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Rubber toughening of practical tetraglycidyl methylenedianiline–piperidine adduct systems

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The inherent brittleness of tetraglycidyl methylenedianiline (TGMDA) based epoxy formulations can be mitigated by the addition of carboxyl-terminated butadiene-nitrile rubbers (CTBNs) if piperidine is used as the curing agent. The problems of toxicity, reactivity and volatility associated with this reagent are overcome by using it in a 'latent' form, as an amino alcohol or urea, after reacting it with a suitable epoxide or isocyanate. The fracture properties, measured by the critical strain energy release rate (G_{Ic}) and the critical stress intensity factor (K_{Ic}), of the new materials were compared to those of the TGMDA-diaminodiphenylsulfone (DDS) system. The best systems gave G_{Ic} values up to 5.5 times those of the standard TGMDA-DDS formulation, while the addition of CTBN further increased this to up to 24 times; in comparison, addition of CTBN to the base formulation effected a threefold increase in G_{Ic}; there is however some lowering of the glass transition temperature and modulus of the modified resins. The morphology of the rubber-toughened materials, their reactivity, latency and water uptake are discussed.

(Keywords: TGMDA; piperidine; rubber toughening)

INTRODUCTION

Use of epoxy resins in the aerospace industry in both secondary and primary structures is increasing. They are used in adhesive formulations and as a matrix for composite systems. Where operational requirements call for high service temperature and the best attainable mechanical properties, particularly in carbon-fibre-reinforced systems, the combination of tetraglycidyl methylenedianiline (TGMDA) resin and diaminodiphenylsulfone (DDS) curing agent in the form of a prepreg has been universally accepted. (Current commercial systems may also include minor amounts of other epoxy resins, to modify certain properties.)

Experience gained from the TGMDA–DDS system has highlighted a number of shortcomings, and perhaps the most serious is its inherently brittle nature. Other concerns relate to the extent of moisture uptake and the resulting depression of the glass transition temperature (T_g).

One way of toughening epoxy resins is by incorporating a discontinuous rubbery phase[1]. Maximum toughening usually occurs if the rubber is present as discrete particles roughly 0.5 to 5 μm in diameter and has functional groups that permit it to form covalent bonds at the rubber–epoxy interface. Significant increases in peel strength, impact properties and fracture toughness have been achieved without serious loss in tensile and thermal properties. The usual way of forming such a system needs a rubber that is initially compatible with the resin but precipitates from the matrix during the cure.

The majority of commercial epoxy formulations are based on the diglycidyl ether of bisphenol A (DGEBA) and the toughness of these resins can be significantly increased by the addition of 5 to 20% by weight of a suitable chemically modified elastomer, usually a carboxyl-terminated butadiene–acrylonitrile rubber (CTBN). Thus studies on improving toughness have been confined mostly to these resin systems, with emphasis on varying the type and concentration of hardener, the initial molecular weight of the resin, the conditions of cure and the amount and nitrile content of the CTBN[2–7]. Elastomer-modified DGEBA-based resins are used extensively in the aerospace industry, particularly in structural applications, when service temperatures do not exceed approximately 120°C.

Although not of commercial importance, materials based on DGEBA and piperidine have been very extensively studied[8,9]. This system can be effectively toughened by the addition of small amounts of CTBN, and large improvements in fracture toughness have been recorded without significant trade-offs in other critical properties. In contrast to the results achieved with DGEBA, attempts at rubber toughening TGMDA, particularly when used with DDS, have resulted in relatively minor improvements in a system with an initially low fracture toughness[10–12].

The aim of this investigation was thus to produce a cured TGMDA system of substantially greater fracture

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toughness without significantly compromising T_g and with minimal modification of key mechanical properties. In addition, usable systems need the same degree of latency, i.e. thermal stability before cure, as current TGMDA–DDS formulations. Our approach has been to study the properties of systems of TGMDA, piperidine and CTBN, a combination not hitherto reported (apart from our preliminary communication[13]). Since piperidine itself is volatile, odorous, toxic and reactive at ambient temperature, we have used derivatives of the curing agent that are non-volatile and relatively inert at room temperature. Related curing agents, such as heterocyclic nitrogen compounds and alkyl-substituted piperidines, were tested to explore the possibility that piperidine and its reactive derivatives have a specific reactivity as curing agents for TGMDA. This report is inevitably incomplete in that the highway has precedence over the by-way, no matter how interesting.

EXPERIMENTAL

Materials

The epoxy resins used in this study, DGEBA and TGMDA, were supplied as Shell Epon 828 and Ciba-Geigy MY720 or MY721 (higher purity), respectively.

Phenyl glycidyl ether (PGE) was obtained from ICI Chemicals; piperidine, *N*-ethylpiperidine, morpholine, phenyl isocyanate and di-n-butylamine from BDH Chemicals Australia Pty Ltd; diaminodiphenylsulfone (DDS) from Koch-Light; 3-(*p*-chlorophenyl)-1,1-dimethylurea (Monuron) from Pfaltz and Bauer Inc., 4-methylpiperidine and piperazine from E. Merck; pyrrolidine from Ajax Chemicals Ltd, ETP (a commercial hardener—see later) from Anchor Chemical Australia Pty Ltd; and 1,4-phenylene diisocyanate and toluene 2,4-diisocyanate from Aldrich Chemical Company Ltd.

The CTBNs were B. F. Goodrich products, 'Hycar' carboxyl-terminated acrylonitrile–butadiene liquid elastomers, types X-8, X-13, X-15 and X-18 containing 17, 27, 10 and 20.5% acrylonitrile, respectively[14].

All materials listed were used without further purification.

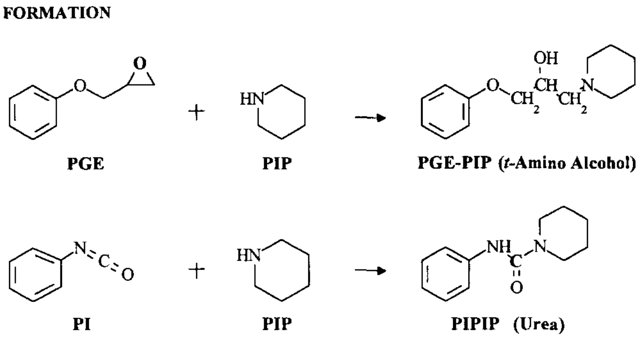
Synthesis of reactive amine derivatives—'adducts'

In the interests of simplicity and readability, the reactive amine derivatives and products are referred to as 'adducts' in the text. The reactions, reactants and relevant abbreviations are shown in *Figure 1.*

Piperidine–epoxy adducts. These various adducts were prepared in the following ways.

Phenyl glycidyl ether–piperidine adduct. (PGE–PIP) was prepared by stirring a mixture of phenyl glycidyl ether (67 g, 0.5 mol) and piperidine (42.5 g, 0.5 mol) at ambient temperature for about 18 h with slight cooling to control the exotherm. The resulting white solid was recrystallized from aqueous ethanol; yield 88 g (80%), m.p. 53°C.

Diglycidyl ether of bisphenol A–piperidine adduct. (DGEBA–PIP) was obtained by stirring a mixture of DGEBA (114 g, 0.3 mol) and piperidine (51 g, 0.6 mol) at 50°C with cooling until the exotherm had subsided (1 h). After standing overnight, the product was warmed to 100°C to ensure complete reaction, stored under refrigeration and used without further purification.



REAGENTS

Amines	
Piperidine	PIP
4-Methyl Piperidine	4-MePIP
Piperazine	PIPAZ
Morpholine	
Di-n-Butylamine	
Pyrrolidine	PYRR
Epoxides	
Phenyl Glycidyl Ether	PGE
Diglycidyl Ether of Bis-Phenol A	DGEBA
Tetragylycidyl Methylene Dianiline	TGMDA
Isocyanates	
Phenyl isocyanate	PI
Toluene Di-isocyanate	TDI
Phenyl Di-Isocyanate	DIPI

Figure 1 Piperidine and related adducts; components and formation

Tetraglycidyl methylenedianiline–piperidine adduct. (TGMDA–PIP) was prepared in the same way as DGEBA–PIP from MY720 (88 g, 0.2 mol) and piperidine (68 g, 0.8 mol).

Adducts from the reaction of amines and isocyanates. These substituted ureas were prepared by methods based on that of Henry and Dehn[15].

Phenyl isocyanate–piperidine adduct. (PIPIP) was prepared by adding phenyl isocyanate (50 ml, 0.46 mol) dropwise over 30 min to a stirred solution of piperidine (45 g, 0.53 mol) in dry benzene (500 ml) maintained at 20–25°C by slight cooling. The mixture was stirred for 1 h at 20°C, and the white precipitate filtered, washed with benzene and dried at 60°C to yield 88 g (94%) of crude product; m.p. 170–171°C, after recrystallization from ethanol.

Phenyl isocyanate–pyrrolidine adduct. (PIPYRR), 89% cured yield, m.p. 125–126.5°C after recrystallization from ethanol.

Phenyl isocyanate–4-methylpiperidine adduct. (PI4MePIP), 70% crude yield, m.p. 113°C after recrystallization from ethanol.

Phenyl isocyanate–piperazine adduct. (PIPAZ), 86% crude yield, no melting point, used without further purification owing to lack of solubility.

Phenyl isocyanate–di-n-butylamine adduct. (PI–dibutylamine), 67% yield after recrystallization from hexane, m.p. 77–79°C.

1,4-Phenylene diisocyanate–piperidine adduct. (DIPIPIP), 78% crude yield, no melting point, used without purification due to lack of solubility.

2,4-Toluene diisocyanate–piperidine adduct. (TDIPIP), 97% crude yield, m.p. 216–217°C after recrystallization from ethanol.

TGMDA–CTBN pre-reacts. The pre-react was obtained by heating a stirred mixture comprising 100 parts TGMDA and 50 parts CTBN at 50°C until full reaction had occurred, i.e. the carboxyl content was negligible (5 h). TGMDA is more reactive than DGEBA and does not need a catalyst to form the TGMDA pre-react.

Preparation of cast resin panels

DGEBA–piperidine combinations were mixed thoroughly, warmed to about 50°C, carefully vacuum degassed and then poured into closed metal moulds that had been coated with a non-silicone release agent and preheated to 50°C. Cure cycle was 16 h at 120°C.

For TGMDA–DDS mixtures, the ingredients were stirred in a Buchner flask maintained at 135°C until the DDS was dissolved. After a thorough degassing the mixture was poured into a coated, closed mould. Cure cycle was 1.5 h at 135°C followed by 2 h at 175°C.

For TGMDA–piperidine systems, TGMDA and CTBN (or the equivalent mixture of TGMDA and prereact) were mixed at 80°C, vacuum degassed and then the piperidine was added using a slow swirling action to minimize air entrapment and loss of amine. The mixture was then poured into an open silicone rubber mould and cured in a laboratory oven. Flat specimens were obtained by careful milling.

The TGMDA–adduct formulations were mixed in a round-bottomed flask, thoroughly outgassed at 100°C using a vacuum rotary evaporator, poured into coated, closed moulds and oven cured.

The selection of appropriate cure cycles for the TGMDA–piperidine and adduct mixtures by thermal analysis is discussed later.

Thermal analysis

A DuPont 1090 Thermal Analysis System, comprising 910 DSC cell, and appropriately modified 941 Thermomechanical Analyzer and 950 Thermogravimetric Balance, was used in conjunction with standard DuPont software for curve analysis. Unless otherwise stated, the thermomechanical analysis (t.m.a.) curves were obtained from samples 2–4 mm thick, heated at 5°C min^{-1} with the hemispherical probe (2.54 mm diameter) under load (10 g). Generally it was desirable to use expansion curves obtained when the sample was reheated after it had been cooled in the instrument from above the transition with the probe in position. Where continuing cure rendered this method impracticable, the maximum in the derivative t.m.a. curve (corresponding to penetration or softening at the end of the transition) was found to be the most consistent temperature for characterization of T_g. In differential scanning calorimetry (d.s.c.) experiments, samples of resin mix (6–12 mg) were heated in open aluminium pans to simulate open mould cure, and in some cases 'hermetic' pans were used to limit loss of volatiles during cure. In isothermal studies the cell was preheated. Thermogravimetry (t.g.) experiments were intended to reproduce corresponding t.m.a. or d.s.c. results, and appropriate samples were used.

Dynamic mechanical thermal analysis

Using a Polymer Laboratories DMTA Mark 1 analyser, T_g was obtained from the peak maximum in the loss tangent ($\tan\delta$) plots measured at 1 Hz at a heating rate of 1°C min^{-1}.

Fracture toughness

Fracture toughness was measured by the critical strain energy release rate (G_{Ic}) and the critical stress intensity factor (K_{Ic}). Double torsion (DT) testing geometry, based on the procedures of Kies and Clark[16], was used and the parameters determined from the following relations:

$$K_{Ic} = \frac{P_L L}{[k_1 w t_n t^3 (1-\nu)]^{1/2}} \tag{1}$$

$$G_{Ic} = \frac{P_L^2}{2t_n}\frac{dC}{da} \tag{2}$$

where P_L is the fracture load; L is the moment arm; w is the plate width; t_n is the crack plane thickness; k_1 is a correction factor[17] used when $w/2t < 10$; ν is Poisson's ratio (taken as 0.35); C is compliance; and a is the crack length. dC/da, which is constant for the DT test geometry, was determined for ungrooved plates and corrected for crack plane thickness. The specimen plate was 75 mm × 30 mm × 4 mm and a constant load was applied using an Instron 1121 universal tensile testing machine with a crosshead speed generally of 1 mm min^{-1}.

Four modes of fracture were distinguished by the profile of the DT test trace: A, continuous, in which the load rose to and maintained a plateau value; B, stick–slip, where the load oscillated between maximum and minimum values, dropping abruptly to give a saw-toothed trace; C, stick–slip rising, unstable crack growth as in the previous case but with the maximum and minimum values slowly increasing; and D, brittle, in which no plateau is reached but crack propagation is virtually instantaneous once a maximum load is reached. For unstable (slip–stick) crack propagation, maximum and minimum values of G_{Ic} and K_{Ic}, corresponding to initiation and arrest of crack propagation, are given. Single values indicate either brittle behaviour or stable (continuous) crack growth. Results were usually based on the average of 4–5 replicates. The 4 mm plate thickness of the DT specimens was well within the requirements of ASTM E399-83 for plane-strain conditions.

Tensile properties

Tensile properties were determined to ASTM test method D638M-84 using an Instron 1121 universal testing machine equipped with a suitable extensometer.

Moisture absorption

Water uptake measurements were conducted on cast specimens measuring approximately 60 mm × 12 mm × 3 mm (weight 3 ± 0.1 g). After drying overnight at 100°C under vacuum, duplicate specimens were weighed and immersed in distilled water at 50°C. At intervals during a period of 25 weeks they were removed, patted dry and weighed to determine the progressive weight gain.

Latency

Three systems were studied to assess their storage

Table 1 Some physical properties of a TGMDA–DDS resin and the effect of CTBN addition

CTBN					T_g (°C)		Tensile properties		
Type	AN (%)	Amount (phr)	G_{Ic} (J m^{-2})	K_{Ic} (MN m$^{3/2}$)	T.m.a.	D.m.t.a.	Strength (MPa)	ϵ_b (%)	Modulus (GPa)
None			38	0.44	210	199	74	2.0	4.0
X-13	27	10	72	0.58	190	202	78	2.8	3.1
X-13	27	20	121	0.66	200	205	62	3.2	2.5
X-13[a]		20	125–143	0.62–0.66		205			
X-18	20.5	10	130			208			
X-8	17	10	60			207			
X-15	10	10	130						

[a] Not pre-reacted

stability; they were prepared either as suspensions, mixed at 60°C and passed through a triple roll mill, or solutions heated at 135, 90 and 125°C depending on the hardener (DDS, TGMDA–PIP and PIPIP respectively). Advancement was estimated by monitoring the disappearance of monomeric TGMDA as a function of ageing time at 23°C. Samples were withdrawn at intervals, dissolved in tetrahydrofuran (THF) and the monomeric TGMDA content determined by gel permeation chromatography (g.p.c.), using 50 μl aliquots of 0.08% solution and an Altex 153 pump, THF at 1 ml min^{-1} as solvent, three Shodex columns (801 + 802 + 803) and a Waters 481 u.v. detector set at 320 nm.

Morphology

The morphology of selected toughened specimens was studied by transmission and scanning electron microscopy (TEM and SEM). In most instances for TEM, one end of a convenient sized block of cured resin was shaped into a square pyramid, stained by immersion in a THF solution of osmium tetroxide[18] and cut at ambient temperature into ultra-thin sections using an LKB Ultratome type 4801a fitted with a diamond knife. The TEM microscope used was a Phillips EM-300. With SEM, after fracture toughness measurements the fracture surface was osmium-stained, coated with an evaporated layer of gold and examined using a S250 Stereoscan SEM microscope.

RESULTS AND DISCUSSION

DDS-cured systems

TGMDA–DDS systems were used as benchmark materials to assess the efficacy of rubber toughening in systems of TGMDA–CTBN with piperidine-derived curing agents. The base formulation comprised MY720 and DDS (28 parts per 100 of resin, phr) and was cured for 1.5 h at 135°C followed by 2 h at 175°C (conditions for optimum properties established by Lee *et al.*[10] except that boron trifluoride–monoethylamine catalyst was omitted). The base formulation displayed a brittle fracture mode at room temperature; the tensile modulus was 4.0 GPa, the tensile yield stress 74 MPa and the fracture toughness (G_{Ic}) 38 J m^{-2}. The values obtained are in close agreement with those previously reported[10].

The effect of addition of CTBN is shown in *Table 1*. It has been suggested[10] that the CTBN with higher acrylonitrile (AN) content (i.e. X-13) would be preferred on the grounds of compatibility, but no clear relation between fracture toughness and CTBN composition was evident. In the case of the X-13 rubber there is some improvement in fracture toughness as the level of rubber addition is increased and an increase of about threefold in G_{Ic} can be obtained at the expense of other mechanical properties, as previously observed[10,18], but in only one instance was there evidence of modification to slip–stick behaviour. Most of these rubbers were pre-reacted and the use of neat rubber makes little difference to the fracture properties because the rubber–resin reaction occurs so promptly. All rubber-containing castings were opaque.

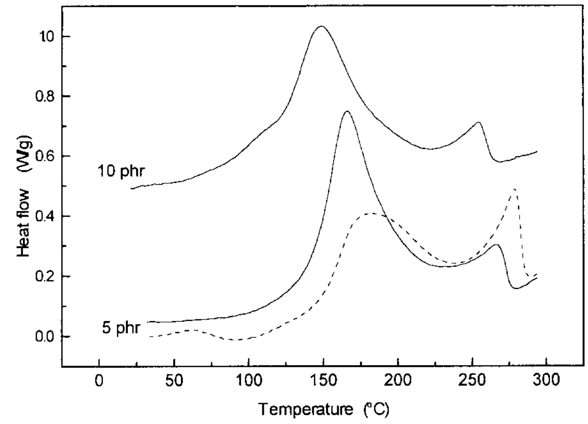


Figure 2 D.s.c. curves of MY720-PIP: 5°C min^{-1}; hermetic pan (—), open pan (– – –). The '5 phr hermetic' sample is not fresh

Piperidine-cured systems

Thermal analysis and cure chemistry. Piperidine is widely used as a hardener for DGEBA in studies of toughening by rubber because it provides a convenient degree of reactivity. D.s.c. of mixtures of TGMDA and piperidine in open or closed pans showed that reaction was facile, beginning at room temperature and reaching maximum rate below 200°C (see *Figure 2*). Two concentrations (5 and 10%) of piperidine were used and the rate of reaction was obviously dependent on the piperidine concentration. The low-temperature reaction is believed to relate to the initial formation of the adduct–a tertiary amino alcohol—which catalyses the homopolymerization of TGMDA. The significant

Table 2 The effect of X-13 CTBN on some physical properties of TGMDA–Piperidine resin

Rubber added				T_g (°C)		Tensile properties		
(phr)	(pre-react, %)	G_{Ic} ($J m^{-2}$)	K_{Ic} ($MN m^{-3/2}$)	T.m.a.	D.m.t.a.	Strength (MPa)	ϵ_b (%)	Modulus (GPa)
0		152	0.76	179	179	81	3.2	3.4
10	(100)	310	0.99	179	179	75	5.1	2.5
20	(100)	525	1.08	174	181	58	5.7	1.8
20	(50)	520	1.13	172				
20	(0)	745	1.09	177				

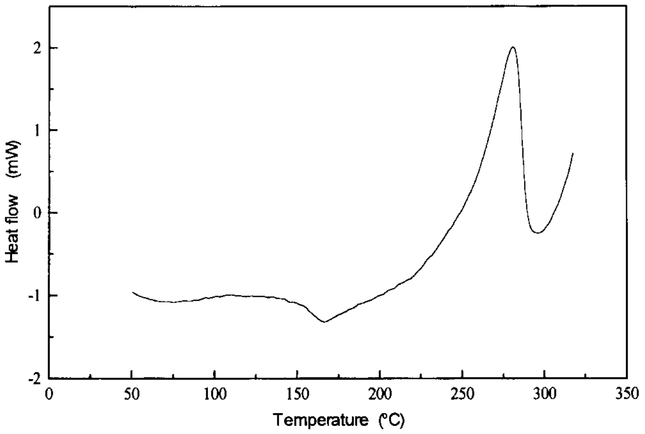


Figure 3 D.s.c. curve of MY720-PIP after cure 1 h/120°C + 1 h/150°C; 10°C min^{-1}, hermetic pan

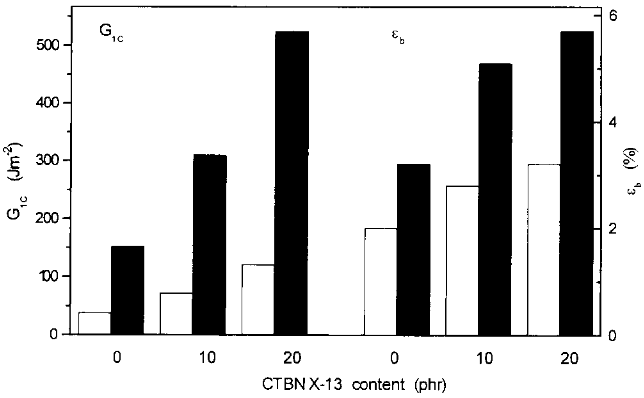


Figure 4 The effect of X-13 CTBN on ϵ_b and G_{Ic} of TGMDA cured with piperidine (shaded) and DDS (open)

difference between these d.s.c. curves obtained in open and hermetic pans is a reflection of the relative volatility of the piperidine and also the facile reaction (the sample of 5% piperidine in the hermetic pan was 15 h old and the low-temperature reaction was complete). MY720 and 5% piperidine cast for 1 h/120°C plus 1 h/150°C gave material of T_g about 150°C, which continued to cure when heated beyond the cure temperature (*Figure 3*). Comparison of *Figures 2* and *3* shows that a high-temperature peak (ca. 280°C) is common to both. Further cure at 150 or 170°C reduces but does not eliminate this exothermic peak, which is attributed to unreactable epoxide groups in the resin, or a subsequent and uncharacterized exothermic decomposition. The 'ultimate' T_g of these materials is close to 190°C (d.s.c., 10°C min^{-1}, end of transition) after considerable cycling to 200°C and above. The T_g and the residual heat of reaction are very similar at both the 5 and 10% piperidine levels, and the concordance between material cured in the d.s.c. cell and cast was good on the limited work done.

The addition of CTBN, up to 20 phr, to the MY720–piperidine mix has relatively little effect on the dynamic d.s.c. curves of samples from slabs cast at 150 and 170°C. At low temperatures the reactivity and volatility of piperidine make meaningful comparison of the curing process difficult, but it is assumed that, as in the case of addition of an epoxy-terminated nitrile rubber (ETBN) to DGEBA[19], or of CTBN to DGEBA adhesives[20], the presence of rubber has little effect on the kinetics of cure.

Piperidine was therefore used for TGMDA at a concentration of 5 phr with a cure cycle of 1 h at 150°C followed by 1 h at 170°C. Compared to DDS-cured systems (*Table 1*), the piperidine-cured systems (*Table 2*) have more than three times the fracture toughness (G_{Ic}), while the tensile strengths are similar, the tensile moduli and T_gs are lower (about 20% and 25°C respectively), and elongation at break are somewhat higher.

Although the fracture properties of the unmodified piperidine-cured system are better than those of the basic DDS system, *Table 2* also shows that the addition of CTBN rubber (X-13) is slightly more effective in increasing G_{Ic} of the former system, with a commensurate influence on the tensile properties (*Figure 4*). Phase separation can be assumed since all the rubber-containing castings were opaque, while those without rubber were transparent.

As a curing agent, piperidine has a major advantage over DDS because the reaction is effectively complete under the temperature cycle employed and a material of stable T_g is produced. In contrast, the reaction between DDS and TGMDA at these temperatures is limited by vitrification, and subsequent heating to higher temperatures leads to further reaction. This is illustrated by the shape of the modulus curves measured by d.m.t.a. *Figure 5* shows representative examples. Above about 180°C further crosslinking evidently occurs in the DDS case resulting in a substantial increase in modulus. At lower temperatures the modulus values were quite similar in the two cases.

Piperidine adduct systems

Piperidine has limited value as a commercial curing agent, particularly in aerospace applications, because it is volatile, toxic with an objectionable odour, and

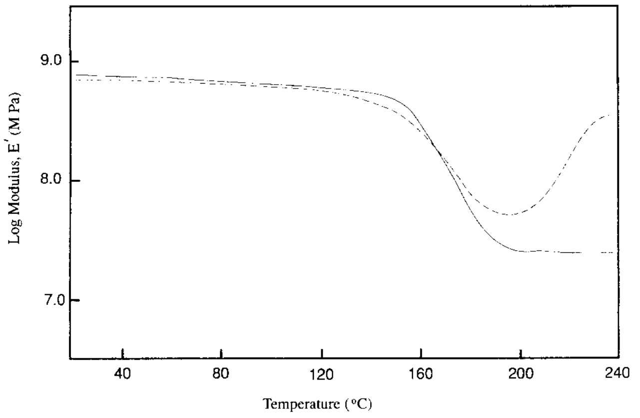


Figure 5 D.m.t.a. curves of TGMDA–DDS (– – –) and TGMDA–PIP (———) cured at 170°C

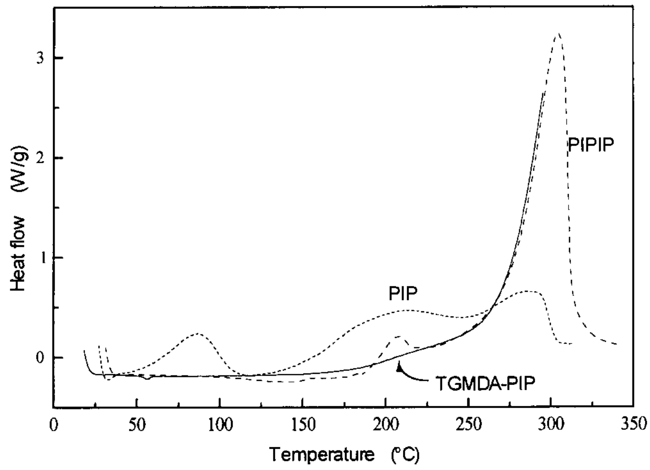


Figure 6 Dynamic d.s.c. curves for MY721 and piperidine 'adducts' (5 phr piperidine equivalent); 10°C min^{-1}, open pan

reactive at ambient temperatures. As a hardener for epoxy polymerization, it is effectively 'catalytic' in action—a secondary amine unable to act as a crosslink in network formation and used in much less than stoichiometric amounts. There are two approaches to the problems of volatility and reactivity at ambient temperature: to preform the initially produced catalytic entity, or to form an adduct that will afford controlled release of piperidine at the curing temperature. Both have been pursued: piperidine has been reacted with glycidyl compounds (epoxy resins, including TGMDA, and phenyl glycidyl ether) to produce analogues of the initial product of the reactions between TGMDA and piperidine; and piperidine has been reacted with various isocyanates to form solid ureas, compounds known to be effective hardeners and catalysts for epoxy cure and suspected of functioning via amine release (see below). These materials are collectively referred to as adducts and were usually used in amounts equivalent to 5 phr piperidine.

Piperidine–epoxy adducts. In *Figure 6* the d.s.c. curve of MY721 and the self-adduct with piperidine (an equimolar mixture of piperidine and MY721) is contrasted with that of MY721 and free piperidine. The facile initial reaction of piperidine with MY721 begins from room temperature, with a pronounced exothermic peak near 70°C, before the bulk reaction above 100°C. (The differences between this curve and the similar curve for MY720 in *Figure 1* can be attributed to freshness of the mixture, heating rate and different composition of the two forms of TGMDA. The d.s.c. curves of the two resins are generally similar but not identical.) In contrast, the reaction with the adduct is slow and the onset of mild exothermic reaction at this heating rate (10°C min^{-1}) is delayed until 150°C; under these conditions TGMDA alone is much less reactive until well above 200°C when there is a sharp, grossly exothermic reaction (homopolymerization?) peaking near 300°C. The high-temperature peaks seen in the d.s.c. curves in *Figure 6* result from this 'uncatalysed' reaction and are relatively less important at lower heating rates.

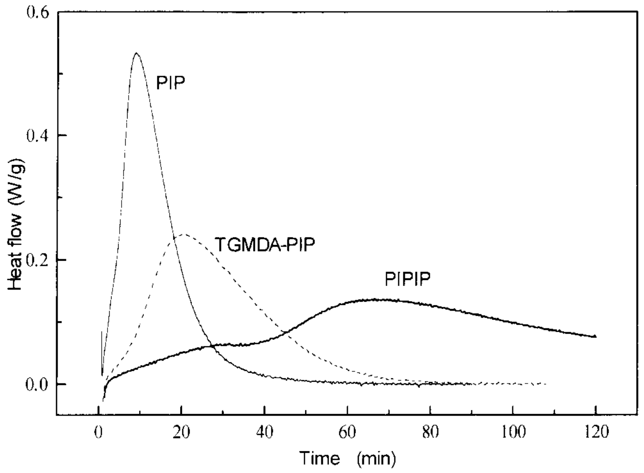


Figure 7 Isothermal d.s.c. curves for MY721 and piperidine 'adducts' (5 phr piperidine equivalent); 150°C, open pan in nitrogen

Isothermal reaction of the same mixtures is more interesting and the d.s.c. curves at 150°C are shown in *Figure 7*. Reheating of the samples after this isothermal cure showed that the same extent of cure was obtained with both the PIP and TGMDA–PIP, although clearly the reaction with the latter was slower and more controlled.

Figures 6 and *7* show that the pre-reaction of piperidine with an epoxide affords an effective 'catalyst' for the cure of TGMDA and obviously mitigates the problems of odour, toxicity and dosage variation associated with the volatility of piperidine. The figures also suggest that a degree of latency at lower temperature can be expected and, incidentally, emphasize that in dynamic d.s.c. it is possible for these systems to 'outrun' autocatalytic reaction if the heating rate is too high and point to isothermal d.s.c. as a useful indicator of reactivity.

The relative mildness of the reaction with TGMDA–PIP is perhaps surprising since the equivalence takes no account of volatility and, in the absence of adduction, some piperdine will be lost from an open pan during warm-up. Williams[21] has observed a loss of the volatile hardener at much lower temperatures, although this is not a sufficient explanation[22] for the variation of T_g of DGEBA–piperidine mixes with cure temperature. Simplistically it might be expected that the facile reaction of piperidine with epoxide, as shown in *Figures 2* and *6*, would lead to a mix of TGMDA–PIP and unreacted

Table 3 Some properties of cured TGMDA systems using various hardeners[a]

				T_g (°C)		Tensile properties		
Hardener	G_{Ic} (J m^{-2})	K_{Ic} (MN m$^{-3/2}$)	Fracture profile[b]	T.m.a.	D.m.t.a.	Strength (MPa)	ϵ_b (%)	Modulus (GPa)
Piperidine	152	0.76	B	179	179	81	3.2	3.4
Glycidyl adducts								
PGE–PIP	80–145	0.58–0.78	B		149	94	4.5	3.4
	111–129	0.70–0.75	B	155	156			
DGEBA–PIP	127–154	0.68–0.75	B	170	172			
ETP	94	0.61	A		157	86	3.5	3.2
TGMDA–PIP	84–123	0.60–0.73	B	181	183			
	102–135	0.61–0.70	B	179				
Isocyanate adducts								
PIPIP	209	0.68	A	175	175	89	3.6	3.2
P14MePIP	366	1.14	D	161	165			
PIPYRR	102	0.65	B	145	170			
PIPIP[c]	25–90	0.60–0.69	B		169			

[a] MY720 and amine equivalent of 5 phr piperidine
[b] Fracture profile in DT tests: A, continuous; B, stick–slip; C, stick–slip, rising; D, brittle
[c] In this case only MY721

resin. This is clearly not so and the complexity of the reaction of secondary amines with resins is confirmed, but has not been studied in any detail.

Other epoxide adducts of piperidine—with PGE, monomeric DGEBA and ETP (a commercial hardener believed to be a product of piperidine and low-oligomer DGEBA, which gave similar results to DGEBA–PIP)—were evaluated in the same way. These were also effective catalysts for the polymerization of TGMDA but less active than piperidine alone. Suitable oven temperature(s) for cure of the large samples (to ensure that reaction was not excessively exothermic but would be complete in a reasonable time) were decided from isothermal d.s.c. cure curves at various temperatures, and subsequent measurement of the T_g and residual heat of reaction of the d.s.c. cured sample.

Table 3 shows that, compared to the other glycidyl adducts, the TGMDA adduct gives a final product with superior high-temperature performance, as evidenced by high T_g, probably because the epoxy functionality does not compromise the crosslink density of the final network. Systems containing the phenyl glycidyl ether–piperidine adduct (PGE–PIP) were clearly inferior in terms of the T_g, presumably because the PGE, being monofunctional, presents an inevitable chain termination. Much the same sort of comment probably attaches to the comparison between DGEBA–PIP and ETP, which may contain non-reactive diluents and oligomers that give longer crosslinks.

Piperidine–isocyanate adducts. Ureas have been commonly used to accelerate epoxy cure, particularly where dicyandiamide (dicy) is the prime curing agent, but are also used in some commercial film adhesives[23] and composites[24] as the sole hardener. These ureas can be synthesized by the (reversible) addition of a secondary amine, usually dimethylamine, to an isocyanate and are believed to function as effective mixtures of the components[25,26]. The solubility of the urea in the epoxy mixture[27] and the particular secondary amine[28] determine its latency and reactivity. Thermal stability may be indicative of the solubility of the urea in the epoxy, but previous studies (thermal analysis, evolved gas analysis (e.g.a.)/infra-red spectroscopy) found no evidence of thermal dissociation in the reactions of dimethylamine-derived ureas with DGEBA[29].

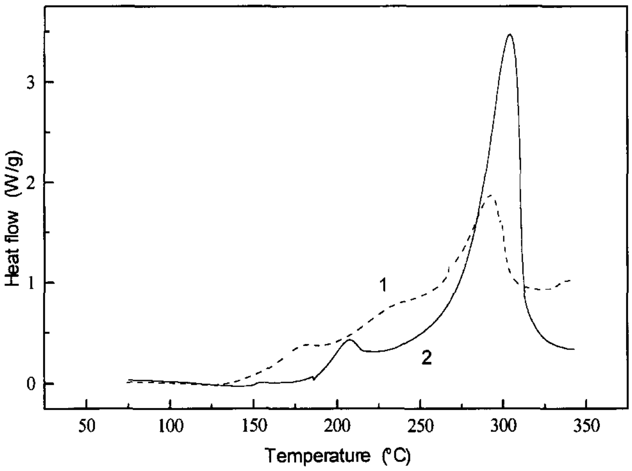


Figure 8 D.s.c. curves (10°C min^{-1}, open pan) of TGMDA and PIPIP: 1, MY720 in air; 2, MY721 in nitrogen

The d.s.c. curves of the simplest of these materials (PIPIP) shown in *Figures 6* and *7* show that it is an effective curing agent for TGMDA, but that it is much less reactive than the equivalent amount of unadducted piperidine and therefore should demonstrate the desired latency. In dynamic conditions the initial reaction is evident somewhat above 170°C, the melting point of PIPIP.

The reaction of MY721 with PIPIP is significantly slower than that of MY720, and the dynamic d.s.c. curves are particularly susceptible to kinetic effects because of the multiplicity of reaction parameters.

Figure 8 shows the curves for different batches of PIPIP reacting with MY720 and MY721 in open pans at 10°C min^{-1} in air and nitrogen respectively. The figure shows a major difference in the baseline (as a result of oxidation at higher temperature), but also there are several obvious reactions and the balance between them is different for each case. In separate experiments it has been found that under isothermal conditions (150°C, cf. *Figure 7*, curve 3) the time to the various maxima and the relative peak heights depend on the TGMDA, on the urea batch (preparation medium, extent of recrystallization), the degree of constraint of the d.s.c. sample (open, crimped or hermetic pan), and atmosphere (inert gas or air, static or flowing gas). In dynamic d.s.c. the distortion and possible leakage of crimped or hermetic pans at higher temperature are further complications.

No serious attempt has been made to elaborate these factors, although it may be speculated that the purer form of TGMDA (MY721) contains fewer extraneous catalysts (including the hydroxyl groups in oligomers)[30], that recrystallization of PIPIP will determine crystal size and dissolution rate in addition to purity, and that constraint and gas flow affect the loss of a catalyst or an alternative reaction (acrolein, but no piperidine, has been identified by e.g.a.[29] and thermogravimetry indicates a small weight loss). The reaction of piperidine with TGMDA, even MY721, is facile (*Figure 6*) and it is improbable that significant loss would occur during the much milder reaction with the urea. Fasce *et al.*[31] generated the urea *in situ* by adding isocyanate to the cooled DGEBA–piperidine mix and noted that the method affords latency and avoids problems of volatility of piperidine: they assume the formation of the secondary amine during cure, but as a by-product of the epoxy–urea reaction rather than by thermal decomposition of the urea, and noted the facile reaction of the secondary amine under these conditions. (*In situ* generation of urea may substitute the risks of workplace exposure to piperidine for those of isocyanates). These workers observed that the incorporation of small amounts of oxazolidone residues in the network had no effect on the T_g of these materials and consider that the reaction was predominantly (anionic) homopolymerization, with an (unidentified) termination reaction that limited the extent of reaction at lower concentrations of piperidine equivalent. More recently[32] the initial stages of the model reaction between PGE and piperidine have been studied in some detail: the facile reaction of the secondary amine and epoxide leads to PGE–PIP, which catalyses the homopolymerization of PGE. PGE–PIP is relatively stable in PGE at room temperature, although, once the reaction has been initiated at a significantly higher temperature (120°C), homopolymerization can proceed at room temperature; intramolecular chain transfer may account for the average molecular weight of the resultant polymer being lower than expected from stoichiometric considerations.

Several other ureas were prepared from piperidine with different isocyanates, and from secondary amines related to piperidine. They were evaluated by attempting isothermal cure at 150°C in the d.s.c. cell using the equivalent of 5 phr piperidine in MY720. If there was no apparent reaction after 2 h, and the subsequent heating at 10°C min^{-1} gave a d.s.c. curve indistinguishable from that of MY720 alone, it was assumed that the urea would have no practical use and no further investigation was undertaken. Piperidine derivatives included the following.

1,4-Phenyl diisocyanate piperidine (DIPIPIP): This hardener, which decomposes above 200°C, did not dissolve completely in the resin during cure. Reaction was slow (90 min to maximum rate at 150°C) and incomplete after 4 h/150°C + 2 h/180°C when the T_g was a low 140°C.

Toluene diisocyanate piperidine (TDI–PIP): Of the several ureas that were not taken beyond the initial investigation, this was perhaps the most interesting, since the results, although suggestive of the possibility of a high T_g, were inconclusive and, in particular, larger-scale preparations and the determination of physical properties were not undertaken. The m.p. of TDI–PIP was about 230°C and it was an effective catalyst for the polymerization of TGMDA with reaction occurring as low as 120°C (at 5°C min^{-1}). Its reactivity appeared to be more complex than PIPIP and depended on preparation (addition of TDI to piperidine in water, dimethylformamide or benzene) and purification (washing, extraction or recrystallization). This difficulty might have been resolved, but no void-free castings were obtained. The porosity may be the result of interference with the degassing procedure and/or chemical reaction and, taken in conjunction with its reactivity, the presence of unreacted hardener and variation of the degree of cure through the thickness of the casting suggested that TDI–PIP was not a promising hardener at this stage.

Other amines were usually, although not always, used as the phenyl isocyanate adducts to avoid any problem with volatility. If the urea appeared to be too insoluble then use of the naked amine was attempted.

Phenyl isocyanate piperazine: Slow and incomplete reaction at 200°C; sedimentation of the hardener can lead to stratified cure; susceptible to oxidative effects at this temperature.

Pyrrolidine: Pyrrolidine reacts quite readily with MY720 at 120°C, at which temperature cure is extensive but not complete; like piperidine it is volatile and has no latency. The adduct with phenyl isocyanate reacted readily at the same temperature, complete reaction could be achieved at 5 phr but not 2 phr PIPYRR.

Dibutylamine: The adduct melts at 84°C and there is no indication of sublimation or decomposition at 150°C. The d.s.c. curve of the mix shows the melting or dissolution of the adduct at 10°C min^{-1} but only very slight reaction at 180–200°C with little effect on the TGMDA homopolymerization. Under isothermal conditions there is some reaction but the T_g does not advance beyond 100°C.

Dimethylamine: Monuron, a 'dimethylamine source', was an effective catalyst for TGMDA polymerization at lower levels than piperidine. High T_g, *ca.* 150°C, was attained with only 2 phr Monuron (Monuron and PIPIP are of approximately the same equivalent weight) in an uncompleted reaction. The reaction is subject to strongly autocatalytic effects and long induction times at low temperatures; at 12 phr and 110°C the induction period was more than 45 min before strongly exothermic reaction, and a slab cast at 115°C suffered significant charring. Although Diuron (3-dichlorophenyl-1,1-dimethylyurea) has been reported as the sole curing agent for a commercial TGMDA–Novolac system[24], the

Table 4 The effect of PIPIP content on the properties of toughened and untoughened TGMDA

PIPIP (phr)	G_{Ic} (J m^{-2})	K_{Ic} (MN m$^{-3/2}$)	Fracture profile[a]	T_g (°C) T.m.a.	T_g (°C) D.m.t.a.
Untoughened					
20	63–151	0.52–0.79	C		162
12	209	0.68	A	175	175
6	118–147	0.65–0.73	B		
2	20–41	0.25–0.35	D	116	
Toughened with 20 phr CTBN X-13					
20	907	1.46	A		148
12	699–907	1.30–1.52	C	175	169
6	490	1.06	A		
2	63–151	0.52–0.79	C	116	

[a] See *Table 3*

reactivity of systems based on dimethylamine seemed less predictable than that of those using piperidine adducts, so further attention was concentrated on the latter.

N-*Ethylpiperidine* (b.p. 130°C): Mixtures of *N*-ethylpiperidine (1, 3, 6 phr) with MY720 were heated at 10°C min^{-1} in both open and hermetic pans. There was some reaction, insufficient to account for all of the epoxide, and the T_g remained low. The effect of evaporation of the hardener cannot be avoided, but attempts to minimize it by establishing the initial homopolymerization during isothermal reaction at 90°C and then heating to 170°C to allow the autocatalytic reaction to proceed further failed to give a product of higher T_g.

Morpholine: There appeared to be exothermic reaction below 100°C (not seen after some days) when a fresh mixture of TGMDA and morpholine was heated at 10°C min^{-1} (as would be expected for reaction with the secondary amine), but the very slight exothermic trend during isothermal heating at 170°C is an indication that any catalytic activity is too weak to be useful.

In general, it can be seen that piperidine, or piperidine-related or -derived materials, are effective agents for the homopolymerization of TGMDA resins provided that problems of reactivity, volatility and miscibility are addressed. The piperidine derivatives appear to be better suited than the more active dimethylamine derivatives because of the higher processing temperatures needed for this relatively viscous resin. The T_g of the resins cured with the same equivalent piperidine concentration varied over a considerable range; one factor is the functionality of the epoxide adduct, but other (unidentified) influences on transfer and termination reactions in the homopolymerization will affect the T_g of the cured resin. The properties of the cured systems that were considered in more detail are shown in *Table 3*. The basic experimental objective was full cure at 5 phr piperidine equivalent, not to optimize the particular system.

Mechanical properties

Table 3 shows that the isocyanate–piperidine adducts show more promise than the epoxide–piperidine materials in terms of increased fracture toughness, while the phenyl isocyanate–piperidine system shows the best overall compromise in terms of increased fracture toughness and high T_g. The effect of variation in the amount of piperidine employed was examined using 2 to 20 phr PIPIP (*Table 4*). The ratio of piperidine equivalent (0.8 to 8 phr) employed was always catalytic, not stoichiometric, but it is clear that at the lowest level there is not sufficient for complete cure. It can also be seen that as in the case of neat piperidine (*Table 2*), the addition of rubber has little, if any, effect on the cure of the system, with the T_g of the toughened material being the same as for the neat resin.

Addition of rubber to piperidine adduct systems

The effect on fracture and mechanical properties of two levels of rubber (X-13) addition using a wider range of the more promising hardeners is shown in *Table 5*; there was no phase inversion at these rubber loadings for this system. The effect on tensile strength and modulus is basically the same regardless of the particular adduct. Glass transition temperature is not really affected by the rubber addition for a particular adduct. The TGMDA–piperidine adduct system results in the highest T_g, about 180°C, which is the same as that without rubber (*Table 3*). As previously noted, pre-reaction of the piperidine and the resin appeared not to affect the final properties.

After the incorporation of rubber, a number of the systems gave a minimal depression of T_g but clear, transparent castings instead of the usual opaque material. This would appear to denote that the second, dispersed phase is of extremely small particle size, since an exact match in refractive index is unlikely. The question of particle size is discussed further below. Attempts to investigate the sub-ambient-temperature transitions of the rubber by d.m.t.a., d.s.c. and t.m.a. were inconclusive. The principal difficulties were the relatively small proportion of the second phase, the presence of the β relaxation of the resin in the same temperature region and deficient sensitivity in the available equipment.

The profile of the fracture curve in double torsion fracture toughness measurement was influenced by the amount of rubber added. With the addition of 10 phr rubber, all systems showed type B (stick–slip) fracture behaviour. With 20 phr rubber a number of systems displayed type A (continuous) fracture. For those still having slip–stick fracture, the excursions in the stick–slip behaviour (the differences between G_{IcI} and G_{IcA} at the initiation and arrest of crack growth respectively) were greatly reduced. For the eight systems listed with 10 phr G_{IcA}/G_{IcI} ranged between 0.45 and 0.80, while for the five systems with 20 phr G_{IcA}/G_{IcI} fell between 0.75 and 0.90, that is, close to type A behaviour.

Fracture behaviour

Considering the fracture data for all systems examined, the value of the measured tensile modulus E can be compared with that calculated from:

$$E = \frac{K_{Ic}^2(1 - \nu^2)}{G_{Ic}} \qquad (3)$$

where K_{Ic} and G_{Ic} were determined by the fracture studies and ν is Poisson's ratio, assumed to be 0.35. This relation assumes bulk linear elastic behaviour and plane-strain conditions. The degree of agreement between the directly measured and calculated values of the tensile modulus can be taken as a guide to the extent to which these assumptions are valid. *Figure 9* suggests good

Table 5 The properties of TGMDA (various hardeners) toughened with CTBN X-13

						T_g (°C)		Tensile properties		
Hardener	Cure[a]	G_{Ic} ($J m^{-2}$)	K_{Ic} ($MN m^{-3/2}$)	Fracture profile[b]	Clarity[c]	T.m.a.	D.m.t.a.	Strength (MPa)	ϵ_b (%)	Modulus (GPa)
Rubber content 10 phr										
PGE–PIP	A	311–627	1.02–1.45	B	O		148	80	4.7	2.8
DGEBA–PIP	A	213–299	0.80–0.93	B	O	172	174			
ETP	A	127–276	0.60–0.92	B	O		159	81	4.1	2.8
TGMDA–PIP	A	181–266	0.75–0.97	B	T	178	181			
TGMDA–PIP[d]	A	183–234	0.75–0.85	B	T	179				
PIPIP	A	166–264	0.74–0.91	B	O	178	169	84	4.8	2.8
PIPIP[e]	A	217–420	0.85–1.18	B	O		160			
P14MePIP	B	183–358	0.76–1.50	B	O	156	163			
PIPYRR	C	141–240	0.70–0.91	B	O	146	160			
Rubber content 20 phr										
PGE–PIP	A	833–1199	1.40–1.70	B	O		149	60	6.7	2.1
DGEBA–PIP	A	360–404	0.94–1.00	A	T	167	172			
ETP	A	544	1.12	A	O		157	61	5.4	2.1
TGMDA–PIP	A	260–314	0.85–0.94	B	T	184	182			
TGMDA–PIP[d]	A	255–312	0.79–0.87	A	T	178				
PIPIP	A	669–907	1.30–1.52	B	O	175	169	61	6.2	2.0
PIPIP[e]	A	572–631	1.27–1.33	B	O		155			
P14MePIP	B	637	1.20	B	O	156	162			
PIPYRR	C	250	0.76	A	O	146	172			

[a] Cure cycle: A, 1 h/150°C + 1 h/170°C; B, 1 h/150°C + 2 h/180°C; C, 2 h/120°C + 1 h/180°C
[b] Fracture profile: A, continuous; B, stick–slip
[c] Clarity of castings: O, opaque; T, transparent
[d] CTBN pre-reacted
[e] TGMDA, MY721 (all others MY720)

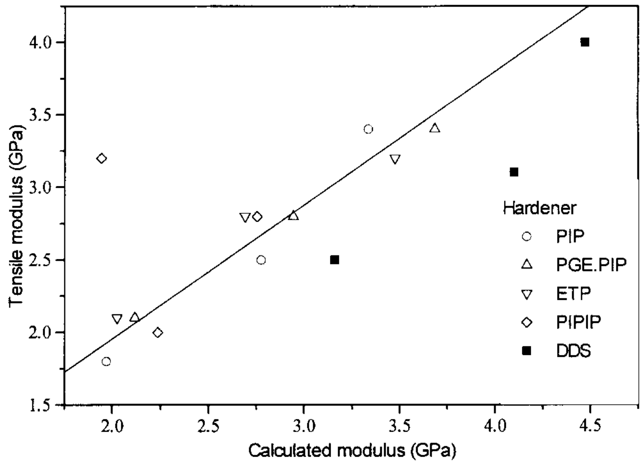


Figure 9 A comparison of experimental and calculated (from equation (3)) moduli for selected toughened and untoughened systems; hardener indicated, see tables for CTBN levels

agreement for the piperidine-based systems and rather poorer agreement for the DDS-cured systems. These assumptions have previously been shown to be valid for the much studied model system DGEBA–piperidine. The line of best fit in *Figure 9* excludes the data for the DDS materials, but also the untoughened PIPIP resin (*Table 3* shows a disturbing divergence between the fracture properties of MY720 and MY721, and exceptionally high values of G_{Ic} for both PIPIP and P14MePIP–MY720 resins). It is interesting that the TGMDA–DDS combination currently in use does not conform so well.

Table 6 Calculated crosslink density (equation (4)) of various unmodified and modified (20 phr CTBN X-13) TGMDA systems

Hardener[a]	M_c (unmodified)	M_c (modified)
Piperidine	390	475
PGE–PIP	440	530
DGEBA–PIP	410	510
ETP	395	
TGMDA–PIP	340	400
PIPIP	455	795

[a] 5 phr piperidine equivalent

The crosslink density (molecular weight between crosslinks, M_c) can be determined, to a first approximation, from the equilibrium rubbery modulus E_r, by means of the relation[33]:

$$\log_{10}\left(\frac{E_r}{3}\right) = \frac{6 + 293\rho}{M_c} \tag{4}$$

where ρ is the density, taken as $1.20\, g\, cm^{-3}$. Values of E_r can be obtained from the d.m.t.a. curves well above the T_g. Values of M_c have been calculated from the modulus curves at 220°C, that is, at least 40°C above the T_g (*Table 6*). These calculations were not possible for DDS systems since, as previously noted, equilibrium was not achieved (*Figure 5*).

The plot of T_g vs. $1/M_c$ can be used to estimate the T_g of the corresponding linear polymer, T_{g0} (refs 33, 34). This approach has been used to estimate the value of

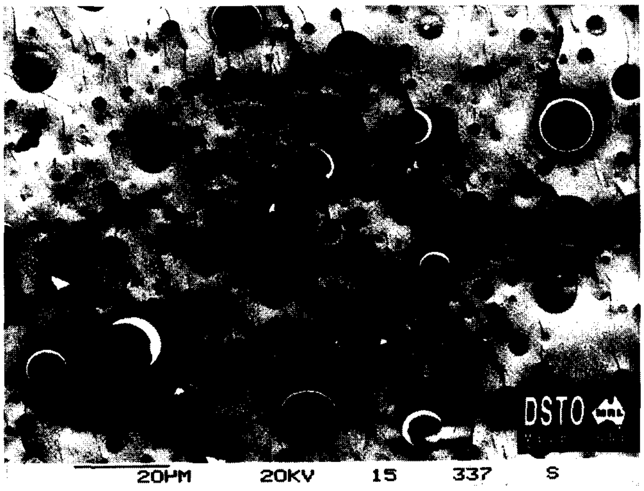


Figure 10 SEM micrograph of the fracture surface of TGMDA–DDS modified by 20 phr CTBN

T_{g0} for DGEBA systems, for which values ranging from 70 to 90°C have been reported[6,22,34]. A more rigorous approach to the calculation of T_{g0} from contributions by structural elements has been found useful for diepoxide systems, giving values similar to those determined experimentally[35]. For higher-functionality epoxides the number of alternative structures means that only indicative values could be calculated. The estimated value for TGMDA from this method was 45°C[35]. A value of 99°C for T_{g0} for TGMDA was obtained by Lau *et al.*[36], using the empirical Nielsen approach and varying the crosslink density by incorporating various amounts of two model resin precursors. In the present case using all available M_c values (from *Table 6*), an estimate of 152°C was obtained for T_{g0}, but it is noted that these data consist of a set of separate systems rather than a systematic series.

Morphology and toughness

In several systems the fracture surfaces (after double torsion testing) were subjected to micrographic study. *Figure 10* shows the fracture surface of the system TGMDA–DDS with 20 phr rubber. A bimodal distribution of rubber particle sizes is apparent (particle diameters approximately 2 and 10 µm). There is clear evidence of very weak bonding at the elastomer–epoxy interface, which doubtless contributes to the poor toughening effect of the rubber.

TEM micrographs of thin sections of the system TGMDA–piperidine–20 phr rubber showed the precipitated rubber particles to be extremely small (~ 0.03 µm) and not uniformly distributed, perhaps suggesting an initial separation into single-phase rubber-rich domains. A similar morphology results when piperidine adducts are used to harden TGMDA–CTBN, and *Figure 11* shows the extremely small extensively agglomerated particles in the system with PIPIP and 20 phr rubber. Furthermore, systems containing TGMDA–PIP and DGEBA–PIP were transparent (*Table 5*), indicating even smaller particle size (less than 0.02 µm, say). A similar situation has been reported for a phenolic epoxy–CTBN system[37].

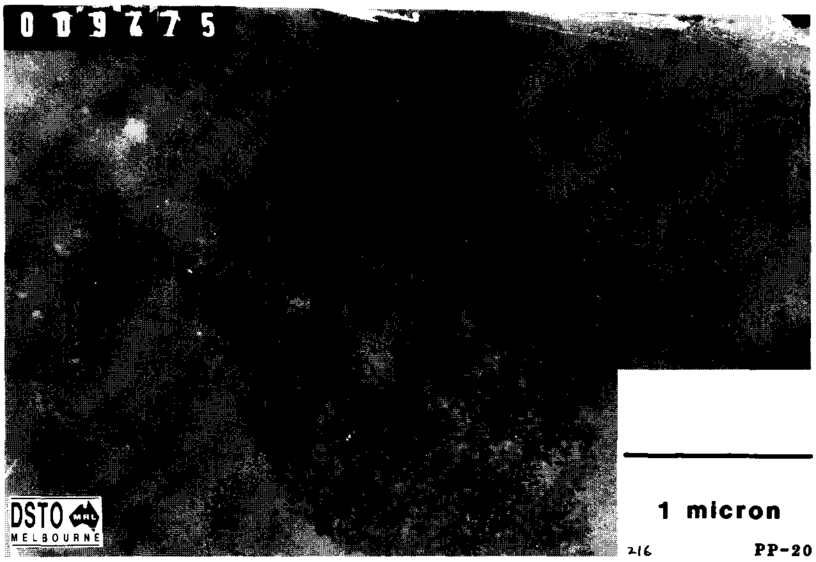


Figure 11 A typical TEM micrograph of section from a TGMDA–PIPIP–CTBN (20 phr) casting showing the small particle size and uneven distribution of the precipitated rubber

Earlier studies on DGEBA systems indicated only a small dependence of fracture energy on rubber particle size[6], but a more extensive study has shown that fracture energy is strongly influenced by particle size[38] and that small particles are more efficient in producing a toughening effect than large particles. The optimal size is suggested to be 0.5 to 5 µm (ref. 3). This is the situation when rubber cavitation–matrix shear banding is the toughening mechanism and is dependent on the ductility of the matrix being sufficient to permit shear yielding. This is so for DGEBA but is very doubtful for TGMDA, which is significantly more brittle. (Neat resin values of G_{Ic} are about 300 J m^{-2} for DGEBA and 150 J m^{-2} for TGMDA, both cured with piperidine, or about 40 J m^{-2} for TGMDA–DDS.) Further, the toughenability of a matrix is dependent on its brittleness, i.e. not only is a more ductile matrix tougher than a less ductile one, but its toughness can be more readily enhanced by the presence of a dispersed rubber phase[6,33,39].

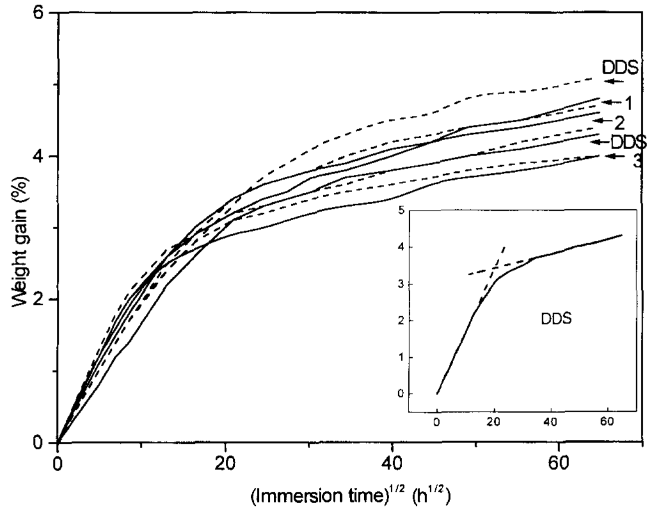


Figure 12 Weight gain in water of toughened (——) and untoughened (- - -) TGMDA resins hardened with DDS and the piperidine 'adducts': PIPIP (1), TGMDA–PIP (2) and DGEBA–PIP (3)

The morphology of rubber–epoxy systems is influenced by the extent of incompatibility between rubber modifier and the matrix resin, by the rate of rubber precipitation and particle growth, and by the rate of increase of matrix viscosity up to gelation, inhibiting particle movement[40,41]. These factors are also associated with the volume fraction of the second phase, i.e. the completeness of separation of the rubber from the epoxy phase and the amount of epoxy caught up in the rubber phase. The former has an important bearing on the ductility of the matrix and on the T_g and overall modulus, while the latter affects the rubber phase modulus and cavitation. For a very brittle material like TGMDA a very small amount of rubber left dissolved in the epoxy phase would be advantageous to enhance its shear yielding ability, but the amount must be small to minimize the deleterious effect that dissolved rubber would have on the T_g. Manipulation of the cure temperature regime would be a way of fine tuning this balance[40]. The effect of these opposing factors can be seen in *Tables 2*, 4 and *5*. For some systems (piperidine, TGMDA–PIP and PIPIP) a three- to fivefold increase in G_{Ic} was obtained with 20 phr CTBN at the expense of up to 2°C in T_g and approaching a 50% reduction in tensile modulus. Other systems, such as P14MePIP, were tougher but of substantially lower T_g. Although CTBN-modified systems are normally characterized by discrete spherical particles (as in *Figure 10*), *Figure 11* shows that the rubber precipitates from TGMDA–PIPIP in irregular agglomerates. The effect and significance of this is unclear.

Moisture absorption

One of the major concerns about TGMDA (or other epoxy) based systems is the reduction in T_g that accompanies water absorption. The rates and extents of weight change, at 50°C over a period of 25 weeks, of cured piperidine-based systems, with and without 20 phr X-13 CTBN, were compared to comparable DDS systems. *Figure 12* shows the overall results and, in the inset, the detail for one system (TGMDA–DDS). All samples displayed broadly similar behaviour; when the weight change was plotted assuming Fickian absorption the curves appeared to show two distinct linear regions with an initial stage, up to about 1 week, after which the rate of water uptake slowed. Generally in the first stage the rubber-containing system gained weight at a slightly faster rate than the corresponding unmodified material, but there were only slight differences at the end of the experiment, when all the systems showed 4 to 5% weight gain (although none had reached equilibrium). The most notable finding is the difference between the modified and unmodified DDS-cured material.

Moisture uptake by TGMDA has been examined by Lau *et al.*[36,42] using diaminodiphenylmethane (DDM) as the hardener. They noted that the rate of uptake depended on the crosslink density but the mode of water absorption did not follow simple Fickian behaviour. They found between 4 and 6% absorbed water, depending on the cure cycle, after equilibration at 40°C. In the present case equilibrium water content has not been determined although there are suggestions that there are two Fickian mechanisms, and that the main differences lie in the early water uptake, with the longer-term moisture behaviour common to all the tested materials. It was not possible to determine T_g of the wet material in t.m.a. runs (expansion or penetration) because of the dimensional instability of the samples—resulting from concurrent drying, stress relaxation, ageing and related effects—although it was noted that the overall effect of these factors was appreciably greater in the DDS-cured materials. It seems probable that the chosen piperidine–TGMDA systems would ultimately take up less water than the modified DDS material and be less affected by the absorption. While it is interesting to speculate that the initial rapid uptake is associated with 'free' water and that there are more defects in the interfacial regions between the relatively weakly bonded inclusion and matrix in the DDS system, no conclusions can be drawn from these initial findings.

Latency

For practical reasons associated with the use of TGMDA in prepregs, candidate curing agents need to possess good latency, i.e. minimal reaction at room temperature. In preliminary studies the latency of a urea (PIPIP) and an amino alcohol (TGMDA–PIP) have been compared to DDS in untoughened resin formulations. Mixtures of TGMDA and the selected curing agents were prepared as suspensions (by milling) and solutions (by stirring at 130°C until dissolved) and stored under ambient conditions. The extent of reaction was assessed at intervals by measuring the decrease of TGMDA monomer—some 60–70% of the 'fresh' MY720 is monomer. The results presented in *Figure 13* show that PIPIP compares very favourably to DDS in suspension and, as expected, both are more latent in suspension. In contrast, the non-volatile TGMDA–piperidine adduct is relatively reactive at ambient temperature and appears to offer little advantage over piperidine (although the direct comparison has not been made) in terms of latency, and would thus be less attractive to the aerospace industry. The latency of dissolved DDS and PIPIP is remarkably similar, and this suggests that there is relatively little reaction during

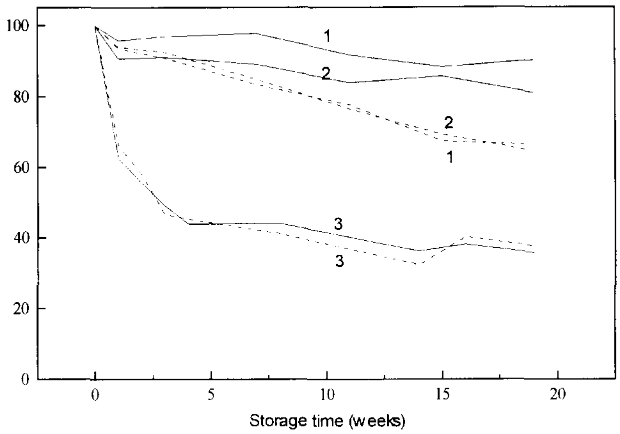


Figure 13 The residual TGMDA monomer content of mixtures of TGMDA and PIPIP (1), DDS (2) and TGMDA–PIP (3) stored under ambient conditions: hardener incorporated by milling (——) or dissolution (– – –)

solution and that the subsequent advancement is largely homopolymerization even for the DDS mix.

SUMMARY AND CONCLUSIONS

A preliminary study to establish the practicality of rubber toughening TGMDA-based resin systems has shown that formulations cured with piperidine are more amenable to toughening by addition of CTBN than DDS-hardened systems. Piperidine is too volatile, odorous, reactive and toxic to be attractive as a curing agent, but these disadvantages can be overcome by reacting it with epoxides or isocyanates—to form amino alcohols and ureas respectively—which are equally effective catalysts for the homopolymerization of TGMDA. The various 'adducts' lead to similar cured products with some differences of T_g, tensile and fracture properties, which are attributed to relatively slight changes in crosslinking density arising from functionality differences in the adducting reagents and possibly from subtle differences in chain termination and transfer reactions during the homopolymerization.

The best fracture properties were obtained by pre-reacting phenyl glycidyl ether with piperidine, but the improved performance was offset by a somewhat lower T_g; the best compromise was shown by the urea PIPIP (phenyl isocyanate and piperidine), which gave—with 20 phr X-13 CTBN—a T_g of 170°C, G_{Ic} of 670–910 J m^{-2}, good latency and low water absorbance, but with some reduction of tensile strength (61 MPa) and modulus (2.0 GPa). This can be compared to the corresponding DDS system, which had much lower G_{Ic} (120 J m^{-2}), similar strength and modulus (62 MPa and 2.4 GPa) and latency, absorbed more water but had higher T_g (200°C). However, the PIPIP-cured system is fully cured whereas the DDS system has temperature-limited cure and has the potential for further reaction, embrittlement and increased T_g.

The CTBN-toughened piperidine-cured TGMDA systems are characterized by the very small size of the precipitated rubbery phase particles, although the T_g is effectively unchanged when up to 20 phr CTBN is added (indicating a discrete second phase); in some cases the castings are transparent. In contrast to micrographs of the DDS system, which show a bimodal distribution of relatively large and poorly bonded rubber particles, those of the piperidine-cured systems show that the very small rubber particles are not evenly distributed. It has not been possible to characterize the size, distribution or mode of fracture of these inclusions. The marked difference between toughened and untoughened DDS–TGMDA with respect to water absorption may be indicative of a weak interface between the two phases in this system. If this is the case, then the very similar water uptake of modified and unmodified PIPIP–TGMDA may be significant. Unfortunately the reasons for opacity and clarity of the castings is not known, and it has not yet been possible to control the morphology of the two phases of TGMDA cured with piperidine adducts by control of the cure schedule, or CTBN and adduct type and concentration.

The optimum level of CTBN appeared to be between 15 and 20 phr and an equivalent concentration of 5 phr piperidine gave a fully cured product. Piperidine offers a level of activity that matches that of TGMDA, so that a well controlled reaction (in effective latent systems) is possible without excessive exotherm, in marked contrast to, for example, dimethylamine (as Monuron). Other related secondary amines are either inactive catalysts for the homopolymerization (di-n-butylamine, morpholine, piperazine) or offer no advantage over piperidine (pyrrolidine, 4-methylpiperidine).

The potential for improving the fracture properties of TGMDA resins by the addition of CTBN rubbers as a second phase, and the practicality of using an 'adducted' form of piperidine as a curing agent, have been established. The G_{Ic} for TGMDA–PIP is four times greater than that for TGMDA–DDS, but G_{Ic} for TGMDA–PIPIP–X-13 CTBN (20 phr) is 24 times that of the base TGMDA–DDS system and seven times that of a modified system.

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