model experiments and post-mortem analysis of fracture surfaces suggest that fracture is initiated by the cleavage of ATH particles. It is postulated that a polymer coating could act as a crack blunting agent, delaying the onset of crack propagation and hence the ultimate failure. Several methods for the application of this coating have been investigated although it should be noted that none of these methods have been exhaustively tested. The ideal coated particle would be a single particle completely encapsulated in the polymer. Coated agglomerations of particles would not be satisfactory for the method to be effective.

3.5.1.2 General observations

It was found that any method that required additional work on the coated filler, i.e. grinding of a sheet, caused cleavage of the particles and thereby destroying the coating. The methods for which this was the case were: (1) solvent deposition, where the solvent is evaporated to leave the polymer (2) precipitation where a poly(vinylacetate) is precipitated from solution with the filler to form a 'cake', and (3) casting methods where a heavily ATH loaded sheet is produced.

3.5.1.3 Fluidised bed

This method is a variation of a fluidised bed agglomerator^[198]. The assembled apparatus is shown in section 2.12.1 (Page 54), a schematic diagram is shown in Figure 83. Normal operation of a fluidised bed agglomerator uses a concentrated feedstock and a low gas velocity. If the feedstock is diluted and the gas velocity raised, any agglomerates formed will be quickly broken up by the lack of binder and the movement of the bed. With suitable conditions the particles will be coated with the polymer in the feedstock while maintaining a low agglomeration level.

Initial trials highlighted two problems: 1) The filler particles were being blasted out of the way of the injection port; and 2) the bed was being saturated with solvent.



The injection pressure and the shape of the injection port were modified to counter the first problem. The wetting of the bed was more difficult to solve quickly. The solvent was causing adiabatic cooling. The addition of heating elements on the outside did not work effectively and there was no space to incorporate heating inside the bed.

This method was not pursued any further. Some problems are associated with scale. The small laboratory size apparatus caused problems that would be easier to solve with the greater space available in larger apparatus. The time required to perfect this method would be prohibitive.

Figure 83 A schematic diagram of the fluidised bed apparatus

3.5.1.4 Nylon coating methods

At first glance Nylon[®] should be the ideal coating, it is compatible with the epoxy resin, without dissolving

in it, and the hydroxyl rich ATH surface. A major draw back is that only very polar solvents (chlorobenzene, DMSO, etc.) will dissolve it. In these experiments DMSO was used.





The concentration of Nylon[®] was followed by infrared spectroscopy; the cut down spectra are given in Figure 84. In practice the nylon, although it does not stay in solution, does not coat the filler. The Nylon[®] forms a separate phase with a few

small particles embedded (Figure 85). The reasons are not totally clear but two reasons could be postulated. 1) The solvent prevents the polymer from contacting the filler's surface. 2) The cohesive energy of the nylon is higher than the adhesive energy of the nylon[®] to the filler. Variations in the cooling rate, concentration and pH were tried but did not improve the results.



Figure 85 ATH filler with Nylon[®] deposited by a solvent deposition method

3.5.1.5 Mechanical mixing

This method was carried out using a 'Moritz' high shear mixer. This is a commercial piece of equipment which is used in applying silane coupling agents to fillers in the powder industry. A schematic diagram is shown in Figure 33 (page 57). The shearing action of the mixer causes frictional heating, this drives off the solvent and causes reaction between the silane and the filler's surface.

A water based poly(vinyl acetate) latex was used as the coating agent. This was added at levels of 0.5, 1, 2 and 5% (w/w) of filler (silanes are added up to a level of, typically, 2% w/w).

This method of application produces even coatings with silane coupling agents and this was the case with the latex as well. Figure 85 shows ATH coated with 5% latex. The polymer is seen to have coated the filler (the extra surface rugosity). In addition the level of agglomerations was low. The level of water was doubled to see if a more dilute solution would improve the coverage. Results of this experiment are shown in Figure 86. The change in the appearance of the filler is remarkable. Some particles seem completely encapsulated but others are not coated at all, but all the particles seem to have a more rounded appearance. The reason for the dramatic change is not clear at the time, but is probably due to the change in the drying conditions when the polymer film-formed.



Figure 86 ATH treated in a Moritz mixer with 5% 9300

Tensile strength measurements were made on epoxy specimens filled with the coated fillers and these results are shown in Table 16. Tensile strengths were not as high as for the uncoated filler but the more rounded particles (5% 9300 diluted) did give marginally better results than its more irregular counterpart.



Figure 87 ATH coated in a Moritz mixer (5% 9300 + water)

Material	Strength (MPa)	Elongation (%)	Modulus (GPa)
ATH	49.3 (1.2)	0.75 (0.1)	7.18 (0.2)
ATH 5% latex	41.7 (1.4)	0.56 (0.1)	7.31 (0.4)
ATH 5% diluted latex	45.4 (3.9)	0.66 (0.1)	7.39 (0.4)
Notes ATH level was 100 phr for all the tests. Standard d given in brackets			

 Table 16

 The tensile strengths of latex coated FRF20 applied by a Moritz mixer

The thickness of the coating in this method was not very great. To build up the thickness, successive applications of latex were made. This was unsuccessful because the second application caused the filler to form a paste which increased torque and caused an overload.

This method has two advantages 1) the dispersion of the coating is very good and 2) agglomerations are not a problem, but gaining a suitable coating thickness would require careful selection of the polymer system.

3.5.1.6 Spray drying

At first sight this is the ideal method. The filler will, by the very nature of the method, be coated provided wetting of the filler's surface occurs. A poly(vinylacetate) latex was used as the coating agent. Levels of latex ranged from 1-10% (w/w). The spray drying method was investigated by the Yarsley Research Laboratories^[167] for the Ministry of Defence. They showed that, with a water soluble polymer, reasonable levels of encapsulation could be achieved.

Initial trials were carried out on a Busch mini spray dryer. Figure 88 shows the results of these trials. The mini dryer produced coated ATH but, agglomerations were a problem. Not only was the particulate ATH agglomerated but the spray dried particles agglomerated together as well (Figure 89). The amount of material retrieved from the dryer was found to be too low to carry out any other experiments. In addition, the feed mechanism was prone to blockages. For these reasons this size of dryer was abandoned in favour of a 2 metre pilot plant spray dryer.



Figure 88 Coated ATH produced in a mini spray dryer



Figure 89 Agglomerations of agglomerates from the mini spray dryer

Initial trials on the pilot plant scale revealed three problems. 1) settling of the filler. This was a simple problem and was cured by stirring the storage tank during the run. The stirring speed was set so that the filler did not settle but cavitation did not occur (cavitation would stop the pump). 2) The thickness of the coating was limited to the maximum latex content that could be added to the slurry. For this equipment the maximum solids was 60%, 10% of which was latex. A higher latex content caused the coated filler to stick to the sides of the drying unit. It is possible that a larger scale rig could handle a larger coating content. 3) Agglomerations. Under the conditions used, the theoretical droplet size from the injection port was

calculated to be approximately 50-65 µm. This was calculated from the empirical equation^[199]:

$$D_{vs} = \frac{1.4 \times 10^{4} \times (M_{L})^{0.24}}{(Nd)^{0.83} \times (nh)^{0.12}}$$
(50)

where: $Dvs = Sauter diameter (\mu m)$, ML = feed rate (Kg/hr), N = head rotation speed (RPM), d = head diameter (m), n = number of vanes and h = vane height (m).

The problem of agglomerations is one of filler selection for the conditions. If the particle size of the filler is greater than that of the droplet, agglomerations are less likely. This can be put simply as "how many particle can fit in the droplet?". For no agglomerations the answer needs to be less than 1. This was tested with ATH of three vastly different particles sizes. Figures 90 to 92 show SEM micrographs of spray dried particles using ATH with mean particles sizes (mps) of 1, 16 and 86µm respectively.



Figure 90 UF25E Spraydried (mps = 1µm)

From the SEM micro graphs the dependence of morphology on the filler particle size can be seen. For the two extremes the dried particles are reasonably spherical but the FRF20 was not as regular. Figure 93 illustrates the morphology of a particle for the three fillers. The spray dried particles morphology is related to the number and arrangement of the particles. The size of the spray dried particles is approximately in the range predicted by equation 50.



Figure 91 FRF20 Spraydried (mps = 16µm)



Figure 92 FRF5 Spraydried (mps = 86µm)

Strength determinations of some of these coated filler were carried out and these are given in Table 17. In general the coated materials showed reduced
strength compared to the uncoated analogue. The agglomerations in the spray dried particles are not mechanically very strong. In the mixing process these are normally broken-up, but if this does not occur the strength suffers dramatically. This highlights the major flaw in this method; agglomerations. Even the large particle size (FRF5) has fine particles below the droplet size and these can agglomerate. The only solution to this would be a mono-size filler or one with a very narrow particle size range.



UF25E

Figure 93

A schematic diagram of the morphology of the spray dried particles for three different particle sizes

(dotted line = droplet size, solid line = particle)

Coating level	Test type	Strength (MPa)	Elongation (mm/%)	Modulus (GPa)
Pure resin		99.8 (7.3)	11.2 (1.7)	2.8 (0.1)
none] [53.7 (2.9)	1.87 (0.05)	7.3 (0.4)
2%		50.7 (4.1)	1.93 (0.12)	6.7 (0.1)
3%	Flexural	51.5 (2.0)	1.84 (0.12)	7.3 (0.4)
4%		82.0 (25.5)	3.4 (1.3)	6.9 (0.1)
4%*		51.7 (1.2)	1.91 (0.09)	6.9 (0.2)
None		56.3 (1.8)	0.84 (0.08)†	6.9 (0.2)
4%		46.0 (3.9)	0.6 ()†	6.7 (0.3)
Polarite 880EW	tensue	37.8 (4.3)	0.4 (0.1)†	7.3 (0.2)
ATH from above§] [55.3 (0.9)	1.0 (0.1)†	7.5 (0.3)
Notes:	filler content PVAc latex († = Elongatio	for all specimens (spray dried). § = S on expressed in %.	= 100 phr. * repeat se Supplied blind by ECC Standard deviations	et. Coating = C International. in brackets.

	Table 17	
The tensile and flo	exural strengths of	various compositions

The flexural tests threw up an interesting result. The first set of tests for 4% latex gave results of: 104, 102, 97, 57 and 52 MPa. Although these results could not be repeated, these are considered to be true results and are not an error in the test or the specimens. The fracture surfaces of the high and low strength specimens are shown in Figure 94. The topography of the high strength specimen (labelled A in Figure 94) shows greater surface roughness than B (low strength). This is consistent with the possession of greater stored elastic energy at failure, as noted by Cantwell *et al*^[70]. The underlying reason for the increased strength could not be determined, but it does serve to illustrate the possible benefits of a polymer coated filler.



Figure 94 The fracture surface topographies of two flexural specimens

A commercial product, Polarite[®], was tested. This is a latex coated ATH marketed by ECC International which they claim^[166] has improved properties, but the tensile strength of the coated filler was lower than that of the uncoated. This is caused by particle agglomerations, which are much larger than the original filler, not being broken up in the mixing stage.

This method shows the potential for producing acceptable coated fillers. An alternative polymer system, that cured during spray drying, would enable a double pass through the dryer. This would serve two purposes; 1) to ensure complete encapsulation and 2) to allow thicker coatings to be built up.

3.5.1.7 In-situ polymerisation

The modification of the surface of a filler has been investigated by Popov et al^[173,174]. All these investigations were in relation to thermoplastics, in an attempt to improve the interfacial strength. Two types of in-situ polymerisation experiments were tried. 1) suspension polymerisation. The polymer chosen to conduct the initial trials with this method was poly(methyl methacrylate). This was selected because of its relative ease of preparation and a procedure was readily available. The experimental procedure is given in the Chapter 2. If these trials were successful a more suitable polymer would be used. 2) interfacial condensation of polyamide 6,6.

Initially the PMMA polymerisation was carried out as normal with the ATH (FRF20) placed in the reaction vessel at the start. This scheme produced mixed results. Figure 95 shows a micrograph of the particles from this experiment after separation with CCI_4 . Some of the particles seem to be coated (arrowed A) but others are not (arrowed B). The particles arrowed C could be mistaken as being pure PMMA, but they must be PMMA / ATH particles because their density must be higher than the CCI_4 (1.5 g/cm³) separating medium.



Figure 95 Particles (FRF20) from the initial PMMA in-situ polymerisation trials (CCl₄ separated)

The probable cause of the observed coating morphology is the formation of normal micelles and not micellular formation at the filler surface. The ATH has a physisorbed layer of water on the surface, this may have stopped the methylmethacrylate monomer from interacting with the hydroxyl rich ATH. To overcome this, the surface needs to be made more accessible and reactively favourable. Popov et al^[174] reacted his filler (talc) with acrylic acid to form a reactive surface coating. This method was tried in this study. The acrylic acid seemed to react with more than just the surface. TGA analysis of the filler (at various reaction times) suggested that the acrylic acid was attacking the crystallographic planes of the ATH (this is discussed further in section 3.5.2.1). A silane treatment was used instead. The silane, vinyltrimethoxysilane, had vinyl functionality.

The results of the vinyl silane coated ATH are shown in Figure 96. The difference is dramatic. The particles are coated completely but the polymerised particles are up to 200µm in size. The original ATH (FRF5) has a particle size of 86µm. This could indicate that there has been some agglomeration of the filler during polymerisation.



Figure 96 PMMA polymerisation using vinyl silane treated ATH (CCl₄ separated)

This method needs some refinements but shows good potential for yielding polymer encapsulated fillers. Time constraints prohibited the development of this method any further.

The interfacial condensation of nylon directly on to the filler's surface was attempted. The ATH was treated with 5% amino-silane (A1100). This was stirred in to a solution of hexamethylene diamine in water, dried and then into a solution of sebacoyl chloride in dichloromethane. This procedure was repeated 10 times. This method was not successful. TGA analysis showed that no coating had occurred.

3.5.2 Characterisation

3.5.2.1 Thermal analysis

Thermogravimetric analysis of a filler gives information on the weight loss and the temperature at which the loss occurred. A typical trace for an uncoated ATH (FRF20) is shown in Figure 97. Further TGA results are given in Appendix 3.



The various conversions that give rise to the peaks in the TGA trace have been assigned previously by Woychesin and Sobolev^[200]. The major water loss occurs at around 280°C and is the reason for the flame retardant properties of ATH. The peak arises from the conversion of α -alumina hydrate to χ -alumina:

$$2AI(OH)_{3}(\alpha) \rightarrow AI_{2}O_{3}(\chi) + 3H_{2}O^{\dagger}$$
(51)

There are also two smaller peaks at 220°C and 500°C, labelled (a) and (c) respectively. Peak (a) at 220°C is due to the conversion of alpha alumina hydrate to boehmite:

$$Al(OH)_3(\alpha) \rightarrow AlOOH + H_2O\uparrow$$
 (52)

Consequently the second peak, (c), is the conversion of boehmite from peak (a) to gamma alumina:

$$AlooH \rightarrow Al_2O_3 (\gamma) + H_2O^{\dagger}$$
 (53)

Woycheshin and Sobolev^[200] showed, using differential thermal analysis, that the size of the first peak varies with particle size. Figure 98 illustrates their results.



The variation in DTA response of the filler with particle size

Table 18 TGA results for various fillers, coatings and methods

	1st P	eak	Total loss	Second peak	Third peak	Extent of	Application
Description	Temp (°C)	loss (%)	(first 2 peaks) (%)	temp (°C)	temp (°C)	Coating (%)	Method
FRF5 Untreated	223.4	1.712	26.62	279.8	495.1	0.00	N/A
FRF5/Acrylic Acid 3 hrs	232.8	1.416	26.71	287.2	509.9	17.3	Pure AA
FRF5/Acrylic Acid 12 hrs	224.5	1.234	26.75	282.2	491.4	27.9	2% AA in H ₂ O
FRF5/Acrylic acid 5 days	224.1	0.633	26.81	238.2	488.7	63.0	Pure AA
FRF5/Acrylic acid 2 months	221.8	0.027	26.43	275.5	485.0	98.4	2% AA in H ₂ O
FRF5/Acryloyl Chloride 12 hrs	224.7	1.129	26.68	282.2	503.6	36.0	Pure AC
FRF5/10% 9300 Latex	234.5	1.216	N/A	294.0	488.9	34.0	Spray Dried
FRF5/3% A1100	225.0	1.01	25.81	284.2	497.2	41.0	Coffee Grinder
FRF5/5% A1100	222.8	0.615	25.33	279.0	489.0	64.1	Coffee Grinder
FRF20 Untreated	232.8	0.472	26.37	286.6	494.0	0.00	N/A
FRF20/10% 9300 Latex	228.0	0.167	N/A	280.2	485.7	64.8	Spray Dried
FRF20 S2 2%	223.6	0.254	25.15	276.1	495.4	25.0	Moritz Mixer
FRF20/5% 9300 Latex	231.0	0.156	25.97	281.4	491.8	66.9	Spray Dried
FRF20/5% 9300 Latex + 5% Water	229.4	0.232	26.05	284.6	489.4	50.8	Moritz Mixer
UF25E/10% 9300 Latex	•	-	-		-	-	Spray Dried
FRF5/PMMA after CCL separation	226.8	0.295		278.4	491.4	79.0	In-Situ Polym'n

The results from thermogravimetric analysis are given in Table 18. The interesting results are for the first peak (a). The weight loss for this peak varied with the time of exposure to acrylic acid.

This peak is the formation of boehmite. It is known that boehmite is formed at around 220°C under pressure^[200]. It is the requirement of pressure that explains the size dependence of this peak on particle size. Wainwright^[8] showed that strong acids attack the crystallographic planes of the ATH particle. The acrylic acid would be expected to have a similar effect, i.e. it attacks the planes which gives an apparent reduction in particle size (with respect to boehmite formation). This is illustrated in Figure 99. This theory does not explain the apparent variation of this peak with the addition of a coating. All the silanated, PMMA and spray dried materials showed a reduction in peak area for peak (a). If the reduction in peak (a) is related to the coating, then this could be taken as an indicator for the extent of coating. This calculation is shown in Table 18.



Figure 99 A schematic diagram of the effect of acid on the ATH particle

The three silanated materials (Table 19) show an extent of coating consistent with their level of silanation. For each of these materials the peak reduction per % of silane agent shows very good agreement. This calculation suggests that approximately 7.7 % silane would give complete encapsulation.

The mechanism by which the coating affects peak (a) is unclear at this time.

Silane level (%)	peak area (1st Peak)	extent of coating (%)	Specific extent of coating		
FRF20	0.472	0	0		
FRF5	1.723	0	0		
2*	0.354	25	12.5		
3§	1.01	41	13.7		
5§	0.615	64	12.8		
Notes:	 * = commercial application method ATH grade = FRF20. § = laboratory application, ATH grade = FRF5 				

Table 19TGA results for silane treated fillers

3.5.2.2 Compatibility

The compatibility of the polymer coating with the filler and the matrix is important issue. These factors determine the strength of the interfacial bonds and therefore, ultimately, the strength of the composite. One method for quantifying the affinity of the polymer for the filler is by how the surface is wetted. A measure of the wetting is the contact angle. Goddard and Bomal^[201] showed that there was good agreement between the contact angle and the filler/matrix failure mode.

Table 20 shows the measured static contact angle of epoxy resin on various materials. The contact angle was obtained by dropping a small quantity of resin (with hardener) on to a pressed ATH pellet. After curing the specimen was cut, polished and analysed in an SEM. An example SEM micrograph is shown in Figure 100.

Substrate	Untreated FRF20	FRF20 S2 (2%)	PTFE	PVAc Latex	
Contact angle	18.5	24.5	61.0	37.0	
Measurements are average of both ends. Notes: S2 = Amino silane. PTFE = Poly(tetrafluoroethylene).					

Table 20The compatibility of epoxy resin with various substrates

These results are empirical, further calculation of b (failure parameter) and M

(wetting parameter) using Lee's unified theory^[202,203] is not possible. Although these results are empirical they serve to rank the different coatings to obtain a 'feel' for the compatibility of the materials.

The results show that the adhesion to untreated ATH should be very good. The adhesion to the silane coated material not as good as the untreated filler but in this case adhesion is enhanced by chemical bonding. The pure latex polymer has a high contact angle. This could be the explanation for the reduction in tensile strength seen with latex treated fillers (Tables 16 and 17, pages 120 and 124).



Figure 100 A micrograph of the contact angle for untreated ATH

3.5.3 Summary

Coating processes that require grinding or additional mechanical work on the filler, to obtain a fine powder again, are not suitable. The additional work causes cleavage of the ATH particle and therefore destruction of the coating.

Methods of coating that showed potential were: Mechanical mixing (Moritz mixer); spray drying and in-situ polymerisation. With suitable polymers and conditions these methods could yield acceptably coated fillers. Coating by in-situ polymerisation shows the greatest potential for customisation of the polymer coating.

Thermogravimetric analysis and contact angles are used to characterise the polymer coatings. TGA analysis also serves as a measure of the extent of coating on the filler.

CONCLUSIONS

- 1. The addition of ATH to the epoxy resin reduced the tensile strength. The largest effect occurred at volume fractions up to 0.1. Above this concentration the tensile strength was relatively insensitive to the filler volume fraction. The inherent weakness of the filler particles, because of their structure, is the source of the reduction in strength. Model experiments suggest that particle fracture constitutes the initiation of failure. Post-mortem SEM analysis of fractured tensile specimens supports this theory. The elongation to failure was also reduced. Current theoretical models do not predict the tensile strength response of ATH-filled epoxy resins. The addition of a reactive rubber toughener (ATBN) to the ATH-filled composite reduced the strength still further but increased the elongation at failure.
- Young's modulus was increased by the addition of ATH, in agreement with previous studies and with theoretical models. The equation of Lewis and Nielsen predicts the modulus of both ATH and ATH-ATBN composites with reasonable accuracy.
- 3. ATH-filled compositions were found to approximate to the criterions for the application of linear elastic fracture mechanics. The fracture energy and fracture toughness are both increased by adding the filler. The fracture energy (G_{lc}) exhibited a maximum at a volume fraction of approximately 0.1. The addition of the rubber toughener increased this further but did not significantly alter the position of the maximum. The fracture toughness (K_{lc}) increases linearly with increasing ATH content. The results follow the prediction of Green when stable propagation was observed but there is some deviation at low volume fractions when the crack propagation was stick-slip. The theory of Green gives a penetrability value, r, of approximately 0.75. This correlates with the widely accepted view that ATH is a weak filler. It is proposed that the dominant toughening mechanism in ATH-filled epoxies is crack-pinning but that the contribution of crack-blunting at low volume fractions of filler increases.

- 4. The addition of ATH to a rubber modified matrix (10phr) initially reduced K_{kc} but as the volume fraction of the filler increased it recovered. The minimum occurred in the filler range of V_f =0.2 - 0.3. Large scale debonding was not observed, so, it is proposed that the increase in constraint on the epoxy resin, imposed by its adhesion to the filler's surface, interferes with the large scale yielding that the rubber otherwise enhances. The fracture toughness of the hybrid ATH-rubber filled composites was always higher than that of the ATHonly composites.
- 5. Large scale model experiments showed that the addition of a polymer coating on the particle could improve the tensile strength by two methods: (1) delaying fracture of the particle by modification of the stress transfer across the particle and (2) when particle fracture occurs, it blunts the crack.
- 6. Methods for applying a polymer coating were investigated. These included: spray drying, mechanical mixing, solvent deposition and in-situ polymerisation. Solvent deposition techniques caused large scale agglomeration of the filler. The mechanical work needed to break up the agglomerations caused cleavage of the filler particles, thereby destroying the coating. Mechanical mixing using a "Moritz" mixer produced a coating but the coating's thickness was limited to the amount of polymer that could be applied in one run. The spray drying method produced reasonably good coatings, but agglomerations were a problem. It was found that matching the particle sizes of the filler to the size of the atomisation droplets minimised the agglomerations. The most promising method was direct polymerisation of the polymer on to the filler's surface. Good coatings were formed if the surface of the filler was first treated with a reactive silane to promote reaction from the surface.

RECOMMENDATIONS FOR FURTHER WORK

The tensile and fracture properties of ATH-filled compositions have been investigated. It has been shown quite clearly that the addition of a reactive Hycar[®]-type rubber toughener improves the fracture resistance of the composite, but does not improve the tensile strength. In fact it reduces the strength further. The tensile strength of ATH-filled epoxies is the major concern with these materials. and should be the subject of further research. The addition of glass fibre to the matrix dramatically improves the strength of the composite, but the crack initiation potential arising from particle fracture of the weak ATH would necessitate a detailed study of the fatigue behaviour of ATH-filled laminates.

It has been shown that the ease of crack initiation in ATH-filled composites is the primary cause of reduced tensile strength. Very fine particle sizes could be used because they have a more regular shape and are stronger in themselves but problems associated with high viscosity mixtures would arise. The method that has been investigated in this study was the application of a rubber/polymer coating around the particles. This study identified the methods that could be used to apply this coating. These methods could be developed further to optimise the coating thickness and properties. Specifically using the spray drying or in-situ polymerisation routes to tailor the coating material directly or by building up a multi-layered coating, with a layer for toughness and an outer shell for adhesion to the host matrix.

The possible areas for further research are:

- 1. A study of the fatigue properties of ATH-filled glass fibre or carbon fibre laminates;
- 2. To study of the effect of ultra fine (sub-micron) particle sizes on the tensile strength and fracture properties;
- Optimisation of the polymer coating around the filler particles with the possibility of interfacial engineering by using a multi-layered coating morphology.

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APPENIDICES

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APPENDIX 1

RAW MATERIALS INFORMATION

1.1 PARTICULATE FILLERS

1.1.1 Alumina trihydrate

Alumina trihydrate (ATH) is a non-toxic, white crystalline powder which is insoluble in water. It is extracted from bauxite by the Bayer process of which it is an intermediate product.

There are a variety of different forms of ATH, all of which have the chemical formula, Al_2O_3 . $3H_2O$ (or $Al(OH)_3$). The ATH used in this study was gibbsite, which is gamma-alumina trihydrate. Its crystal structure consists of layers of $Al(OH)_3$, built up by the edge sharing of $Al(OH)_6$ octahedra to give a pair of approximately close packed OH layers with Al atoms in two thirds of the octahedral interstices. The OH groups on the under side of one layer rest directly above the OH groups of the layer below. ATH particles are made up of a series of hexagonal plates, loosely packed together, to give a particle with an approximate aspect ratio of 1. Above 200°C, ATH decomposes into alumina and water:

$2AI(OH)_3 \rightarrow AI_2O_3 + 3H_2O_3$

The two grades of ATH used in this study were FRF20 and FRF5 (ex Alcan Chemicals Ltd). These have mean particle sizes of 16µm and 86µm respectively. The other grade mentioned, ON920v, has a range of 1-70µm with a mean diameter of 15µm. ON920v was supplied by Croxton and Garry Ltd, Dorking, Surrey. Particle size distributions are shown in Figures 1 - 3. These were determined using a Malvern E laser diffractometer.



Figure 1 The particle size distribution of FRF20



Figure 2 The particle size distribution of FRF5



Figure 3
The particle size distribution of ON920V

Table 1							
General	General properties of some particulate fillers						

Property	Units	ATH	Silica	Glass Beads	
Einstein Coeff. (K _E)	η_{sp}/υ_{f}	6-10	4-5	2.5	
Thermal conductivity	$(cal/g.s.^{\circ}C)$ x10 ³	0.2	7	1.7	
Specific heat	cal/g.°C	0.19	0.19	0.27	
Coeff. thermal expansion	(linear unit/unit /°C)x10 ⁶	4-5	10	8.6	
Young's modulus	Kg/cm ² x10 ⁻⁶	3	3	6	
Poisson's ratio	dw/dl	0.3	0.3	0.23	
Hardness	Mohs	2	6.5-7	5	
Absolute	relative force	8	80	40	
Dielectric constant	$\epsilon = D/E$	7	4.3	5	
Density	g/cm ³	2.4-2.42	2.65	2.48	
Notes:	Data from reference 5				

1.1.2 Glass beads

Three types of glass beads were used in this study, a solid glass bead and two hollow beads. The solid bead (CP3000) was supplied by Croxton and Garry Ltd of Dorking but is a Potters-Ballotini product, marketed under the "Spheriglass" trade name. Hollow beads were obtained from Potters Industries and Croxton and Garry. These are marketed under the "Sphericel" and "Scotchlite" names respectively and have product codes of, 110P8 and B23/500 respectively. A glass flake was also used. This was supplied by Croxton and Garry as Microglas RCF-015(manufactured by Nippon Sheet Glass Company). A particle size analysis for the two spherical beads is shown in Figures 4 and 5. Table 2 shows a comparison of the measured particle size and the manufacturers' quoted sizes and Table 3 shows further technical data.



Figure 4 The particle size distribution of CP3000 glass beads

Table 2 Particle size comparisons for the glass fillers

D 17	Measured			М	lanufacturers' Da	ita
Bead Type	10%	50%	90%	10%	50%	90%
RCF-015	1.5	12.4	41.8	-	15	-
CP3000	0.9	8.4	33.4	-	12-26	~50
B23		-	-	-	60	
110P8	3.7	10.4	20.4	3.8	8.0	15
Notes:	B23 could not Mastersizer E	be measured. I (Courtesy of A	Particle size dete lean Chemicals	erminations mac Ltd).	de using a Malve	rn



Figure 5 The particle size distribution of hollow glass bubbles

Table 3General properties of the glass fillers

Property	RCF-015	B23	110P8	CP3000
Shape	Flake		Sphere	
Specific density (g/cm ³)	2.52	0.23	1.1	2.45-2.55
Composition	C glass			
Crush Strength (psi)	-	500	-	10,000*
Young's Modulus (GPa)	-		-	68.9
Poisson's Ratio	-	-	-	0.21
Notes:	After reference 41			

1.2 EPOXY RESIN

The epoxy resin system was Epikote[®] 816 (supplied by Stag Resins and Sealants, West Drayton). This consists of the following components:

(1)	Epikote® 828	85%
(2)	Cardura [®] E10	15%

Epikote[®] 828 is a diglycidyl ether of bisphenol-A and epichlorhydrin and has the structural formula:



Cardura[®] E10 is a glycidyl ester of a mixture of monocarboxylic acids having a mixture of branched C₁₀ isomers, and has the following structural formula:



The physical and structural properties of the components of Epikote[®] 816 are listed in Table 4 (page154).

 Table 4

 The properties of Epikote[®] 816 and its components

Component	Molar mass (g/mol)	Density @ 25°C (g/cm ³)	Epoxy group content (mmol/Kg)
Epikote [®] 828	364	1.16	5490
Epikote [®] 816	344	1.13	5130
Cardura [®] E10	228	0.96	4100

1.3 CURING AGENTS

Three curing agents were used: Epikure[®] T, piperidine and a bismaleimide. Epikure[®] T (supplied by Shell Chemicals U.K.) is a mixed primary, secondary and tertiary amine and has a density at 25°C of 1.14 g/cm³. It consists of the following components:

- (1) $HN-(CH_2CH_2NH_2)_2$ 30% w/w
- (2) $HO-CH_2CH_2N(CH_2CH_2NH_2)_2$ 70% w/w

Piperidine (obtained from Merck, Poole) is a heterocyclic secondary amine having the following structural formula:



The bismaleimide (supplied by Shell under the trade name Compimide[®] 353) is a eutectic mixture of the following constituents:



4,4 Bismaleimido diphenylmethane (55%)



These react via the double bonds on the imido end groups.

1.4 RUBBER TOUGHENERS

The amine terminated liquid reactive rubber used was Hycar[®] ATBN 1300×16 which was supplied by BF Goodrich Ltd. This is a random copolymer of butadiene and acrylonitrile and has the following schematic structural formula (which does not reflect the random distribution of butadiene units along the chain):



The carboxyl terminated rubber was CTBN 1300x8 the structure is:



The general properties of these rubbers are given in Table 5.

Property	CTBNx8	ATBNx16	
Molecular weight (g)	3.600	3,600	
Density (g/cm ³)	0.948	0.956	
Refractive index		1.5172	
Viscosity (mPa.s) @27°C	150,000	200,000	
Acrylonitrile content (%)	18	16	
Notes:	Data taken from suppliers literature		

Table 5General properties of the reactive rubbers

1.5 DISPERSING AGENT

The dispersing agent evaluated and used in the glass fibre laminates was Hypermer[®] FP4 (ex ICI) which is believed to be poly-hydroxy stearic acid. Analysis by EDX could not detect any halogens at the 1% detection limit of the instrument.

APPENDIX 2 SAMPLE CALCULATIONS

2.1 Void content

The void content of the specimens was expressed as the volume fraction of air required to lower the density calculated from the true ATH content (by ashing) to the true density of the casting, measured by a helium pycnometer. The void content must be related to the difference between the expected density and the true density. Any air in the specimen is at the expense of the matrix (because the ATH content has been measured by ashing). The void content can therfore be expressed as:

$$\rho_{calc} - \rho_{true} = Volume_{(air)} \times \rho_{(resin)} - Volume_{(air)} \times \rho_{(air)}$$
(2)

where: ρ_{calc} = expected density from measured ATH content ρ_{true} = density measured using the helium pycnometer and the volume of air is the void volume fraction

this can be rearranged to:

$$\rho_{(calc)} - \rho_{(true)} = volume_{(air)} \times \left(\rho_{(resin)} - \rho_{(air)}\right)$$
(3)

therefore the void volume can be calculated from:

volume (air) =
$$\frac{\left(\rho_{(calc)} - \rho_{(true)}\right)}{\left(\rho_{(resin)} - \rho_{(air)}\right)}$$
(4)

Example 1 - 20 phr ATH cured with Epikure® T

ATH content = 20.0

Expected density =	= 1.282 g/cm ³	Cured resin density =	1.1713 g/cm ³
True density =	1.2780 g/cm ³	Density of air @ 23°C =	5.83x10 ⁻⁵ g/cm ³

Void volume fraction =
$$\frac{1.282 - 1.2780}{1.1713 - 5.83 \times 10^{-5}}$$

Example	2 -	250	phr	ATH	cured	with	piperidine
---------	-----	-----	-----	-----	-------	------	------------

Į	oid volume fraction	=		
True density = 1.8360 g/cm^3		Density of air @ 23° C = 5.83×10^{-5} g/cm ³		
Expected density =	1.851 g/cm ³	Cured resin density = 1.1593 g/cm^3		
ATH content =	253.2			

= 0.0129

 $1.1593 - 5.83 \times 10^{-5}$

2.2 Crack-blunting/crack-pinning contributions

The relative contributions of crack-blunting and crack-pinning were determined as follows:

- The predictions of Green^a *et al* for particles with a rectangular cross section with break-away values of 0.5 and 1.0 were determined from figure 3 (of their paper).
- 2. An approximate prediction of the toughening effect for a break-away position of 0.75 were calculated. This was done by assuming linearity of the toughening effect between r=0.5 and r=1.0. i.e. r=0.75 lies half way between r=1.0 and r=0.5 at the same interparticle separation. This was done for 15 points on each curve. A polynomial curve fit was used to calculate the relative KIc for any value of r/c.
- 3. The contribution of crack-pinning is assumed to be the value predicted by Green *et al*, and therefore the contribution of crack-blunting is the difference between the measured value of KIc and the prediction of Green.
- For spherical particles, the same methodology was applied except that the predicted and actual values of K_k for Spanoudakis and Young^b were read off of Figure14 of their paper.

a DJ Green, PS Nicholson and JD Embury, J. Mater. Sci., 14, (1979), 1657.

b J Spanoudakis and RJ Young, J. Mater. Sci., 19, (1984), 473.

Example 1 - 20 phr ATH

r/c = 0.145 predicted relative KIc =1.4166

therefore:

$$crack - blunting = \frac{1.81 - 1.4166}{1.81} \times 100$$

= 21.73%

measured value of rel KIc = 1.81

r/c = 0.725 predicted relative KIc =2.21 measured value of rel KIc = 2.23

therefore:

$$crack - blunting = \frac{2.23 - 2.21}{2.23} \times 100$$

= 0.897 %

Example 3 - 0.392 V_f glass beads from Spanoudakis

r/c = 0.967 predicted relative Klc = 2.51 measured value of rel Klc = 2.63

therefore:

crack - blunting =
$$\frac{2.63 - 2.51}{2.63} \times 100$$

= 4.56%
APPENDIX 3

THERMOGRAVIMETRIC ANALYSIS GRAPHS

The TGA analysis of various samples was carried out using a Perkin-Elmer TGA7 system with computer control and analysis facilities. All specimens were run at a heating rate of 10°C per minute in air. The thermograms provided here were digitally scanned from the original traces









Figure 9 FRF20 coated with poly(vinyl acetate) latex by spray drying



Figure 10 FRF20 treated with A1100 silane (commercial material)



Figure 11 FRF5 coated with poly(methylmethacrylate) by in-situ polymerisation



Figure 12 Pure poly(vinyl acetate) latex film



Figure 13 Pure film of A1100 silane coupling agent



Figure 14 FRF5 treated with acrylic acid after 12 hours



Figure 15 FRF5 treated with acrylic acid after 5 days



Figure 16 FRF5 treated with acrylic acid after 2 months