Toughening procedures, processing and performance of bismaleimide–carbon fibre composites*

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Toughening procedures, processing optimization and performance evaluation of bismaleimide (BMI)–carbon fibre composites are reported. The BMI matrix was 4,4'-bismaleimidodiphenylmethane (BMPM)/*O*,*O'*-diallyl bisphenol A (DABPA). Toughening procedures involved (i) characterization and optimization of the BMI cure reactions to produce 'defect-free', fully cured crosslinked networks, and (ii) incorporation of viscoelastic toughening poly(ether imide) (PEI) particulates and film interleaves and crack deflector Kevlar 49 whiskers into the BMI–carbon fibre composites. Optimization of composite processing conditions is reported. The effects of toughening procedures on composite performance in terms of G_{Ic} toughness, impact penetration, compression after impact and open hole compression as a function of temperature are discussed. The conflicting requirements of these performance tests upon desirable polymer matrix properties are critically discussed.

(Keywords: bismaleimides; cure reactions; network structure; toughening; composite processing; composite performance)

INTRODUCTION

Future commercial and military aircraft require structural polymer matrix–fibre composites that exhibit good composite (i) high-temperature/high-moisture ('hot–wet') properties, (ii) processibility and (iii) mechanical performance over long time periods. High-temperature composite matrices such as thermoplastic polyimides have exhibited both processing and toughness limitations, whereas thermoset bismaleimides (BMI) are more processible but have exhibited a more brittle mechanical response.

The two principal mechanisms for toughening carbon fibre–polymer matrix composites involve (i) polymer matrix viscoelastic flow and (ii) crack deflection by the incorporation of microscopic second-phase additives into the polymer matrix.

For high-T_g polymer matrices, because of increasing yield stress with decreasing temperature below T_g, high yield stresses under service environment conditions limit viscoelastic flow. Optimization of viscoelastic flow in a crosslinked, thermoset matrix, in addition, requires a fully reacted defect-free network[1]. Networks containing defects in the form of unreacted groups cause overloading and network segmental chain scission at lower strains that ultimately transforms into crack formation and propagation early in the deformation process, which truncates significant viscoelastic flow. Hence, there is a need to characterize the cure reactions and kinetics involved in the formation of BMI networks, in order to optimize network structure for high toughness. Also, a ductile, second-phase, lower-yield-stress, thermoplastic additive that deforms viscoelastically can circumvent the yield stress–temperature dependence dilemma of the polymer matrix continuous phase[2].

Small, submicrometre additives, with dimensions well below the critical matrix flaw size, can cause a tortuous crack propagation path in the polymer matrix, resulting in an increased matrix fracture energy. Appropriately oriented organic micro-whiskers that readily split longitudinally, and which are incorporated in the composite inter-fibre tow regions, would seem the most promising from a surface energetic viewpoint.

The specific objectives of this study were (i) to toughen BMI–carbon fibre composites, while maintaining their processibility and thermal properties, and (ii) to seek correlations between toughening procedures and the desired, practical service performance properties.

Our studies were based on 4,4'-bismaleimidodiphenylmethane (BMPM)/*O*,*O'*-diallyl bisphenol A (DABPA) systems (Matrimid 5292, Ciba-Geigy) (*Figure 1*). The

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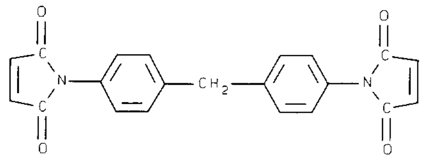
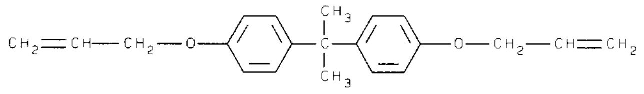


4,4′-Bismaleimidodiphenylmethane



O,O′-Diallyl Bisphenol A

Figure 1 The chemical structures of BMPM and DABPA monomers

toughening procedures, composite processing areas and service performance evaluation studies were as follows:

(i) Toughening procedures involved (a) characterization of the BMI cure reactions in order to produce 'defect-free' crosslinked networks based on full chemical cure, and (b) incorporation of viscoelastic toughening poly(ether imide) (PEI) particulates and film interleaves and, also, crack deflector Kevlar 49 whiskers into BMI–carbon fibre composites.

(ii) Composite processing optimization involved the composite prepreg, lamination and post-cure conditions.

(iii) Composite service performance evaluation involved G_{Ic} toughness, impact penetration, compression after impact and open hole compression as a function of temperature.

EXPERIMENTAL

Materials

The BMI resin system utilized was the BMPM/DABPA (1:1 molar ratio) (Ciba-Geigy) system (*Figure 1*). (BMI resin toughness has been reported[3] to be higher at a BMPM/DABPA molar ratio of 2:1.) AS4 carbon fibres (Hercules), 6000 filaments per tow with a sizing, were used to fabricate composites.

Kevlar 49 micro-whiskers were manufactured from Kevlar 49 fibres. Kevlar 60 nm diameter microfibrils were fabricated in two stages. Kevlar short fibres were first obtained by acid-induced hydrolytic degradation through the fibre fast periodic transverse diffusion planes[4,5]. Kevlar 49 fibres were refluxed at 100–105°C with a 37 wt% HCl aqueous solution for 52 h and the short fibres were then collected on a filter paper and dried. In the second stage the short fibres were ball-milled to produce submicrometre micro-whiskers.

PEI (Ultem, General Electric) thermoplastic, T_g ~210°C, was incorporated into the composite as a particulate or interleaf toughening agent.

Methods

The characterization of the cure reactions was carried out by systematic Fourier-transform infra-red spectroscopy (*F*Ti.r., Nicolet) and differential scanning calorimetry (10°C min^{-1}, N_2 atmosphere) (d.s.c., DuPont 910) as a function of cure conditions and BMPM/DABPA composition. Molecular models (CPK Atomic Models) were utilized to ascertain the steric viability of possible network structural entities.

The viscosity (η)–time–temperature characteristics of the BMPM/DABPA BMI resin and those resins containing toughening agents were optimized for prepregging and lamination composite processing conditions by viscometry (Brookfield Viscometer) and dynamic mechanical analyses (d.m.a., DuPont 982). Composite prepregs were prepared at a resin pot temperature of 90°C (Research Tool Prepregger). Composite laminates were fabricated in 'clam-shaped' moulds (miniclave) in a press in which the temperature, pressure and vacuum imposed on the composite can be controlled (Tetrahedron Press).

G_{Ic} mode I interlaminar toughness measurements were carried out on BMPM/DABPA (1:1 molar)–AS4 carbon fibre composite specimens with a $(0°)_{24}$ configuration. The test specimens were 1 inch wide and 6 inch long (2.5 cm x 15 cm) with a central 1/2 inch (~13 mm) Teflon spacer. G_{Ic} is determined from the equation[6]:

$$G_{Ic}=\frac{1}{2b\Delta C}(P_1\delta_2-P_2\delta_1) \qquad (1)$$

where b is specimen width, ΔC is the crack growth distance between recorded data points, P is the load and δ is the crack opening width. The crack was propagated from the Teflon spacer by stressing the specimen in an Instron testing machine, and the crack growth characteristics were monitored by VCR (video) coverage.

The composite impact energy absorption characteristics for penetration impact were determined by a Rheometrics High Rate Impact Tester, 1/2 inch diameter (~13 mm) semi-spherical impacter, with an associated computer data monitoring acquisition system. The composites had $[0/90]_8$ geometric laminate configurations.

Compression after impact tests (CAI) were conducted on composite panels with a $(45/0/-45/90)_{4s}$ geometric configuration (Boeing B557260 Test, Class 1 Impact). Impact was performed on a 4 inch x 6 inch (10 cm x 15 cm) laminate with an impact energy level of 680 kg. Subsequent compression testing was performed on the impacted composite laminates. Prior to testing, two strain gauges were applied onto the laminate for the purpose of detecting laminate buckling.

Open hole compression testing was conducted on a 3 inch x 1 inch (7.5 cm x 2.5 cm) untabbed composite with a $(\pm 45/90/0_2/\pm 45/0_2/\pm 45/0)_s$ geometric configuration and a 1/4 inch (~6.5 mm) hole in the middle of the specimen. Prior to testing, specimens were subjected to moisture conditioning by placing the specimens in boiling water for 4 days. The conditioned specimens were tested in the 23–177°C temperature range.

Composite damage and failure modes were monitored by both ultrasonic C-scan (Physical Acoustics) and scanning electron microscopy (SEM) (Amray).

RESULTS AND DISCUSSION

Toughening procedures

Cure reactions. Systematic *F*Ti.r. and d.s.c. studies of the cure reactions of the BMPM/DABPA BMI resin system as a function of chemical composition and temperature–time cure conditions, together with literature data, led to the following findings[7–9].

There are three principal temperature regimes associated with the cure reactions, namely (i) 100–200°C range, (ii) 200–300°C range and (iii) 300–350°C range. In *Figure 2* a d.s.c. plot of a BMPM/DABPA (1:1 molar)–AS4 carbon fibre composite prepreg exhibits exotherm peaks in each of the three regimes.

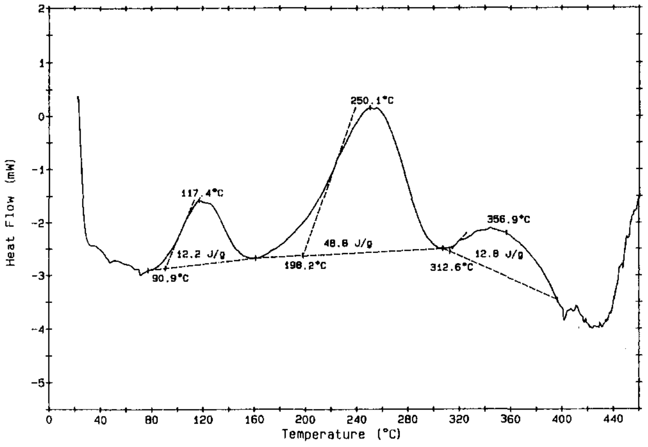
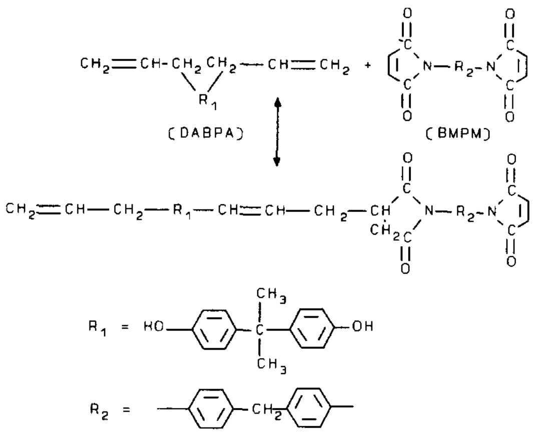


Figure 2 D.s.c. plot of BMPM/DABPA (1:1 molar)–AS4 carbon fibre composite prepreg

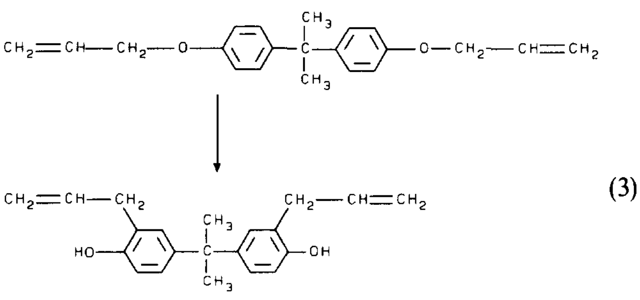
(i) In regime (i) in the 100–200°C range the 'ene' reaction (2) occurs slowly and there is evidence that it may be reversible. Gel permeation chromatography indicates that only a small molecular-weight increase occurs (from 520 to 680) for the BMPM/DABPA system after 16 h at 100°C. Viscosity–time–temperature observations indicate that this reaction only occurs at significant rates above 180°C.

'Ene reaction



(2)

Prior to the 'ene' reaction the *O,O′*-diallyl bisphenol A (DABPA) rearranges upon heating via the Claisen rearrangement to form the allyl phenol form:



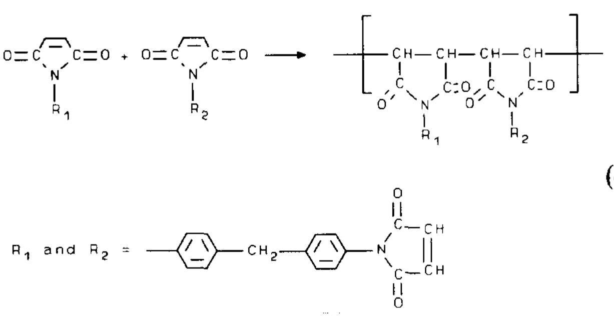
(3)

(ii) In regime (ii) in the 200–300°C range a number of chemical reactions occur in the following sequence:

(a) The 'ene' reaction (2) occurs at a significant rate.

(b) BMPM homopolymerization, reaction (4), occurs.

BMPM homopolymerization



(4)

or a longer-chain 'ene' reaction product

A d.s.c. plot of the BMPM monomer alone exhibits a reaction peak centred in the 205–210°C range.

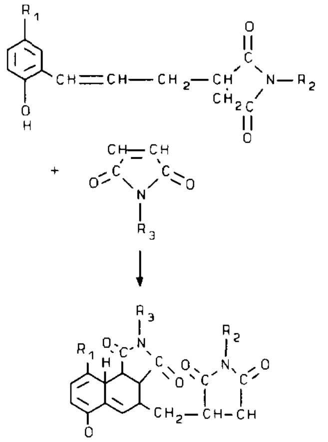
(c) At higher temperatures both 'ene' homopolymerization, reaction (5), and 'ene'–BMI double-bond crosslinking polymerization (Diels–Alder reaction), reaction (6), occur as indicated by the d.s.c. peak centred at 254°C for the prepreg in *Figure 2*. A low-temperature shoulder exhibited by this peak is associated with BMPM homopolymerization.

'Ene' homopolymerization

$$n\,R_1\text{—}CH{=}CHR_2 \longrightarrow \text{—}\!\left(R_1CH\text{—}CHR_2\right)_n\!\text{—} \qquad (5)$$

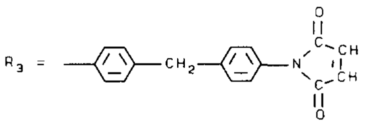
where R_1 and R_2 are chain continuations of the 'prepolymer' formed in the 'ene' reaction

Diels–Alder reaction



(6)

where R_1 and R_2 are chain continuations of the 'prepolymer' formed in the 'ene' reaction, and



or a longer-chain 'ene' reaction product

(d) Above 240°C, dehydration of the hydroxyl groups of the DABPA starts to occur to form ether crosslinks, reaction (7).

$$HO\text{—}R\text{—}OH + HO\text{—}R\text{—}OH \longrightarrow HO\text{—}R\text{—}O\text{—}R\text{—}OH \qquad (7)$$

where R = polymer chains formed from reactions (2) through (6)

A d.s.c. plot of the DABPA monomer alone starts to exhibit thermal activity above 240°C, associated with dehydration. There is no indication of the Claisen rearrangement in the d.s.c. plot. T.g.a. weight loss and *FT*i.r. studies confirm that ~75% of hydroxyl groups undergo dehydration with an associated 1.8 wt% H_2O loss in this temperature region. In *Figure 3* a simultaneous decrease in the i.r. hydroxyl band ($3473\,cm^{-1}$) and increase in the i.r. ether band ($1179\,cm^{-1}$) for the BMPM/DABPA BMI resin system as a function of cure time at 250°C is observed. In *Figure 4* t.g.a. and d.s.c. plots for the BMI resin also reveal a 1.8 wt% loss and maximum cure activity near 250°C.

(iii) In regime (iii) in the 300–350°C range further cure occurs as the specimen cure temperature exceeds the T_g of the resin. It is important from the network-toughness viewpoint that the reaction is allowed to proceed to completion, thus eliminating network defects in the form of unreacted groups[1]. D.s.c. studies as a function of post-cure conditions on BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites $(0°)_5$ indicate that the crosslinked network structure only attains full cure after a 300°C/2 h post-cure with a final T_g near 350°C (*Table 1*). However, the high post-cure temperature does result in transverse resin microcracking in 0/90° composites.

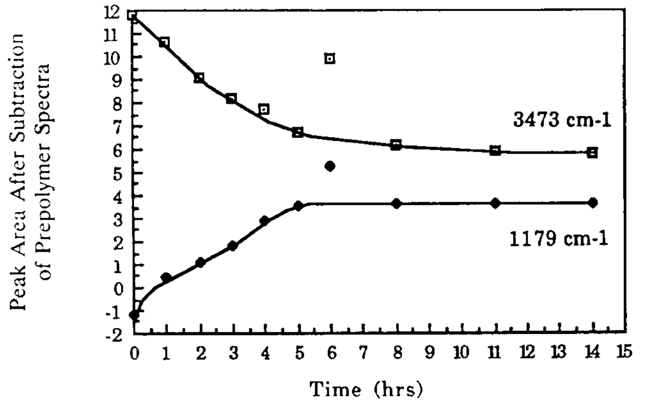


Figure 3 I.r. hydroxyl ($3473\,cm^{-1}$) and ether ($1179\,cm^{-1}$) band relative intensities for BMPM/DABPA (1:1 molar) BMI resin as a function of cure time at 250°C

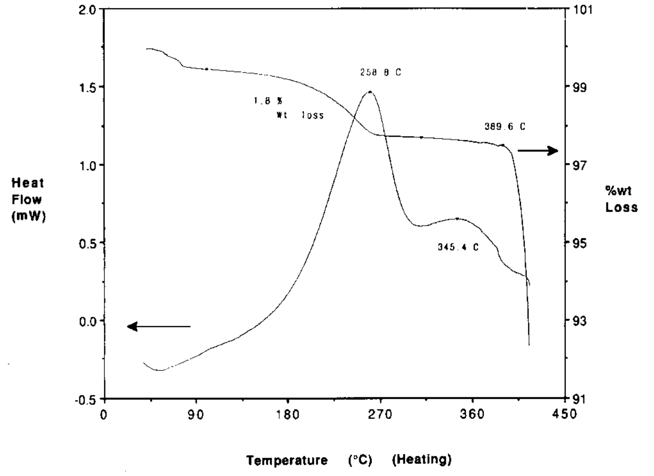


Figure 4 T.g.a./d.s.c. plots of BMPM/DABPA (1:1 molar) BMI resin in a N_2 atmosphere at a heating rate of $10°C\,min^{-1}$

Table 1 T_g *versus* cure conditions for BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites $(0°)_5$

Specimen	Post-cure cycle	T_g (°C)
1 Prepreg (4 ply)	None	313
2 Composite	200°C/2 h; 250°C/6 h	323
3 Composite	200°C/2 h; 250°C/6 h; 300°C/1 h	347
4 Composite	200°C/2 h; 250°C/6 h; 300°C/1 h	353

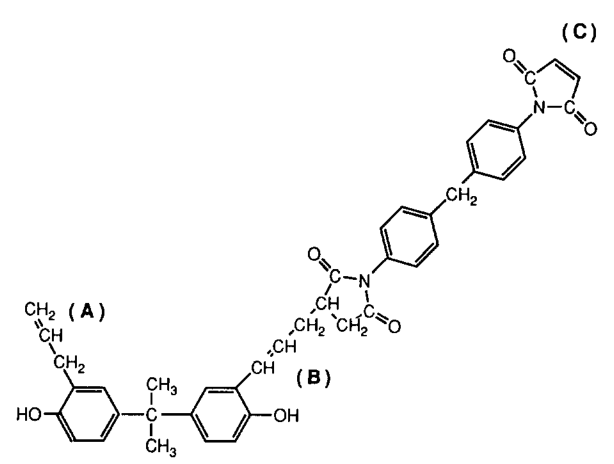


Figure 5 The chemical structure of the BMPM/DABPA 'ene' adduct prepolymer. (A), (B) and (C) are active double bonds capable of polymerization

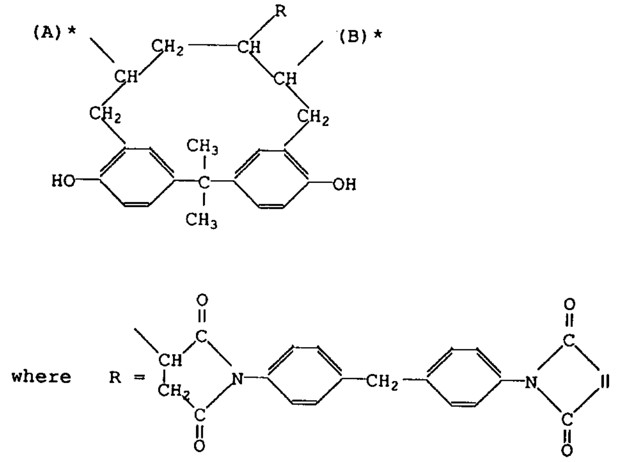
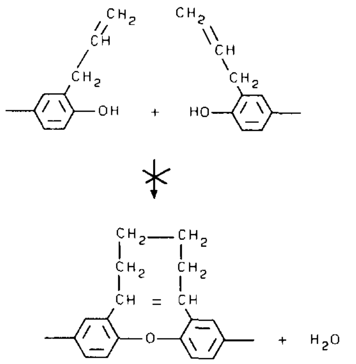


Figure 6 Intramolecular cyclization via (A)–(B) double bonds of an 'ene' molecule. (The (A)* and (B)* are structural intermolecular connections to neighbouring 'ene' molecules)

BMI network modelling. Based on our understanding of the BMPM/DABPA cure reactions, network molecular modelling studies were carried out. The chemical structure of the BMPM/DABPA 'ene' adduct is illustrated in *Figure 5*. The 'ene' adduct is pentafunctional as a result of (i) three double bonds, capable of chain extension and crosslinking, designated (A), (B) and (C) in *Figure 5*, and (ii) two hydroxyl groups capable of etherification by hydroxyl dehydration.

For the pentafunctional 'ene' molecule to achieve nearly full cure would require sequential polymerization of all three double bonds. Molecular models indicate that inter- and intramolecular double-bond polymerization via the (A) and (B) double bonds of the 'ene' molecule is sterically possible. In *Figure 6*, the 'ene' molecule intramolecular cyclic structure as a result of (A)–(B) intra- and intermolecular polymerization is illustrated.

Molecular models also indicate that synergistic ring formations by two 'ene' molecules reacting via (A) and (B) double bonds and adjacent hydroxyl groups, reaction (8), is not sterically possible.



(8)

Based on the molecular modelling studies, network formation could occur by the formation of ring chains via (A)-(B)-(A)-(B) and (C)-(C) double-bond polymerization (*Figure 7*), followed by ring chain crosslinking via etherification by hydroxyl group dehydration.

Thermoplastic toughening. Thermoplastics such as poly(ether imide) and poly(arylene ethers) have been used[10–13] to toughen BMIs with variable improvement. The thermoplastic additive usually compromises the T_g, modulus, processibility and organic solvent susceptibility of the BMI resin. The concentration of thermoplastic additive, its morphological characteristics within the BMI and its molecular weight are all critical factors that modify BMI toughness. The specific type of composite deformation and failure mode and the effect of BMI toughening procedures and compromises upon overall composite performance have not all been addressed.

PEI was chosen as the thermoplastic toughening agent because its solubility in methylene chloride allowed (i) intimate mixing of the PEI with the DABPA unreacted monomer for PEI particulate formation within the composite matrix during processing, and (ii) the casting of PEI sheets from solution to serve as composite interleaves.

For the introduction of PEI particulates into the BMPM/DABPA BMI resin, the PEI was dissolved in methylene chloride with the appropriate amount of DABPA (BMPM is not soluble in methylene chloride). Then the methylene chloride was evaporated at 40°C and the DABPA/PEI is mixed with the BMPM at 130°C to form a mixture amenable to composite prepregging.

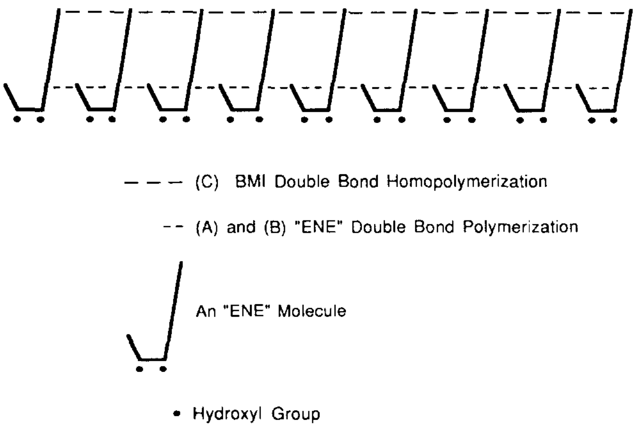


Figure 7 Ring chain structure from 'ene' double-bond polymerization

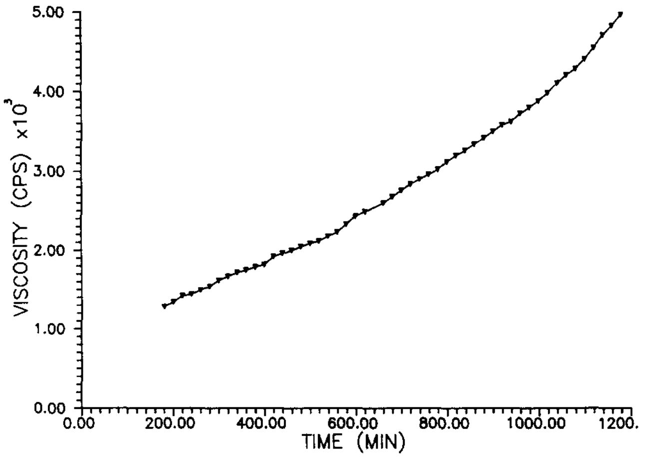


Figure 8 Isothermal viscosity changes *versus* time, at 91°C, for BMPM/DABPA (1:1 molar) BMI resin

For PEI composite interleaves, thin sheets (0.025–0.050 mm thick) were formed by casting from PEI–methylene chloride solutions. Commercially available PEI sheets, PEI 1000 and PEI 5000, 0.025 mm thick with T_g values of 217 and 225°C, respectively, were also used.

The incorporation of PEI particulates and sheets into the composite is described in the following composite fabrication section.

Kevlar 49 whisker crack deflectors. Organic, liquid-crystal Kevlar 49 based whiskers with submicrometre diameters that readily fibrillate could add an additional synergistic composite toughening mode to complement BMI network structure optimization, and PEI thermoplastic toughening.

Composite processing

For any polymer matrix materials developments to be successful in terms of composite performance requires that such materials modifications meet limitations imposed by the physical, chemical and rheological composite processing requirements.

Prepregging. Isothermal viscosity profiles in the 85–95°C prepregging temperature range indicate that initial viscosities of the BMPM/DABPA (1:1 molar) resin are in the 700–1200 cP range and only increase slowly with time. For example, the viscosity of the BMPM/DABPA (1:1 molar) system only increases to 5000 cP after 1200 min at 91°C, thus indicating adequate viscosity–time profiles for prepregging in the 85–95°C temperature range (*Figure 8*). The addition of ~10 wt% toughening agents such as PEI or Kevlar whiskers causes the viscosity of the BMPM/DABPA (1:1 molar) system to increase to nearly 5000 cP at 90°C. Satisfactory prepregs were fabricated for the toughened systems despite the higher viscosities.

The BMPM/DABPA systems were prepregged with adjustable wedge slit dies each developed specifically for 3000, 6000 and 12 000 filament tow AS4 carbon fibres. The carbon fibres contain epoxide sizings[14], which would chemically degrade during post-cure conditions of the BMI composite, causing poor fibre–matrix interface integrity. Hence, during the prepreg process the sizing is burnt off the fibre at 400°C in air. (This thermal processing condition is based on systematic t.g.a.-based weight loss studies as a function of heating rate and temperature.)

The prepregs were characterized for reproducibility in terms of (i) resin weight percentage, (ii) fibre areal weight, (iii) prepreg areal weight and (iv) fibre volume fraction (V_f). The resin weight percentage was determined from the densities of fibre and matrix.

Lamination. The optimization of conditions to fabricate the BMPM/DABPA (1:1 molar) BMI–carbon fibre composites from unidirectional prepreg is critical for meaningful evaluation of the resin toughening procedures on composite performance.

The composite prepreg 'lay-ups' were laminated into composites at 177°C. The viscosity–time–temperature characteristics of the resin were monitored by direct viscosity–time–temperature measurements and d.m.a. The d.m.a. plots exhibited broad minima in damping in the 160–190°C temperature range, which suggests a relatively constant viscosity for adequate time periods to achieve laminate consolidation and associated controlled composite resin and void content. In *Figure 9*, the BMI resin viscosity in the absence of carbon fibres is shown as a function of temperature (100–185°C) and exhibits a minimum near 160°C as a result of competing viscosity decreases with increasing temperature and increases as a result of cure reaction-induced molecular-weight increases. Based on this type of data, optimum composite laminate conditions, shown in *Figure 10*, were developed. These lamination conditions were further optimized for the toughened composite systems. The quality of the laminates was characterized by (i) H_2SO_4 acid digestion–density measurements, giving void contents in the 0.64–1.01% range, (ii) SEMs of polished composite surfaces, (iii) ultrasonic C-scan and (iv) d.m.a. The laminates fabricated were of standard acceptable quality, with the exception of some of the thicker laminates that contained toughening PEI interleaves or Kevlar 49 whiskers, which exhibited a higher degree of porosity and/or surface undulations.

The viscosity in the 110–170°C temperature range of the BMPM/DABPA (1:1 molar) BMI resin containing 8–10 wt% PEI was observed to increase ~6× faster during cure than in the absence of PEI, which suggests that the BMI resin system actually reacts chemically with the PEI. Also, for this PEI-modified BMI system a T_g associated with the PEI in the 210°C region indicates that the PEI, at least in part, exists as a separate phase within the BMI resin. SEMs of composite fracture topographies reveal PEI particulates in the 1 μm diameter range.

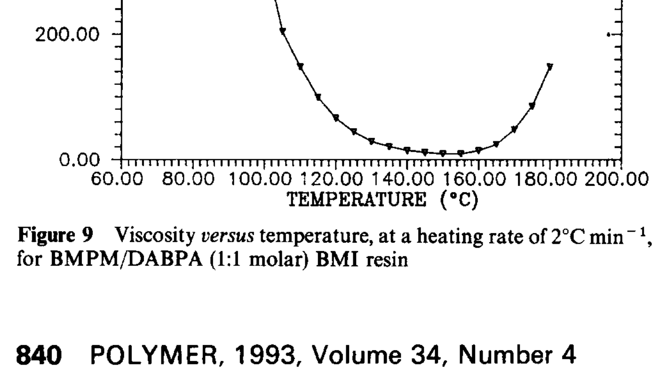


Figure 9 Viscosity *versus* temperature, at a heating rate of 2°C min^{-1}, for BMPM/DABPA (1:1 molar) BMI resin

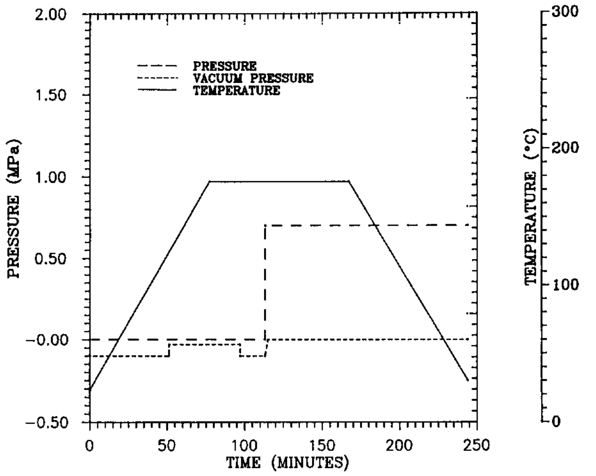


Figure 10 Optimum composite lamination conditions for BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites

For BMPM/DABPA (1:1 molar)–AS4 carbon fibre–PEI interleaf composite $[0/\overline{PEI}/90]_{4s}$ laminates, unusual porosity patterns were observed in ultrasonic C-scans (*Figure 11*). It was subsequently established that such composite porosity was eliminated by preannealing the PEI interleaves at 250°C, which caused ~25% shrinkage of the PEI. Relaxation of fabrication strains in the PEI interleaves evidently caused cavitation within the composite interleaf during lamination and post-cure.

Composite performance

The BMI polymer matrix toughening procedures were evaluated in terms of the following critical mechanical property service performance composite evaluation measurements.

G_{Ic} toughness. For a 300°C post-cured composite and resultant T_g near 350°C, the baseline 23°C G_{Ic} values were 330 J m^{-2}. Post-curing at 300°C did not deteriorate the 23°C G_{Ic} toughness relative to post-curing at 250°C despite a 30°C increase in the resin T_g (see *Table 1*). This observation suggests that the BMI resin is toughened after a 300°C post-cure as a result of a more fully cured 'defect-free' crosslinked network. (It is assumed that for a constant test temperature of 23°C a polymeric matrix with a higher T_g would be more brittle as the test temperature is further from the T_g if there were no modifications of the crosslinked network structure.)

For composite fibre volume fractions of ~65% the incorporation of PEI particulates increased G_{Ic} values ~30% for a 300°C post-cured composite. The PEI particulates in this composite deformation mode act as viscoelastic crack bridgers, based on the PEI fibrillation observed by SEM in the composite fracture topographies.

With PEI interleaves the composite G_{Ic} was ~20% greater than for the unmodified composite. (However, the fibre volume fractions for these composites were only near 50% compared to ~65% for the unmodified composites.) We observed that there is a 5% decrease in G_{Ic} toughness for a 1% increase in fibre volume fraction (V_f) in the 63–71% V_f range.

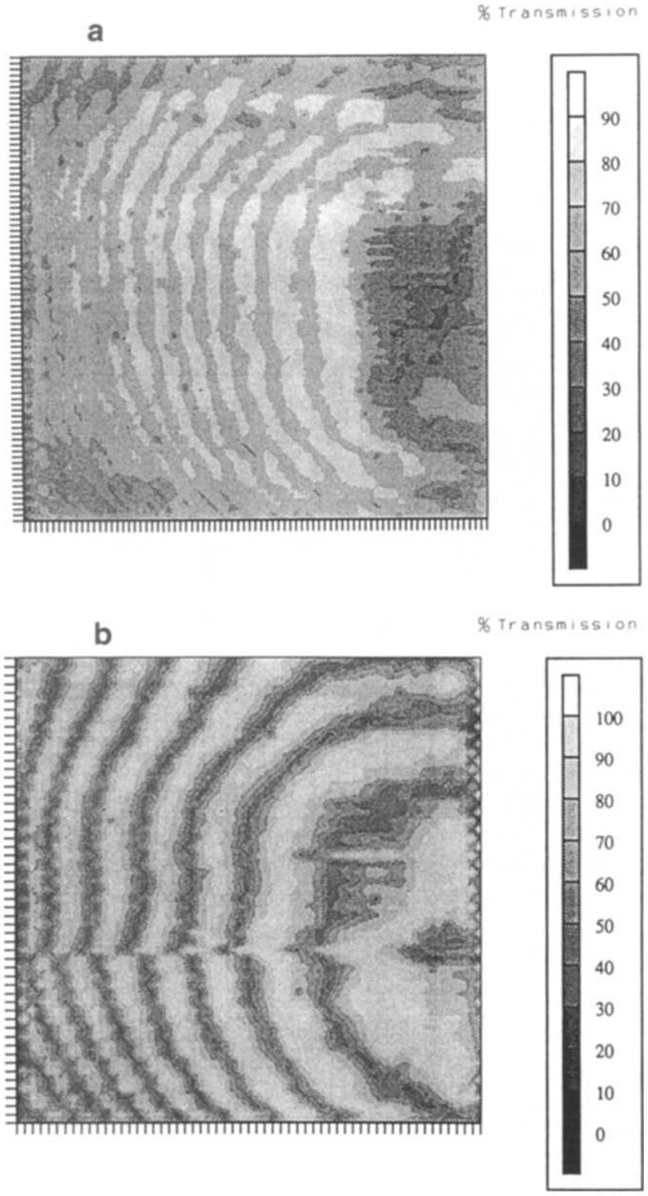


Figure 11 Ultrasonic C-scans (signal amplitude received from echo travelling back through the laminate thickness; 5 MHz probe) of BMPM/DABPA (1:1 molar)–AS4 carbon fibre–PEI interleaf composite $[0/\overline{\text{PEI}}/90]_{4s}$ laminate (a) non-post-cured and (b) post-cured at 200°C for 2 h and 250°C for 6 h

For BMI composite matrices containing 8.6 wt% Kevlar 49 whiskers, the composite G_{Ic} was increased 15% for a composite V_f of 66.5%. However, in the notched G_{Ic} test the crack propagation initiation stress was 25% lower for Kevlar 49 whisker-modified composites compared with that of the unmodified BMI composite. This observation implies that whisker clusters, which also possess a poor whisker–polymer matrix interfacial adhesion, allow easier crack initiation but do cause a more tortuous propagation path once the crack propagates. In the case of both PEI particulate- and interleaf-modified composites, the G_{Ic} crack propagation initiation stress was increased 25% compared with the unmodified BMI composite as a result of enhanced 'energy-absorbing' PEI viscoelastic flow during the slow crack growth initiation process.

Impact penetration. For impact penetration the average normalized total impact energies were similar for all types of 'toughened' BMI composites (~60–65% V_f), with the exception of the PEI interleaf composite (~50% V_f), which exhibited a 20% greater impact energy. In *Figure 12*, the force–displacement plots that were used to ascertain the total impact penetration energies are illustrated. The majority of the energy in impact penetration involves fibre fracture, with matrix interlaminar deformation only playing a significant role in the outer layer of the specimen through backface delamination.

Residual properties after impact. The unmodified BMPM/DABPA (1:1 molar)–AS4 carbon fibre composite exhibited low compressive strength after impact of 98.5 MPa (generally a value of 200 MPa is acceptable) (*Figure 13*). The low compressive strength value is attributed to composite fabrication strains as a result of further resin shrinkage and microcracking as a result of the high composite post-cure temperatures. However, BMI–carbon fibre composites cured at lower temperatures will thermally age at 190°C and lose 50% of their impact energy[15] as a result of further curing and associated resin shrinkage and microcracking. (BMI composites could be exposed to service temperatures of 190°C in future commercial high-speed civil aircraft[16].)

Interleaf PEI toughening was the most successful in enhancing the compressive strength after impact to over 200 MPa (232.9 MPa) for the high temperature post-cured BMI composite. The other toughening procedures

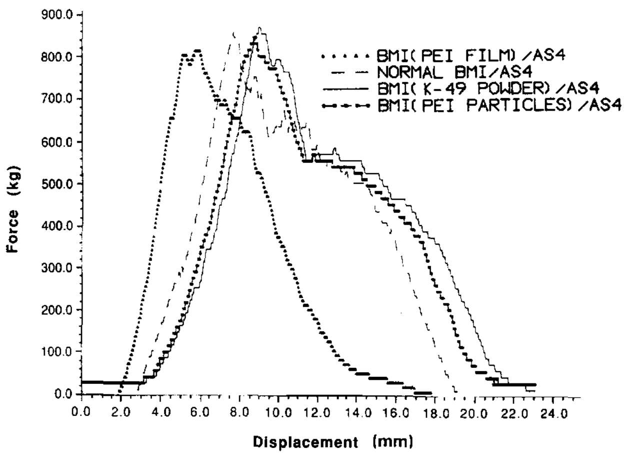


Figure 12 Force–displacement plots for impact energy penetration of BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites

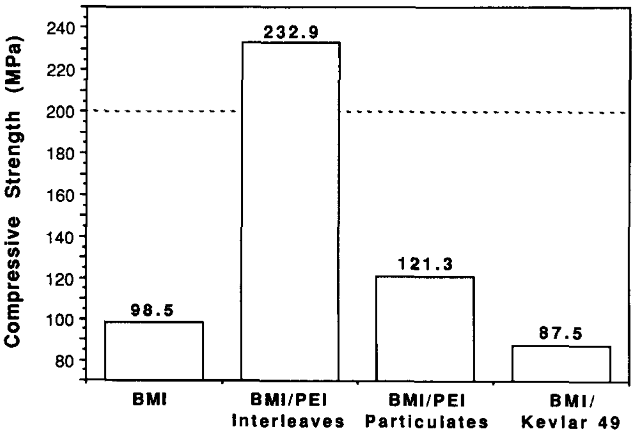


Figure 13 Compressive strength after impact for BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites

had minimal modifications on compressive strengths, with the PEI particulate- and Kevlar 49 whisker-modified composites resulting in only a 15% increase and a 10% decrease respectively.

Open hole compression. For the open hole compression composite test specimens, ~95% of equilibrium absorbed moisture was attained after 1 day exposure to boiling water. The average maximum moisture content after 4 days in boiling water was 1.66 wt% for the unmodified BMPM/DABPA (1:1 molar)–AS4 carbon fibre composite. The composite specimen with the PEI interleaves absorbed ~2.5 wt% moisture after 4 days exposure to boiling water. The higher polymer matrix volume fraction and porosity of the interleaf composites must cause the higher moisture absorption of the PEI interleaf-modified composites. The unmodified composite had a fibre volume fraction of 62%, whereas the interleaf composites had a fibre volume fraction in the 57–58% range.

In *Figure 14*, the open hole compression test data for BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites are illustrated as a function of test temperature for both unmodified and PEI interleaf-modified composites. For the unmodified BMI composite, 85% of the 23°C compressive strength was retained at 191°C (wet). The PEI interleaf composites retained at least 70% of their ambient properties at 177°C (wet). At 191°C (wet), however, interleaf composites lose 40–50% of their ambient compressive strengths, because of the lowering of the interleaf modulus as the test temperatures approach the interleaf T_g.

CONCLUSIONS

The cure reactions of BMPM/DABPA bismaleimide are complex. In the 100–200°C range, the BMPM and DABPA react to form an 'ene' prepolymer. In the 200–300°C range, the 'ene' molecule polymerizes and crosslinks by (i) cooperative reactions between the three double bonds in the 'ene' molecule and (ii) dehydration through hydroxyl groups, with associated moisture evolution. In the 200–250°C range, full cure is not attained because of diffusion restrictions associated with the glassy state. Full cure is essentially attained after a 300°C/2 h post-cure resulting in a final T_g of near 350°C. The crosslinked network structure is complex as a result of the pentafunctional nature of the 'ene' prepolymer.

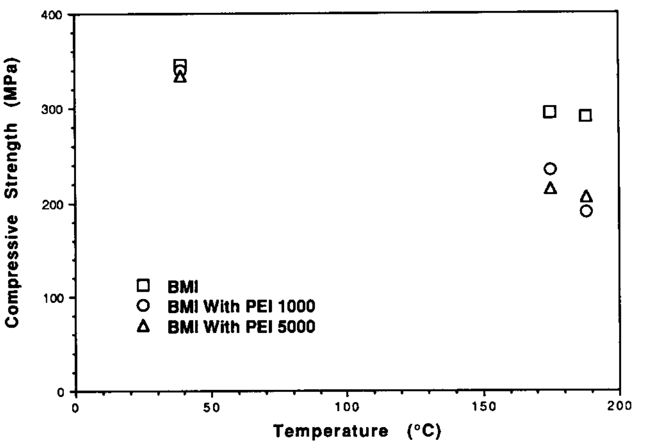


Figure 14 Open hole compressive strength *versus* temperature for BMPM/DABPA (1:1 molar)–AS4 carbon fibre composite and its composites with PEI interleaves

Optimum prepreg, lamination and post-cure conditions were ascertained for processing BMPM/DABPA (1:1 molar)–AS4 carbon fibre composites and the introduction of toughening agents, namely, poly(ether imide) (PEI) particulates and interleaves and Kevlar 49 whiskers. However, some of the thicker laminates with additives exhibited porosity and surface undulations. Viscosity–time measurements indicate that there is a chemical reaction between the BMPM/DABPA resin and the thermoplastic PEI. Post-curing in the 250–300°C range produced transverse resin microcracking in 0/90° laminates as a result of high post-cure temperatures and the mismatch in the resin and fibre thermal coefficients of expansion.

In the composite performance area, it is difficult to toughen the composite and meet all the requirements associated with G_{Ic} toughness, impact penetration, compression after impact and open hole compression tests.

A fully cured composite with minimal BMI network defects possesses a T_g of near 350°C without compromising the ambient G_{Ic} toughness of 330 J m^{-2}. However, compression after impact properties are sacrificed and they are 50% lower than is generally acceptable. The G_{Ic} and compression after impact are acceptable when PEI interleaves are used in the composite; however, the softer interleaves cause a loss of high-temperature, wet, open hole compression properties.

Increased fibre volume fractions were found to decrease G_{Ic} toughness, but increase impact penetration, where the polymer matrix plays a minimal energy absorption role.

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