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The cohesive mechanical properties of a toughened epoxy adhesive as a function of cure level

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Abstract

The cohesive performance of an epoxy adhesive as a function of cure applied is evaluated through the use of mechanical testing, thermal analysis and electron microscopy techniques. These material characterisation techniques allow a complete analysis of the reference material in terms of mechanical behaviour, surface topography and thermally induced events during cure. The effect of cure level within the adhesive was explored by examining all the material properties as a function of post cure duration and temperature. Post cure temperature and duration were both found to be directly proportional to the amount of curing reactions taking place within the system, with increases in post cure duration found to lower the temperature required to cure to a specific level. The mechanical properties of the adhesive varied as a function of post cure harshness with a number of mechanisms contributing to the strength during the post cure. The elastic modulus of the material was found to decrease with increases in post cure temperature, more so than with increases in post cure duration. Large increases in ductility were witnessed at certain post cure levels for each mode of loading. As curing levels are increased the glass transition temperature increases, until a point where the energy required to cause the transition then falls and the T_g is lowered. The morphology of the toughening phase has also been characterised with spherical elements ranging from approximately 0.06 to 0.75 μm, and inter-phase spacing also noted along with the distribution of the elements. Basic mechanical testing of the adhesives was carried out in the form of lap shear and T-peel testing upon mild steel substrates, the correlation with glass transition temperature being stronger in these modes.

Keywords: Epoxy/epoxides; Thermal analysis; Cure/hardening; Cohesive properties

1. Introduction

As the performance of bonded joints improves and expectations of bonding become higher, the requirement for high strength adhesives becomes greater than ever. This is fuelled partially by an increasing demand for composite structures, which naturally lend themselves to fastening techniques such as bonding. With correct process and application controls adhesive products can now exhibit extremely high bond strengths.

The mechanical strength of the adhesive in the bulk (or cohesive) mode is an important parameter in preventing unexpected failure of adhesive products. Failure in the cohesive mode is often promoted due to the very high bonding strengths that can be achieved with modern bonding techniques.

This work aims to evaluate the cohesive properties of a reference epoxy adhesive through the analysis of mechanical behaviour as a function of curing conditions. The ability to characterise and benchmark the cohesive performance of other adhesives is made possible by the creation of a 'portfolio' of tests, and as the performance of the material is increasingly understood, future improvements to formulations can be made. A brief series of traditional adhesive strength tests are also performed to augment the characterisation.

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1.1. Toughening of adhesives

The purpose of toughening a material is to increase its ductility and decrease the possibility of brittle fracture. Toughened adhesives are more resilient to the progress of cracks and resist the propagation of such flaws. Thermosetting materials such as epoxies are naturally brittle materials and the use of a toughening agent (or plasticiser) creates a material able to withstand impact and absorb more energy when loaded, hence improving the peel and shear performance.

Toughening differs from flexibilisation where an elastomer is completely soluble in the uncured and cured states. With toughening the elastomer may partially or fully 'phase out' to form insoluble particles (although they remain well bonded [1]) that are incompatible with the host resin matrix whilst flexibilisation can result in large increases in the extension to failure of the material [2]. Crack front pinning results when a crack front meets a number of toughening particles. The crack is forced to propagate around the particulates as they resist its progress. This creates a deformation in the crack and an increased level of energy is required by the crack to maintain progress. This mechanism can also cause particle de-bonding in severe cases, which helps to blunt the crack tip and increase the fracture toughness of the material. An increase in the energy required to maintain the propagation of the crack is seen here too which helps to improve the peel strength of the material [3]. In this research the main toughening agent is a reactive liquid polymer amine-terminated butadiene acrilonitrile material (Hycar$^{\mathrm{TM}}$ RLP ATBN). The morphology of this phase and its influence on the mechanical properties of the adhesive is highly dependent on the curing condition as noted by Hong [4] and also Chikhi [5].

The influence of the size and distribution of the phases upon the material properties has been examined; Shieu [6] argues that the ratio of inter-phase spacing to particle size is important for toughened glassy polymers and Chikhi et al. [5] found that properties can change significantly as a function of ATBN concentration. In that research it was found that the majority of mechanical properties deteriorate as the proportion of ATBN is increased. Elastic modulus, tensile strength and the glass transition temperature are all reported to decrease, but resistance to impact damage and shear strength are improved.

The contribution to mechanical strength from the ATBN phase has been examined [7] and was found to be highly dependent on the effect of cure temperature. Not only was the cure temperature noted to be important in the 'phase out' process but proper dispersion and segregation of the plasticiser throughout the epoxy matrix was also observed to be essential. Agglomeration therefore greatly reduces the effectiveness of the ATBN phase.

Initiation of crack tip deformation processes is found to occur through the translational motion of the entire crack front [8]. Plastic shear yielding is the mechanism by which the epoxy matrix experiences highly localised plastic flows which dissipate energy and occur more readily for a toughened epoxy system than an unmodified epoxy. As this region translates the rubber particles frequently debond or fracture causing small voids to cavitate [9]. Cavitation is a major mechanism of increasing the fracture energy of adhesives. Stress is further dissipated through the growth of such voids until ultimately coalescence occurs [1,6,5,10]. Crack bridging can occur as particles are stretched from their initial sites and the progress of the crack inhibited. Overall, however, brittle epoxies are resistant to global plastic deformation with only small amounts witnessed locally around the crack tip [11].

In house research has previously examined the effectiveness of various toughening agents, their optimal addition level and whether or not any synergistic effects between tougheners occur [12]. This work identified that polymer polyols could be used to increase toughening quite successfully. Although more commonly found in foams, these particles are finding increased usage in other applications. It has been shown that combining toughening phases with a range of sizes results in a synergistic contribution to some material properties [13]. The extent of this is dependent on the individual system and the curing conditions employed.

1.2. Influence of cure upon mechanical properties

The relationship between degree of conversion and mechanical properties is complicated by a number of factors:

- Degree of cross-linking and network interactions between polymer chains.

The amount of heat energy supplied and also the rate at which it is provided are determining factors of the degree of cross-linking that occurs within the polymeric molecular network; as the adhesive hardens it changes its physical form from a liquid material to an infusible, thermoset solid by a thermally induced chemical reaction. A material with low conversion has a network of cured, cross-linked polymer chains surrounded by uncured material, resulting in increased flexibility (Fig. 1). This effect is replicated when a non-stoichiometric mix ratio is used, resulting in excess hardener and an adhesive with a lower elastic modulus [14].

- Curing agent employed.

A major attraction of epoxy adhesives is that they can be used with a great number of curing agents, modifiers and additives. The curing agent used will affect the cured structure and the manner in which interactions or bonds are made. Therefore the wide number of curing agents allow for a wide range of cured properties. For example, polyamide curing agents are known to perform well when bonding oily substrates [15].

- Vitrification through curing below maximum T_g.

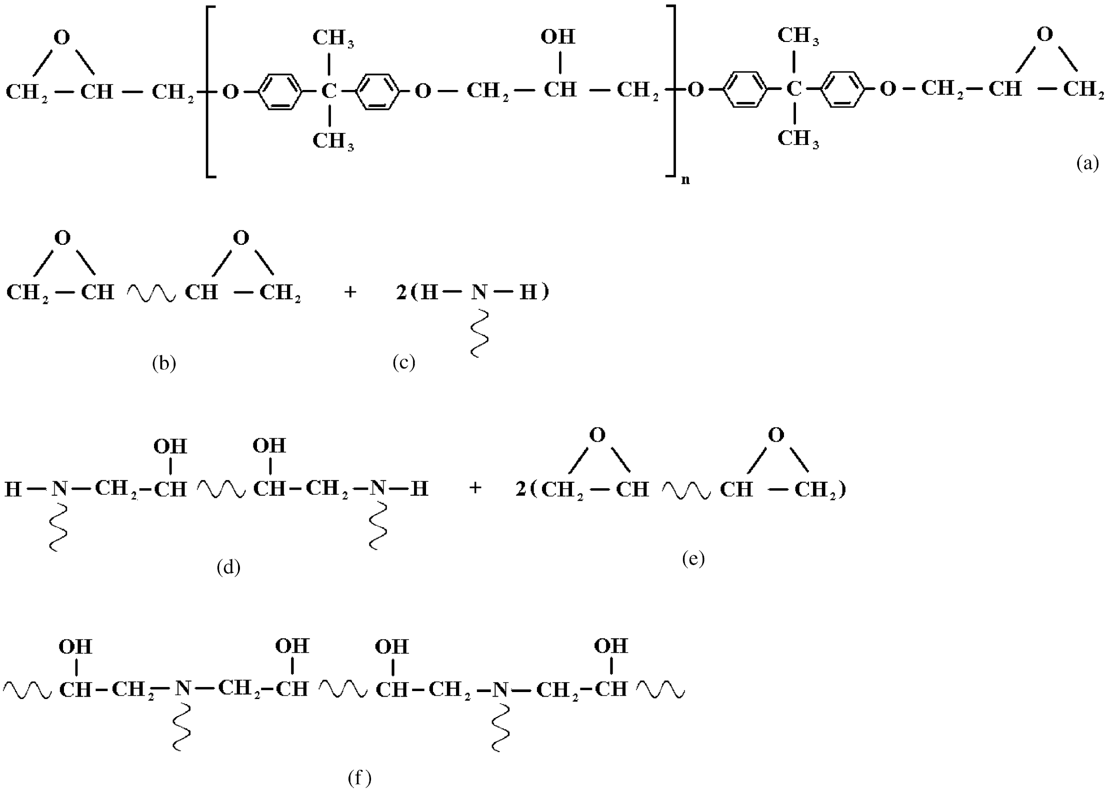


Fig. 1. Typical epoxy/amine hardening reaction: (a) DGEBA resin; (b) un-reacted resin; (c) terminal amine group; (d) partially cross-linked resin; (e) un-reacted resin; (f) fully cross-linked resin.

An effect witnessed by Ludbook [16] and later Lapique [17] occurs when the material is cured below the maximum glass transition temperature that it can achieve, and is manifested by an inhibition in the rate of curing. At its simplest the process known as 'vitrification' retards the rate of reaction through a decrease in molecular mobility. Lapique validates this by showing that longer periods of time are required to reach the conversion rates displayed at higher cure temperatures.

- Reactive liquid polymer and polymer polyol.

The phase out process of the toughening agent has been noted to be heavily dependent on cure temperature and time. As the epoxy resin matrix begins to cure, the reactive liquid polymer ATBN quickly becomes increasingly incompatible and starts to phase out into small inhomogeneities. The inclusion of the polyol phase complicates the microstructural behaviour of the material, but has been used previously with epoxy nanocomposites to successfully increase the impact performance by up to 160% [18].

2. Experimental

2.1. Material

Epoxy adhesives can demonstrate lap shear strengths up to 50 MPa at room temperature, with properties diminishing as service temperature is increased up to a maximum of approximately 200 °C [19]. Epoxies can be formulated to have excellent chemical resistance and have a low propensity for the absorption of moisture. Such materials are, however, inherently brittle with low elongations to fracture (approximately 1%) although increased fracture toughness and impact resistance can be achieved through the use of toughening agents. Epoxy adhesives have found such widespread use due to their ability to be readily modified by many different types of fillers, tougheners, flexibilisers, adhesion promoters, thixotropic agents and especially curing agents [1,20,21]. The ability to manufacture bespoke epoxy adhesives makes a wide range of potential properties available.

The adhesive to be analysed is a toughened two-part (Parts A and B) epoxy manufactured by Bondmaster (E3334). The Part A component comprises a blend of DGEBA and DGEBF resins primarily for viscosity control, whilst the Part B component contains a polyoxyalkyleneamine curing agent, a aliphatic polyamide curing agent and the ATBN toughening agent (a HYCAR$^{\mathrm{TM}}$ reactive liquid polymer). The resin component also contains a polymer polyol, a component usually found in foams where increased hardness, flexibility and lower density are required [22]. In this application the polyol acts with the liquid rubber ATBN phase to toughen the cured adhesive, which is manifested by a significant increase in peel strength.

2.2. Mechanical testing

A series of mechanical tests were performed in order to characterise the behaviour of the material. Tensile, compressive and flexural modes of loading were employed to evaluate the various strengths and moduli of the adhesive, the deformation behaviour was also observed. The cohesive mechanical tests performed and the relevant standards are listed in Table 1. All cohesive mechanical testing was performed on an Instron 1190 Series Tensometer, and where applicable a clip gauge extensometer was used.

Bulk mechanical test specimens were manufactured using a refined casting process in which an aluminium alloy mould was employed to create consistent, reproducible results. The rigid mould ensured dimensional stability whilst a silicone fluid release agent facilitated the removal of the test pieces after curing (see Fig. 2). Previous work has suggested that deleterious effects may result from using such a product [23] but questions the extent and depth of penetration. Others have discovered problems with void formation that can often blight the creation of bulk test specimens especially when using adhesive films [24]. Use of the spray was kept to a minimum throughout the program of testing to avoid any large scale plasticising. Tensile and flexural test pieces were created with the mould whilst compressive test specimens were sectioned from a cylindrical casting taken from a polypropylene syringe body (Fig. 2). Flexural test specimens were sectioned from the gauge length of the tensile ‘dog-bone’ specimens. Four tests were performed for each set of test parameters.

A series of bond strength experiments were also undertaken so that a correlation between bulk and joint behaviour as a function of cure level could be established. These experiments consisted of a lap shear test with degreased, grit blasted and degreased mild steel substrates (DGD condition) and T-peel aluminium alloy DGD substrates. Test pieces were cured under the same regime as the bulk test specimens (see Section 2.6) and experimentation was performed as dictated by BS ISO 4587:2003 (lap shear) and BS 5350-C12:1994/ISO 11339:1993 (T-peel). The T-peel test pieces had 200-μm diameter wire installed transverse to the loading axis in order to control the bond line thickness. This wire does not interfere as the test pieces are peeled open and any reduction in the load required to propagate a crack can be detected from the load-extension output trace. A Lloyd Instruments series LR 50-K tensometer was used with NEXYGEN test software to measure the shear and peel strengths and extension behaviour. Four tests were performed at each cure level and for each mode.

Table 1
Mechanical test standards

Mode	Property to be evaluated	Relevant standard
Cohesive	Tensile strength (UTS)	ISO EN 527-2:1996
	Tensile modulus	ISO EN 527-2:1996
	Compressive strength (yield)	BS EN ISO 604:1997
	Compressive elastic modulus	BS EN ISO 604:1997
	Flexural strength	BS EN ISO 178:2003
	Flexural modulus	BS EN ISO 178:2003
	Tensile strain at failure	ISO EN 527-2:1996
	Flexural strain at failure	BS EN ISO 178:2003
Adhesive	Lap shear strength	BS ISO 4587:2003
	T-peel strength	BS 5350-C12 1994 (ISO 11339:1993)

2.3. Thermal analysis

Differential scanning calorimetry (DSC) was used in order to further understand adhesive performance. This technique permitted the evaluation of glass transition temperatures (T_g) of the reference adhesive and a quantitative assessment of the state of cure. The test procedure for this technique involves the accurate dispensing (± 0.01 mg) of the adhesive into aluminium hermetic pans, which are crimped in a press to give a uniform contact between the constantan disc in the DSC and the pan, avoiding any discontinuities that may lead to anomalous heat flows. The reference adhesive was cured to the desired level by an isothermal run in the DSC. The material was then scanned with the temperature increasing from -50 to 200 °C at a heating rate of 20 °C/min. A TA Q1000 T-zero$^{\text{TM}}$ DSC machine was used throughout to perform the thermal analysis.

2.4. Degree of cure

Previous work has shown that this technique can be used to show that both time and temperature of the cure are directly proportional to the degree of cure [15,17,25] with conversion occurring more quickly as cure temperature is raised.

Polymeric materials can display significant changes in the heat capacity over a range of temperatures, the glass transition being the obvious step change, but with the gradual changes in the heat capacity present on the heat flow trace, analysis must be carefully made to appreciate the non-flat nature of polymer baselines. Again the DSC software provides several options for interpolating the baseline underneath the exotherm. The degree of cure for each cure level was calculated from the same scans run to evaluate glass transition temperatures.

2.5. Microscopy

Electron microscopy techniques were used to study the morphology of the sample adhesive, specifically upon flexural fracture surfaces in order to examine potential evidence on the mechanism and nature of failure. This permitted characterisation of a number of phases within the reference material. A scanning electron microscope manufactured by JEOL was used throughout this work

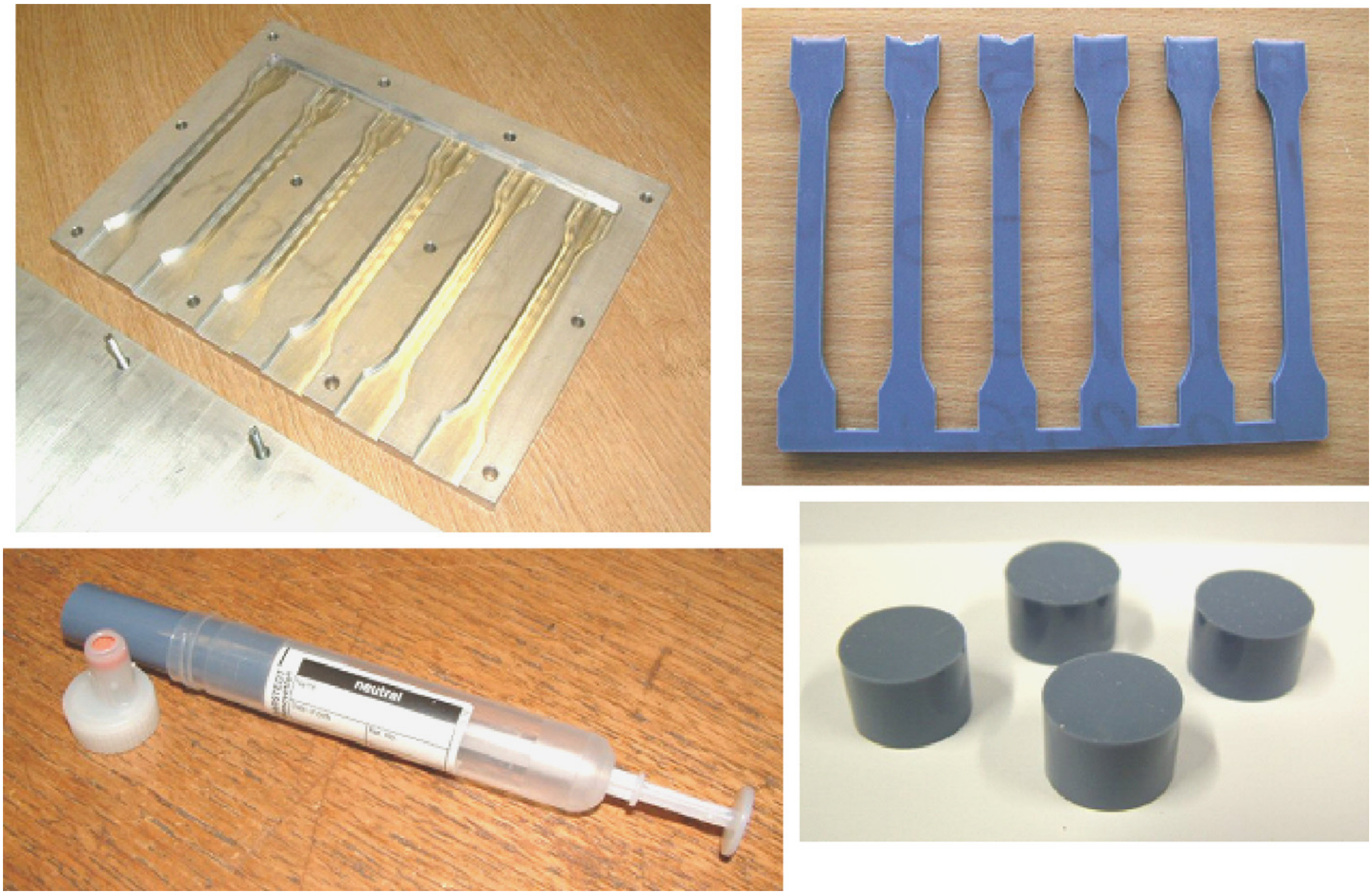


Fig. 2. Compressive and tensile test pieces.

(JEOL SEM—5910). A gold sputtering machine was used to deposit a conductive layer ($\sim$0.1 μm [26]) upon the surface of the electrically non-conductive polymer adhesive.

2.6. *Cure levels used in experimentation*

The adhesive material tested was cured at ambient temperature for 24 h and then subjected to one of nine possible post cures, from three durations ($\frac{1}{2}$, 2 and 4 h) and three temperatures (40, 60 and 90 °C). These permutations were designed so that 'undercooked' and 'overcooked' states existed about the manufacturer's current recommendation. As the test pieces are placed in the oven, a period of time has to pass before the test pieces reach the desired temperature. This time varies with the dimensions of the test piece and also with the nature of the fixture used to hold the test pieces in place. An aluminium mould acts as a bigger heat sink than a small lap shear test piece for example. The difference has been assessed and quantified in previous studies [16], with lap shear test pieces taking approximately 5 min to equilibrate to 200 °C. For complete accuracy the parameter 'stoving time' should be used; however, convention will be followed here and the standard term of 'curing time' will be used in this work. As the conditions were identical for each batch of test pieces in this work, the effect shall not be quantified further.

3. Results

3.1. *Thermal analysis*

The values of T_g for the cured material are shown in Fig. 3(a, b). The glass transition of a cross-linking thermosetting material will rise as the cure level is increased in both duration and temperature; as more thermal energy is supplied to the system more curing reactions can take place more frequently and a higher degree of cross-linking within the network can occur. This rigid, more tightly knit molecular network requires more energy to permit chain motion and as such an increased glass transition temperature is manifested.

Fig. 3 clearly shows that as the temperature of the post cure increases, the rate at which the glass transition increases begins to retard, and for cures of 2 and 4 h durations T_g actually begins to decrease. This suggests a mechanism has allowed the network to become more freely mobile, whereas at lower temperature cures the structure is more rigid. This is potential evidence of thermal

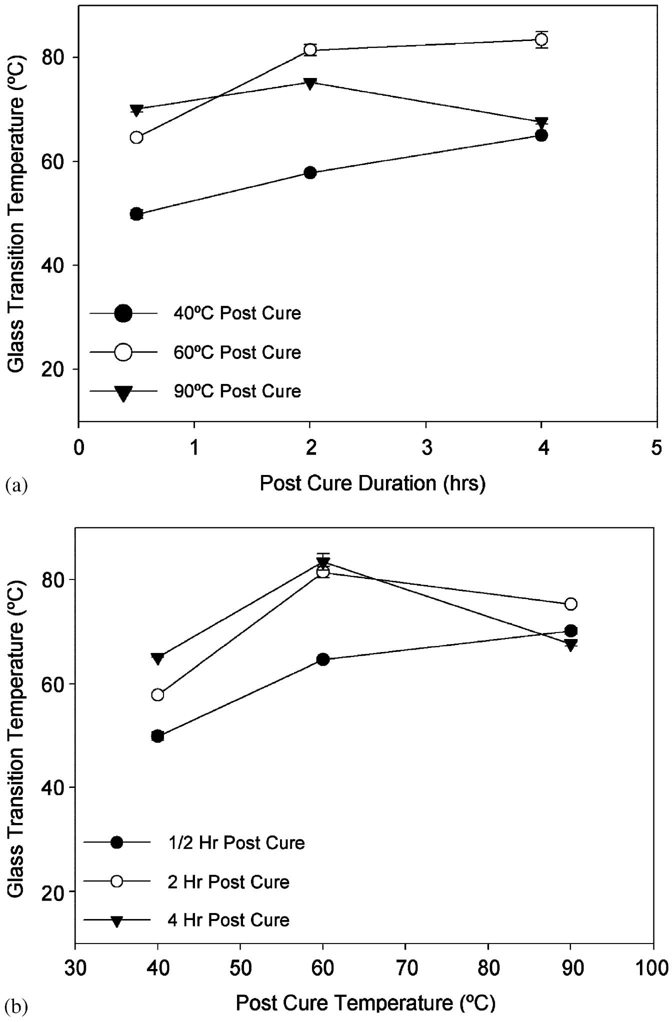


Fig. 3. Thermal analysis—glass transition temperature.

degradation that may occur at the more extreme cure levels. The exothermic curing reactions occur as the polymer chains start to cross-link and chain mobility reduces, which is activated more aggressively at the higher temperatures. The process was noted to be more dependent on the temperature of the post cure than it was upon the duration, as at lower temperatures a 'residual' amount of curing remained past the time at which for higher temperatures the net heat flow had approached zero. This is to say that at greater post cure temperatures, the material cures more fully and more quickly.

3.2. Degree of conversion

The degree of cure within the material is raised more through increases in curing temperature than by increases in cure duration (Fig. 4(a, b)). It can be seen that for all the durations of post cure, a similar conversion rate is seen for each cure temperature. Fig. 4(a) shows that material post cured at 90 °C reaches a conversion rate of 99% after just 30 min, with a 4 h cure at the same temperature providing only a 0.6% increase in the level of conversion. A similar effect is seen for both the 60 and 40 °C cure levels, with conversion rates steady at approximately 96% and 90%, respectively. This result suggests that for this room temperature curing epoxy, a large proportion of full conversion could potentially be reached after just 24 h at ambient temperature.

It is important to realise that material plasticity is influenced by both changes to the toughening phase and an elevated or decreased glass transition temperature, which itself is a function of the degree of conversion. More intense curing regimes ensure a more complete phase out of the toughening agent (increased plasticity) whilst also ensuring a high degree of cross-linking (increased brittleness). This inverse proportionality can cloud the analysis and should be appreciated.

3.3. Bulk mechanical testing

The flexural and tensile strengths correlate well as both modes display similar behaviour over the post cure

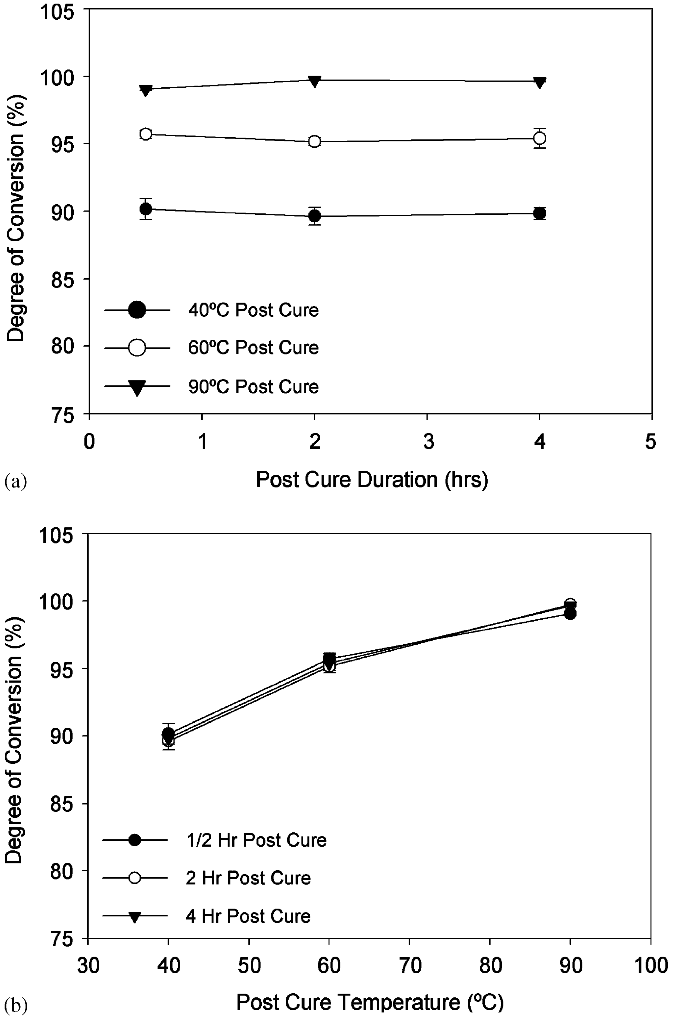


Fig. 4. Thermal analysis—degree of conversion.

schedules (Fig. 5). Strength decreases and then rises as curing temperature is increased for 30-min post cures, the strength increases slowly with temperature for all 2 h cures and for 4 h post cures the material strength increases and falls as curing temperature is increased. Compressive properties are less susceptible to variation in post cure duration but are significantly affected by higher temperature curing. All 90 °C post cures significantly decrease the strength of the material (approximately 20%) for all post cure durations. In tension strengths are developed of approximately 20–30 MPa whilst 50–65 MPa is developed in flexion and compression.

Elastic modulus of the material generally decreases as the post cure temperature is increased (Fig. 6). The reduced values of stiffness concur with the retardation in the rate of increase of the glass transitions witnessed at elevated post cure temperatures (Fig. 3).

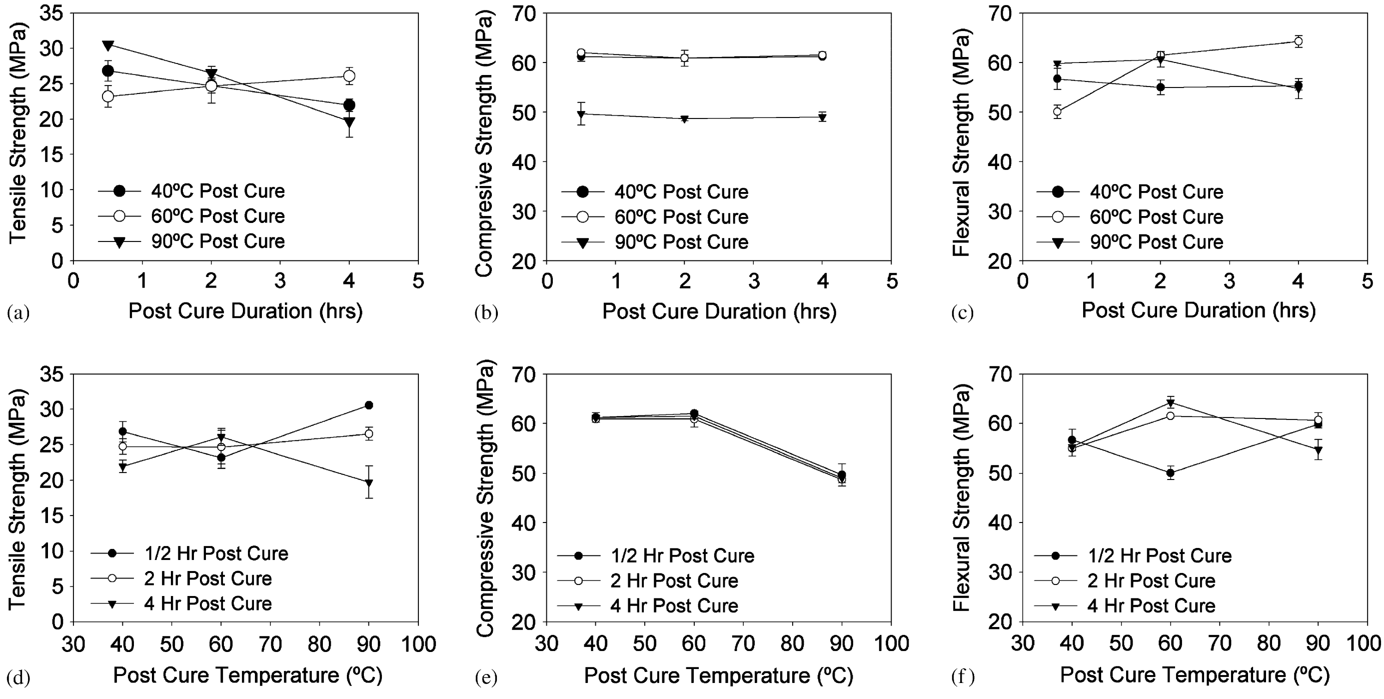
From Fig. 7 it can be seen that the material generally displays increased elongation at failure as the curing temperature is increased. This suggests greater ductility when cured at higher temperatures, which is in agreement with the results from the elastic modulus tests. The reduced level of brittleness may also be attributable to the complete phase out of the toughening agents.

It can be suggested therefore that the adhesive material has a less rigid molecular structure when cured at higher post cure temperatures, this manifests itself by a reduced T_g, decreased elastic moduli for all modes of loading and increased levels of ductility with greater elongations to failure. However, the fact that material strength has no simple correlation with the glass transition temperatures (and hence indirectly the level of chain network rigidity) suggests that there are other microstructural features or mechanisms acting to affect the material properties.

3.4. Mechanical testing of joints

Evidence of a correlation between the glass transition temperature of the adhesive and the lap shear strength can be seen in Figs. 3 and 8. For all post cure durations the material is weakened in lap shear strength when cured at 60 °C, and at this temperature (for each duration of cure except at $\frac{1}{2}$ h) the material has the highest T_g. This suggests that the material must display a degree of elevated chain mobility (although not the extreme level at 40 °C) in order for high lap shear strengths to be achievable. It is important to emphasise here that the strength of a joint is dependent on both the cohesive strength of the material and the bond strength to the substrate. The effect of the variation in T_g upon the adhesion forces, be they adsorption, diffusion or otherwise, will not be examined here; however, in our efforts to analyse the relationship between cohesive and adhesive behaviour it must be remembered that contributions to strength are made from different sources in each mode.

The T-peel test results are shown in Fig. 8(c, d). It can be seen that the material cured at 90 °C is the strongest for all cure durations. For all cure durations (except $\frac{1}{2}$ h) a decrease in strength is seen with material cured at 60 °C, as with lap shear performance for all durations. The performance of adhesives in peel can be increased significantly when a toughening agent is employed and for the highest temperature cure levels in this research the material displays very good peel performance (~7 N/mm).



(a) (b) (c)

(d) (e) (f)

Fig. 5. Mechanical properties—strength.

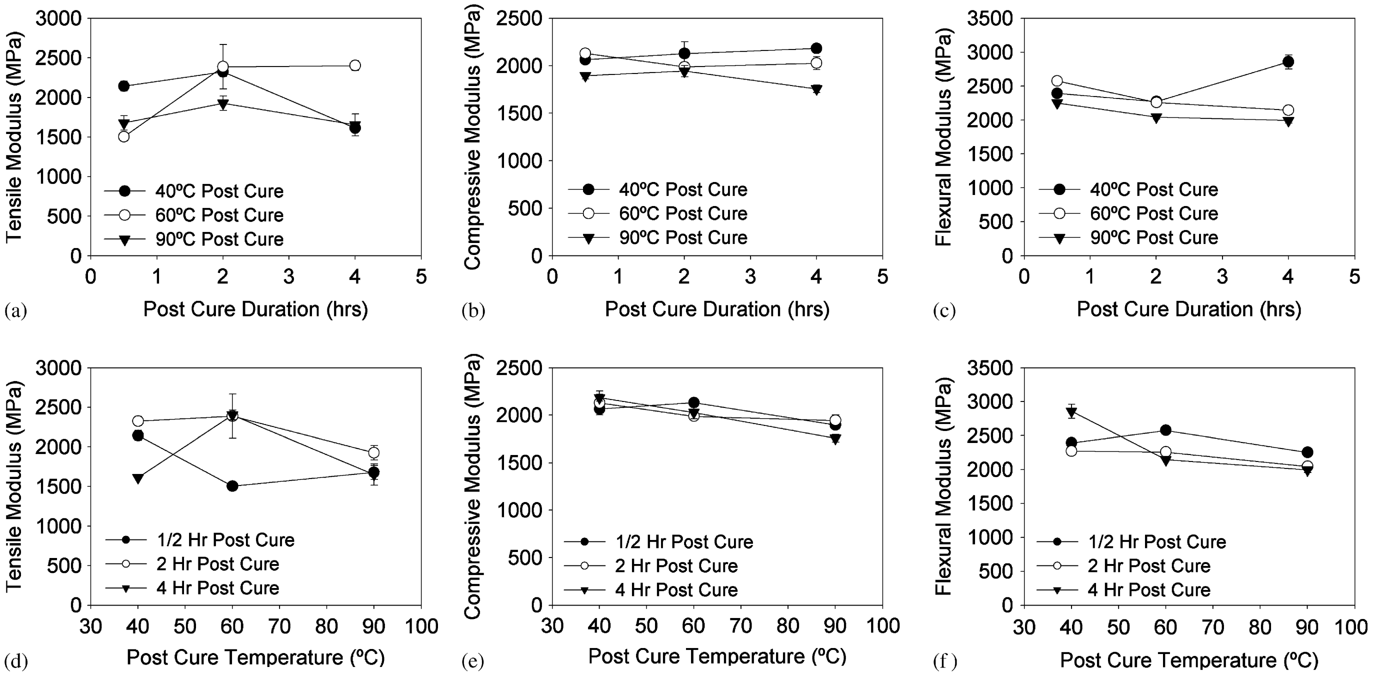


Fig. 6. Mechanical properties—elastic modulus.

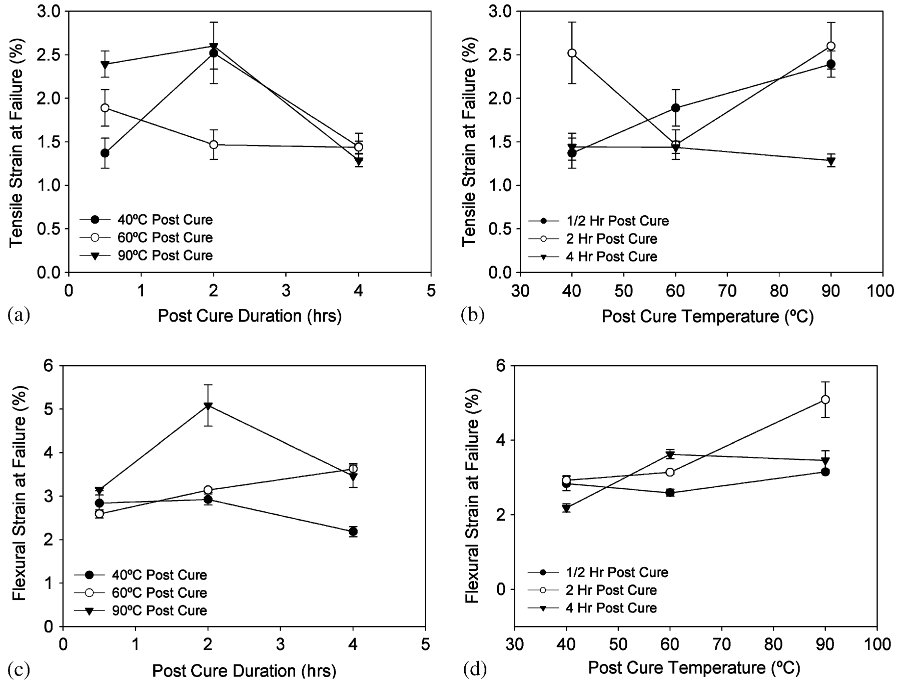


Fig. 7. Mechanical properties—strain and elongation.

This suggests that the plasticiser is completely phased-out and operating efficiently for material subjected to 90 °C cures which correlates well with the glass transition temperature experiments in which material cured at 90 °C displayed a lower T_g. The plasticiser works to promote the onset of the transition, and expressed simply for this system, a higher volume of non-agglomerated plasticiser causes a lower T_g and an increased peel performance.

3.5. Microscopy

Scanning electron microscopy techniques were used to examine fracture surfaces to establish if any mechanisms of failure were promoted or hindered as a function of cure level. Failed flexural surfaces were analysed as compressive and tensile loading modes occur through such a cross-section. Table 2 shows images of material cured at all cure

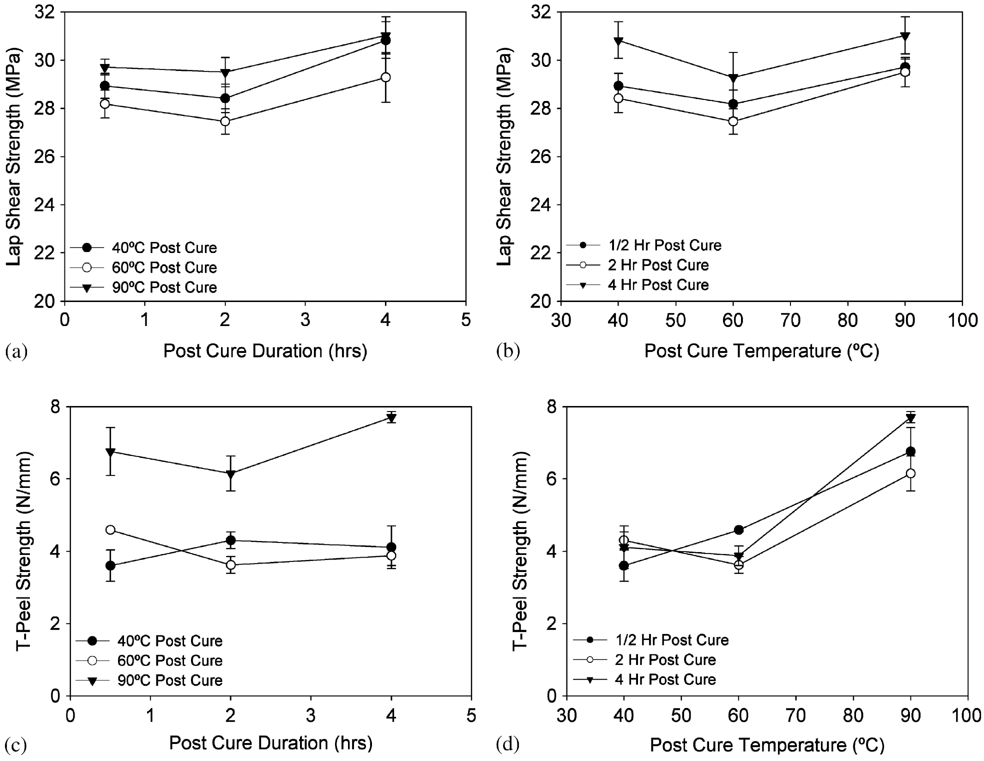


Fig. 8. Mechanical properties—adhesive tests.

levels, accompanied by the cohesive data generated during this research. Quantification of toughener morphology was made possible and Fig. 9 illustrates the distribution of the main plasticiser phase (ATBN phase: 375–750 nm diameter) and also the smaller polymer polyol particles (60–125 nm diameter). The colours have been inverted to illustrate the cavitated particles. The inter-particle spacing is also apparent from Fig. 9 and it can be seen that the polyol phase is more densely populated than the larger less frequently occurring ATBN particles.

No significant evidence of typical compressive and tensile loading traits were detected across the fracture surfaces in the experimental examinations. The SEM techniques used were, however, successful at identifying phases within the epoxy matrix and will be used in the future to evaluate the progress of the 'phase out' process in more detail.

3.6. Discussion and conclusion

The performance of the material in a number of modes has been measured and analysed. The influence of the toughener has been demonstrated through the peel tests and the DSC glass transition measurements. As cure temperature is increased up to 90 °C the plasticiser fully phases-out and acts to lower the glass transition and increase the energy required to cause fracture in peel. The elastic modulus measurements and the strain at failure tests show that as cure temperature increases material stiffness is reduced whilst elongation rises.

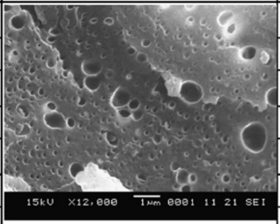
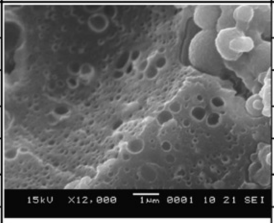
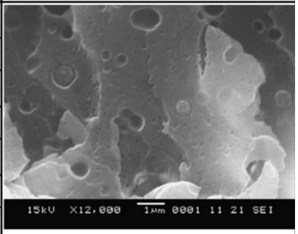
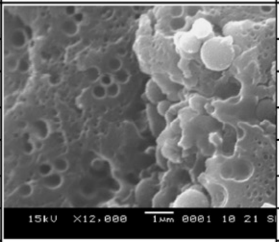
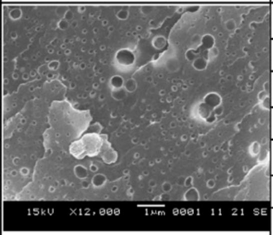
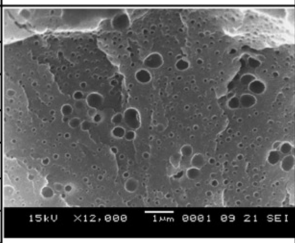
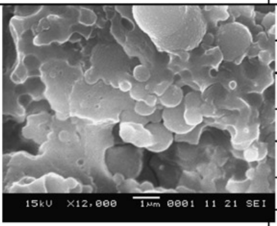
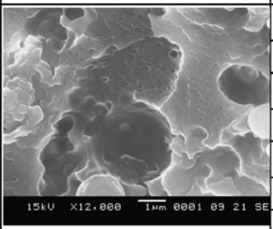
The behaviour of cohesive strength of the material in both flexural and tensile modes is somewhat erratic. Perhaps this is an indication of the problems with creating flaw free test pieces, as during the compressive testing a lower yield strength was seen for material cured at 90 °C (as compressive loading naturally 'closes' cracks around flaws, and failure would be less susceptible to defects). This correlates well with the demonstration of full plasticiser phase out shown through the T-peel and T_g experiments.

The relationship between rigidity on a molecular scale and glass transition is a function of the degree of cross-linking with the toughening phase acting on a larger structural scale. Increased chain stiffness requires a higher energy input to make the polymer chains more freely mobile, with a greater glass transition.

A low glass transition temperature therefore corresponds to a polymer with low molecular scale stiffness and this is borne out by the correlation between lower elastic modulus and reduced glass transition temperatures.

As an indicator of mechanical performance the degree of conversion figure is at best limited, as two very different cure schedules can produce material with identical conversion figures but with diverse microstructural features resulting in dissimilar mechanical performance. This reinforces the findings of Lapique and also Ludbook [15,16], where vitrification at low temperatures makes more complete curing dependent on increased cure durations, and the that heating rates during cure are important as the adhesive is cured through both the gel point and the vitrification. The fact that duration is not greatly influential

Table 2
SEM images plus data—all values are stated in MPa except T_g (°C)

Cure temp	Prop.	Val.	Cure duration = $\frac{1}{2}$ hr	Prop.	Val.	Cure duration = 2 hr	Prop.	Val.	Cure duration = 4 hrs
40 °C	σ_{UTS}	26.85		σ_{UTS}	24.74		σ_{UTS}	21.96	
	E_T	2143		E_T	2324		E_T	1312	
	$\sigma_{C.y}$	61.2		$\sigma_{C.y}$	60.8		$\sigma_{C.y}$	61.2	
	E_C	2065		E_C	2128		E_C	2183	
	σ_{flex}	56.7		σ_{flex}	55		σ_{flex}	55.3	
	E_{flex}	2393		E_{flex}	2273		E_{flex}	2857	
	T_G	49.9		T_G	57.8		T_G	65	
60 °C	σ_{UTS}	23.19		σ_{UTS}	24.65		σ_{UTS}	26.09	
	E_T	1503		E_T	2387		E_T	2402	
	$\sigma_{C.y}$	62		$\sigma_{C.y}$	60.8		$\sigma_{C.y}$	61.5	
	E_C	2130		E_C	1987		E_C	2028	
	σ_{flex}	50		σ_{flex}	61.5		σ_{flex}	64.25	
	E_{flex}	2575		E_{flex}	2259		E_{flex}	2145	
	T_G	64.6		T_G	81.4		T_G	83.4	
90 °C	σ_{UTS}	30.57		σ_{UTS}	26.52		σ_{UTS}	19.72	
	E_T	1678		E_T	1927		E_T	1651	
	$\sigma_{C.y}$	49.6		$\sigma_{C.y}$	48.7		$\sigma_{C.y}$	49	
	E_C	1896		E_C	1944		E_C	1757	
	σ_{flex}	59.9		σ_{flex}	60.7		σ_{flex}	54.7	
	E_{flex}	2252		E_{flex}	2044		E_{flex}	1994	
	T_G	70.1		T_G	75.3		T_G	67.6	

Units: σ_{UTS}, E_T, $\sigma_{C.y}$, E_C σ_{flex}, E_{flex} in MPa and T_G in °C.

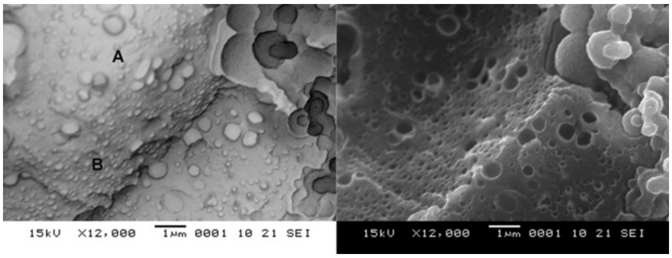


Fig. 9. SEM images of failed flexural surfaces. Picture on left is negative of right, giving representation of particles from cavitated sites. Point A illustrates area rich in larger ATBN toughening phases (375–750 nm diameter) whilst point B shows the smaller polymer polyol phases (60–120 nm diameter).

on the degree of conversion figure over the ranges used in these experiments is significant but it is important to clarify that different cure schedules cause the material to display dissimilar mechanical performance, even when conversion rates are identical.

Bulk compressive strength, lap shear strength and elastic modulus are all reduced when the material is cured at 90 °C. This is similar to previous work where mechanical properties were seen to fall with increases in toughener content; the complete, efficient phase out of the toughener (added to all material at a constant content of approximately 10%) also reduces a number of the mechanical properties. This work demonstrates that it is not merely the plasticiser content that dictates the mechanical performance but also that the morphology of the plasticising agent has a potentially high effect upon the cured properties, which itself is related to the severity of cure. The performance of a toughened adhesive therefore is a function of not only the proportion of toughener employed, but also how completely it has phased out and the resultant morphology.

Great benefits in toughening an adhesive are seen when joints are to be subjected to peel forces. A caveat exists, however, and the reduction in other properties created by the addition of plasticiser must not be ignored. The trade-off between various properties must be appreciated when tailoring a structural adhesive specifically when selecting a cure regime, as material properties can vary on average by 60% (with this system) between the minimum and maximum values. This makes the degree of cure a vitally important consideration in the use of structural epoxy adhesive.

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