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Characterization of the cure reactions of bismaleimide composite matrices

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The cure reactions of 4,4′-bismaleimidodiphenyl methane (BMPM)/*O*, *O*′-diallyl bisphenol A (DABPA) bismaleimide composite matrices are characterized by systematic Fourier transform infra-red spectroscopy and differential scanning calorimetry studies as a function of isothermal exposures from 130 to 300°C for time periods from 1 to 14 h. The BMPM and DABPA monomers initially react to form an 'ene' adduct. The allyl, propenyl and maleimide double C=C bonds of the 'ene' adduct are completely reacted after 3 h at 250°C. These cure reactions of the 'ene' molecule can initiate intra- or inter-molecularly and, hence, the cure path sequence is dependent on viscosity–time–temperature cure conditions. However, only 50% of the hydroxyl groups of the 'ene' adduct that form ether crosslinks via dehydration are reacted at 250°C, over 10^4 h time periods, resulting in T_g increases and mechanical property deterioration. The degree of cure, α, as determined from d.s.c. measurements is less sensitive to the dehydration reaction because of a lower heat of reaction compared to the double C=C bond cure reactions. Additional BMI cure induced T_g increases in future aerospace service environments are discussed. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: bismaleimides; cure reactions; dehydration)

INTRODUCTION

Utilization of high temperature polymer matrix–carbon fibre composites for structural applications in future commercial, such as High Speed Civil Transport (HSCT), and military aircraft will be exposed to prolonged and often extreme service environment conditions[1,2]. These complex service environment conditions of combined stress, time, temperature, moisture, chemical and atmospheric environments require a thorough understanding of potential physical, chemical and mechanical-induced composite degradation mechanisms, and their synergistic effects that could lead to the most probable critical failure path. An understanding of the critical fundamental aging mechanisms is necessary for credible long-term composite performance predictions from experimentally observed shorter time service environment induced composite performance deterioration mechanisms.

Two of the leading high temperature polymer matrix–carbon fibre composites consist of either (i) crosslinked bismaleimide (BMI) thermoset and (ii) thermoplastic polyimide (PI) matrices. Such composites are utilized in present aerospace structures and are being evaluated for structural applications in future commercial and military aircraft. The thermoplastic polyimides have exhibited both processing and toughness limitations whereas the thermoset bismaleimides are more processible but have exhibited a more brittle mechanical response.

Based on our previous studies[2–9] we have identified the most likely potential, critical aging mechanisms that control damage initiation in BMI and PI carbon fibre composites based on a systematic durability evaluation methodology illustrated in *Figure 1*.

In the case of BMI–carbon fibre composites, the BMI cure reactions are incomplete after standard composite fabrication and post-cure procedures and further cure can occur in service environment conditions resulting in increases in glass transition temperature (T_g) and associated composite mechanical property deteriorations. Loechet and Rothschild[10] have observed real time T_g increases for commercial BMI–carbon fibre composites (BASF 5260) of up to 70°C after isothermal exposure in the 150–200°C temperature range for up to $\sim 10^4$ h. Li[11] reported a 50% decrease in impact energy after thermal aging of BMI–carbon fibre composites for 1000 h at 190°C.

Commercial BMI resins, such as Matrimid 5292, Ciba Geigy and BASF 5260 are based on the 4,4′-bismaleimidodiphenyl methane (BMPM)/*O*, *O*′-diallyl bisphenol A (DABPA) system (*Figure 2*). In our previous studies[4] we conducted systematic Fourier transform infra-red spectroscopy (*FT*i.r.) and differential scanning calorimetry (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 and together with literature data[12–15] it was concluded:

(i) In the 100–200°C range the BMPM and DABPA monomers react via the 'ene' reaction to form the 'ene' adduct, illustrated in *Figure 3*. The 'ene' adduct is pentafunctional as a result of three double –C=C– bonds, capable of chain extension and

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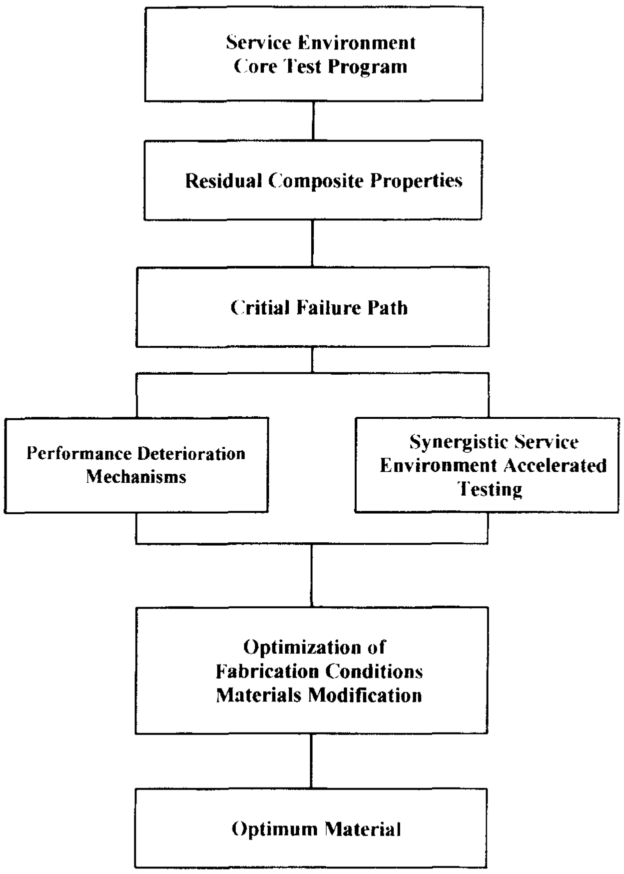


Figure 1 Durability program plan

crosslinking, designated (A), allyl, (B), propenyl and (C) maleimide in *Figure 3a* and two hydroxyl groups capable of etherification by hydroxyl dehydration *Figure 3b*.

(ii) The principal cure reactions occur in the 200–300°C range via the –C=C– double bonds with etherification occurring above 240°C at d.s.c. heating rates of 10°C min^{-1}.

(iii) Cure was incomplete due to glassy-state diffusion restrictions at 250°C and further cure at 300°C for 1 or 2 h produced a constant T_g near 350°C. Residual d.s.c. exotherm experiments indicate <10% unreacted groups remain after 2 h at 200°C, 6 h at 250°C and 2 h at 300°C cure schedule.

Recent isothermal BMI cure studies by Mijovic and Andjelic[16] by remote fibre optic near infra-red spectroscopy in the 140–250°C range have been conducted. They report the relative rates of allyl and maleimide consumption and that essentially complete conversion of these groups occurs at 200°C. Also, they observe the onset of dehydration at low temperatures, 140°C, over periods of hours.

In this paper we have extended our systematic *FT*i.r. and d.s.c. studies to 1–14 h isothermal exposures in the 130 to 300°C range. These studies were carried out in order to ascertain (i) the sequence and relative rates of the cure reactions and (ii) the nature of chemical reactions that are capable of further reactions, with associated thermal and mechanical property modifications, in future aerospace service environment conditions.

EXPERIMENTAL

Materials

The BMI resin system utilized was the BMPM/DABPA (1/1 molar ratio) (Ciba-Geigy) system (*Figure 2*).

Methods

The characterization of the BMI cure reactions was carried out by systematic *FT*i.r. (Nicolet) and d.s.c. (DuPont 910) at 10°C min^{-1} in an N_2 atmosphere as a function of isothermal cure conditions.

For the *FT*i.r. studies the BMI mixtures were placed between NaCl crystals that were separated by a 0.5 mm spacer. The BMI mixtures were isothermally cured between the NaCl crystals in an oven, allowed to cool to 23°C and then introduced into the *FT*i.r. spectrometer and the infra-red spectra recorded. The spectra were obtained from 100 scans at a resolution of 1 wave number (cm^{-1}). Between isothermal cure cycles for consecutive isothermal cures the NaCl–BMI specimens were stored in a dessicator at 23°C. Spectral stripping, which reveals differences in the spectra recorded at different stages of cure, was utilized to monitor the disappearance of the reactants or the formation of the products during cure.

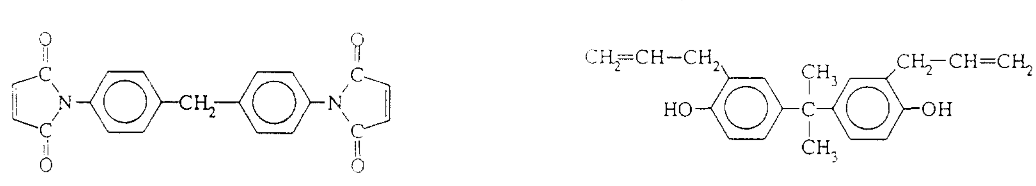
D.s.c. kinetic analysis was used to characterize the cure reaction kinetics. Isothermal scans were run up to 10 h in the 130–300°C range. There was no significant change in heat flow after 10 h cure at each temperature within the limit of equipment resolution. The degree of cure, α, was determined from the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \qquad (1)$$

whereΔH_t is the partial heat of reaction at time t and ΔH_∞ is the total heat of reaction, ΔH_∞ was determined from a dynamic d.s.c. scan at a heating rate of 5°C min^{-1} and had a value of 389 J g^{-1}.

The T_g of the BMI system as a function of isothermal exposure conditions was determined by thermal mechanical analysis (t.m.a.).

^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy was used to monitor the early stages of the BMI cure. A Bruker EM-360 Fourier transform n.m.r. spectrometer equipped with a dual carbon-13/proton probe was used in this study.



4,4' Bismaleimidodiphenylmethane (BMI)

O,O'-Diallyl Bisphenol A (DABPA)

Figure 2 The chemical structures of BMPM and DABPA monomers

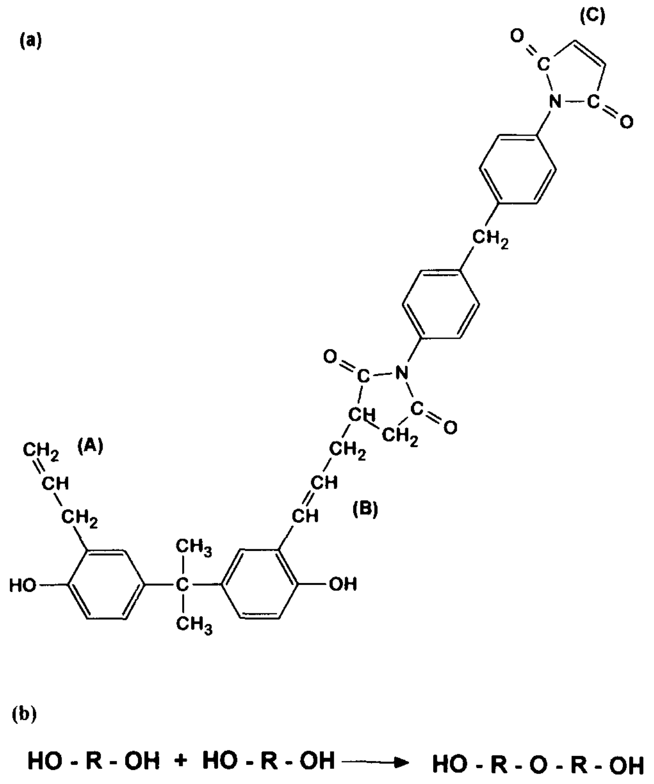


Figure 3 (a) The chemical structure of the BMPM/DABPA 'ene' adduct prepolymer. (A), (B) and (C) are double bonds capable of polymerization. (b) Dehydration of the hydroxyl groups to form ether crosslinks

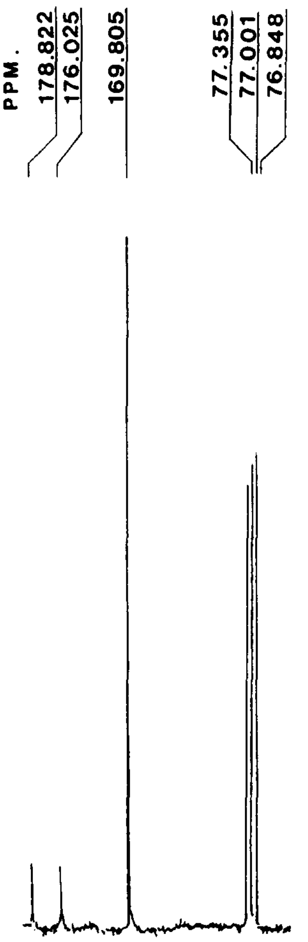


Figure 4 ^{13}C n.m.r. spectrum of the BMDPM–DABPA (1/1 molar ratio) prepolymer after a 165°C, 5 h cure

RESULTS AND DISCUSSION

FT *i.r. and n.m.r. characterization of the cure reactions*

For the BMPM/DABPA BMI system the 'ene' reaction initially occurs in the 100–200°C range. Gel permeation chromatography (g.p.c.) indicates that only a small molecular weight increase occurs (from 520 to 680) after 16 h at 100°C[12–14]. Viscosity–time–temperature data indicate that this reaction only occurs at significant rates above 180°C[4]. We observe after 5 h cure at 165°C only organically soluble reaction products. ^{13}C n.m.r. spectrum, illustrated in *Figure 4*, shows a doublet between 176 and 179 ppm for the BMPM/DABPA BMI system which is associated with the two unsymmetrical carbonyl C-atoms of the 'ene' adduct, that differs from the spectrum of the unreacted BMPM molecule which exhibits only a single peak at 169.8 ppm associated with the carbonyl C atoms.

In *Figure 5*, we show typical *FT*i.r. spectra of the BMPM–DABPA BMI system as a function of cure conditions. The i.r. bands at 820 cm^{-1}, 915 cm^{-1}, 1183 cm^{-1} and 3473 cm^{-1} are assigned to the maleimide, allyl, ether and hydroxyl groups respectively, that are associated with the cure reactions[4,17–19]. The band intensities were normalized against the CH_3 group in DABPA. This CH_3 group has two characteristic regions of absorption at 2970 cm^{-1} and a doublet for the dimethyl group at 1365 and 1385 cm^{-1} [17–19].

From the normalized i.r. bands are plotted in *Figure 6* reaction percentages of the maleimide and allyl double C=C bonds and the ether appearance caused by hydroxyl dehydration as a function of sequential, accumulative cure conditions from 130 to 250°C. The maleimide and allyl double C=C bonds associated with the 'ene' adduct are completely reacted after 3 h at 250°C. The commercially recommended cure of the BMPM–DABPA BMI system is 6 h at 250°C. The maleimide and allyl double C=C bonds react at very nearly the same rates but for certain cure sequences the maleimide consumption can be up to 10% greater than the allyl consumption, as illustrated for isothermal cure at 130°C in *Figure 7*.

The relative rates of the allyl, propenyl and maleimide double C=C bond cure polymerization reactions can be complex and depend on the cure history sequence. Previous d.s.c. studies of the reaction exotherms of the BMPM and DABPA monomers and their mixtures showed that the BMPM exotherm was centered at 210°C, whereas the BMPM–DABPA mixture exotherm was 45°C higher at 255°C. The lower BMPM exotherm is equivalent to a 25 × faster reaction rate for the maleimide–maleimide double C=C bond polymerization compared to other double C=C bond polymerization combinations that involve allyl, propenyl and maleimide combinations. However, as the viscosity increases during cure intermolecular reactions will become restricted and intramolecular reactions will be favoured. Previous molecular modelling characterization of the BMI cure reactions showed the intramolecular 'ene' allyl-propenyl cyclization is possible (*Figure 8*)[4]. The (A)–(B) double radical cyclization structure shown in *Figure 8* is considerably more reactive than the maleimide double C=C bond. Hence, cure path

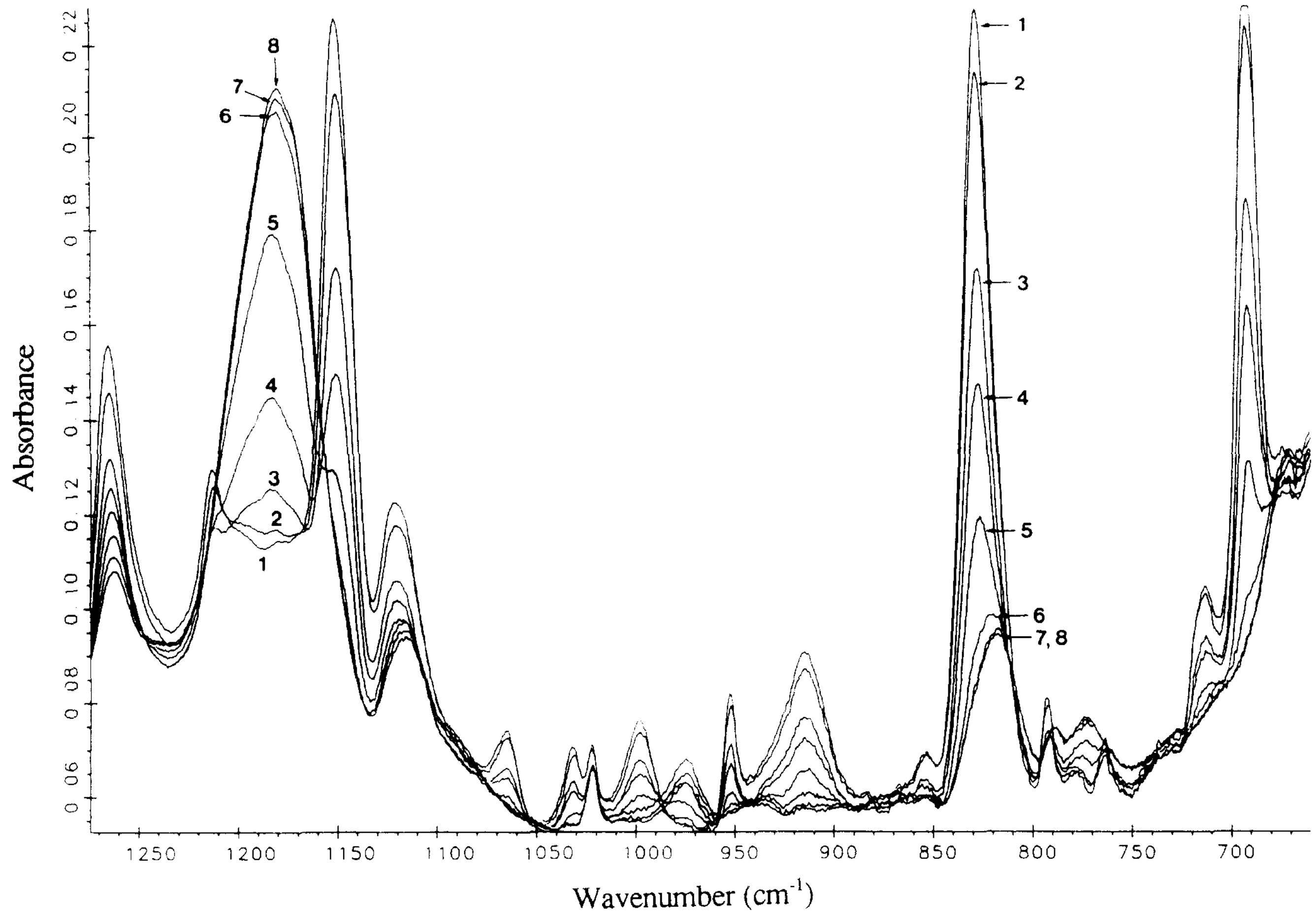


Figure 5 *FT*i.r. spectra of BMPM–DABPA (1/1 molar) system as a function of sequential cure conditions. 1, Prepolymer 0.5 h, 130°C mixing; 2, 3, 4, 5, 6, 1 h, at sequential temperatures of 130, 150, 175, 200, 225°C respectively; 7, 8, 3 h and 9 h at 250°C respectively

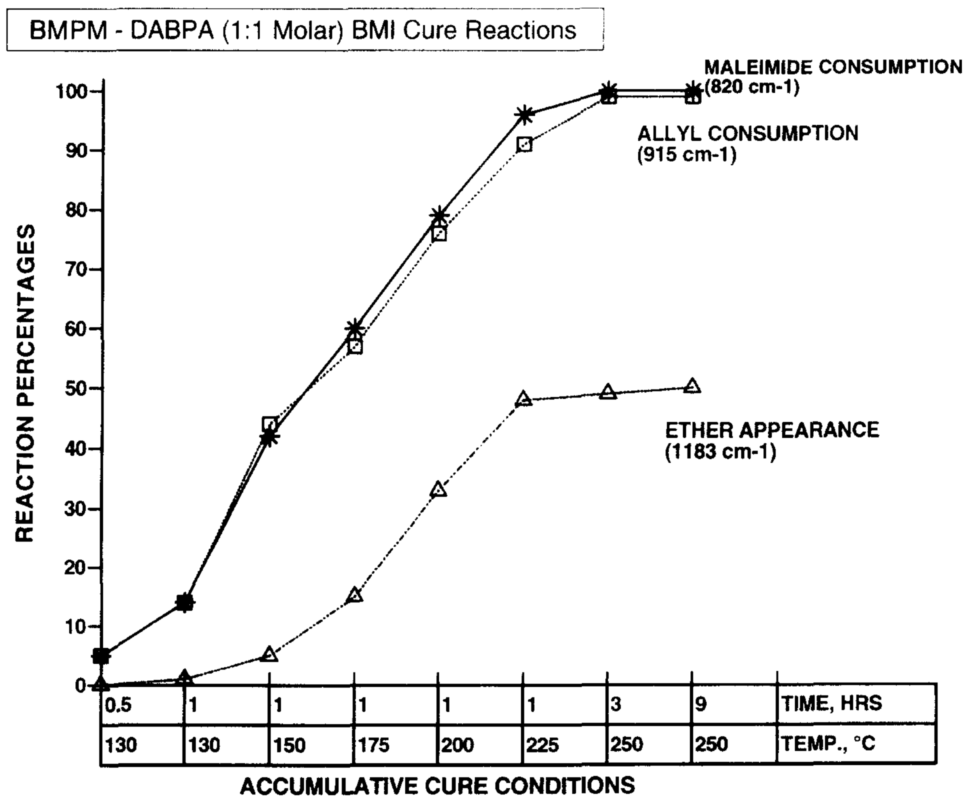


Figure 6 The consumption of the maleimide (*) and allyl (□) groups and appearance of the ether group for the BMPM–DABPA (1/1 molar) system as a function of sequential, isothermal cure conditions

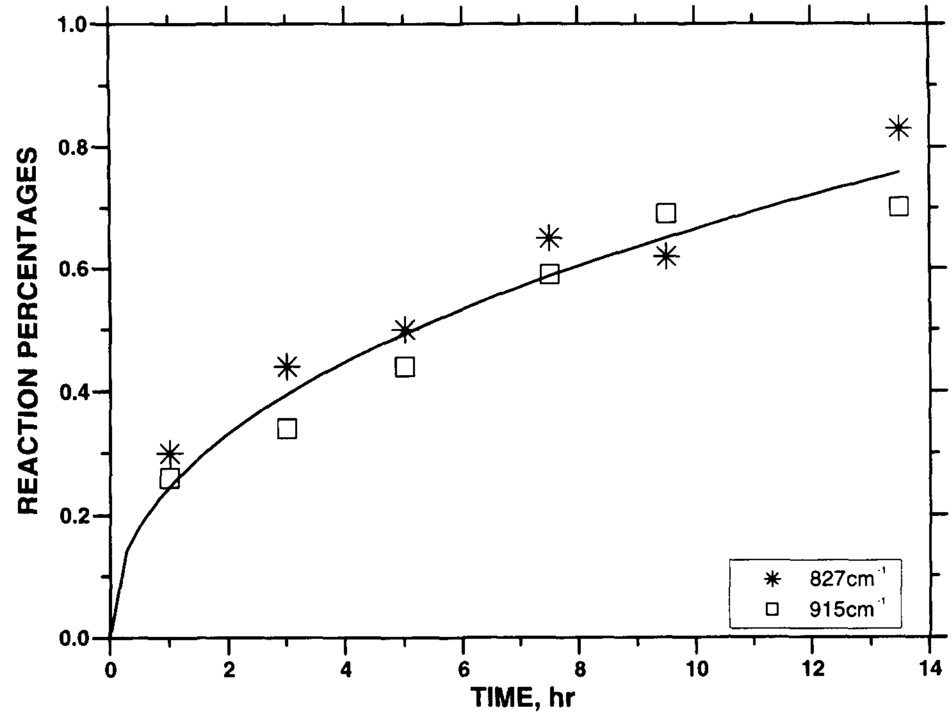


Figure 7 The consumption of the maleimide (*) and allyl (□) groups for the BMPM–DABPA (1/1 molar) system as a function of time under 130°C isothermal cure conditions

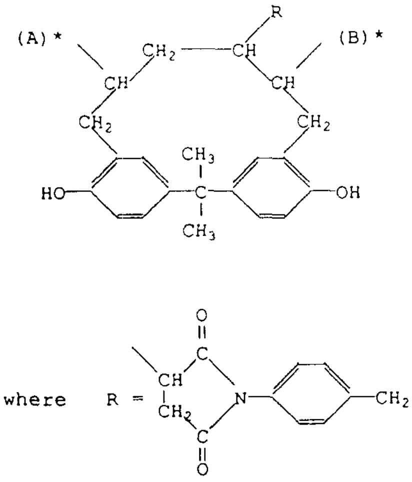


Figure 8 Intramolecular cyclization via (A)–(B) double bonds (*Figure 3*) of the 'ene' molecule. (The (A) and (B) radicals further react intermolecularly with other 'ene' species)

sequences and associated viscosity–time–temperature histories may affect observed relative reaction rates of the three 'ene' double C=C bonds and the resultant BMI network structure.

The ether crosslink reaction via hydroxyl dehydration is only 50% complete after the sequential isothermal cure and 9 h at 250°C as illustrated in *Figure 6*. This crosslink reaction is inhibited by glassy-state diffusion and molecular network topography restrictions. Further post-curing at 300°C for 9 h results in a further ~10% increase in ether crosslinks, as monitored by the intensity decrease of the i.r. hydroxyl band at 3473 cm^{-1}, and an associated T_g increase from 280 to 350°C. However, at the 300°C cure conditions the ether crosslinks become thermally unstable and partially dissociate into other species, as indicated by the lack of further ether i.r. band intensity increase that correlated directly with the hydroxyl i.r. band decrease at lower cure temperatures. Previous systematic *FT*i.r. studies of diaminodiphenyl sulfone cured tetraglycidyl 4,4′-diaminodiphenyl methane epoxies as a function of cure conditions and initial monomer ratio show that dehydration formed ether crosslinks start to thermally dissociate in the 300°C temperature range[20].

The *FT*i.r. studies indicate the BMI network is not fully cured under standard recommended composite cure conditions. The cure reaction rates and the resultant network structure could be dependent upon cure path history sequence, with intramolecular reactions favoured at higher viscosity conditions.

D.s.c. characterization of the cure reactions

In *Figure 9*, the increase in the T_g, as monitored by t.m.a., as a function of isothermal exposure temperatures from 130 to 300°C for up to 30 h is illustrated for the BMPM–DABPA (1/1 molar) BMI system. For all isothermal cure temperatures the T_g increases rapidly at

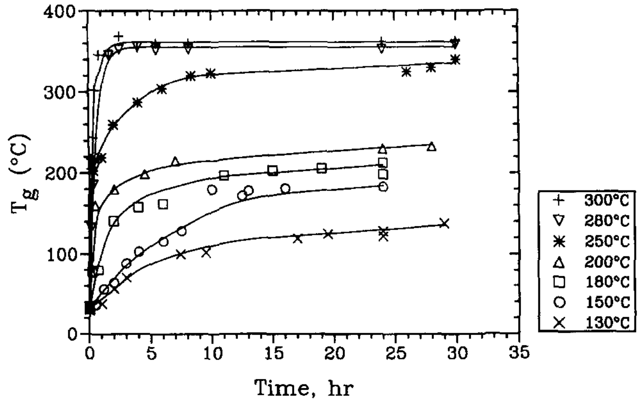


Figure 9 T_g vs isothermal cure time for temperatures ranging from 130 to 300°C for the BMPM–DABPA (1/1 molar) BMI system

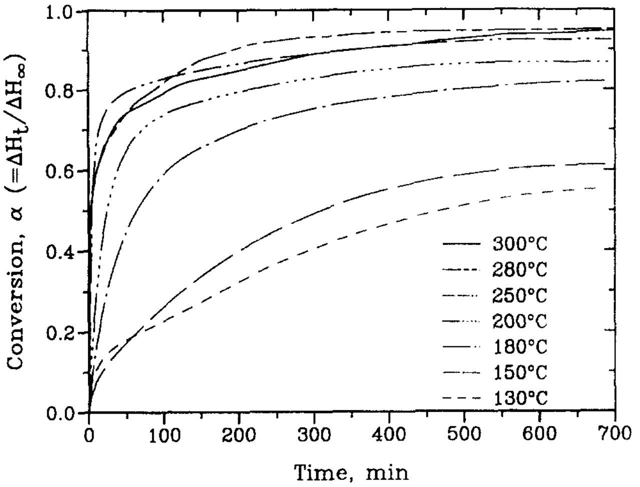


Figure 10 Degree of cure, α, ($\Delta H_t/\Delta H_\infty$) vs isothermal cure time for temperatures ranging from 130 to 300°C for the BMPM–DABPA (1:1 molar) BMI system

short times in the liquid state and only increases slowly at longer times in the glassy state as a result of diffusion restrictions. There is an abrupt increase in T_g between isothermal 200 and 250°C cure temperatures over similar time periods, which is consistent with the maximum rates of the double C=C polymerization cure reactions occurring in this range.

The degree of cure, α, determined from the d.s.c. exotherm $\Delta H_t/\Delta H_\infty$ ratios is shown as a function of isothermal exposure temperatures from 130 to 300°C for cure time periods up to 10 h for the BMPM–DABPA (1/1 molar) BMI system in *Figure 10*.

Based on the data plotted in *Figures 9* and *10* T_g vs α as a function of isothermal cure temperature is illustrated in *Figure 11* for a constant cure time of 10 h. This plot clearly indicates that T_g for a specific α, is cure history path dependent, as the isothermal T_g–α plots do not fall on one common plot. For example, for a 90% degree of cure at isothermal cure temperature 250°C the T_g is 280°C; however, for the same degree of cure at isothermal cure temperatures of 280°C and 300°C, the T_g is 70°C higher at 350°C. The lack of sensitivity of α to T_g, particularly at the higher cure temperatures indicates that the crosslink reactions in this range do not exhibit as strong ΔH_t exotherms as at lower temperatures. We associate this lack of sensitivity of the $\Delta H_t/\Delta H_\infty$ ratio to the T_g increase to the lower heat of reaction of the dehydration reaction that exclusively occurs in the latter stages of cure in the 280–300°C range. A d.s.c. scan of the DABPA monomer (*Figure 12*) exhibits an endotherm followed by an exotherm in the 250–300°C range with resultant little overall heat evolution.

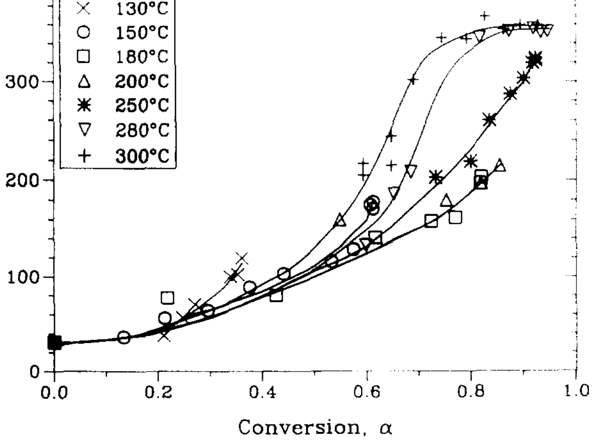


Figure 11 T_g vs degree of cure, α, ($\Delta H_t/\Delta H_\infty$) for isothermal cure temperatures in the 130–300°C range for a constant cure time of 10 h for the BMPM–DABPA (1/1 molar) BMI system

In the 130–250°C temperature region, the T_g at final cure temperature was observed to be essentially independent of cure history path, as illustrated in *Figure 13*. The T_g is, therefore, not sensitive to any network structural differences that may result from a range viscosity–time cure history profile differences that would affect intermolecular vs intramolecular cure reactions.

Service environment aging

Based on the *FT*i.r. and d.s.c. cure studies of the BMPM–DABPA BMI system, it is evident that the resin can undergo further cure via dehydration with associated T_g increases and mechanical property deteriorations.

In *Figure 14*, real time T_g increases for commercial BMI–carbon fibre composites (BASF 5260) are shown for isothermal temperature exposures in the 150–200°C range for times up to $\sim 10^4$ h[10]. In *Figure 15* these data are replotted in the form of isothermal plots of ΔT_g changes *versus* log *t*. For the HSCT a T_g shift of less than 5% for 120 000 h service environment exposure is required (twice the service environment lifetime of the HSCT). However, regressive analysis of these data utilizing a model equation (2),

$$\Delta T_g = B_1(1 - e^{-B_2 t})^{B_3} \qquad (2)$$

reveals that for a 5% T_g shift the isothermal service environment exposure temperature could only be 120°C; well below the expected HSCT service environment temperatures.

However, for a more scientifically sound prediction of service environment induced T_g increases, and associated mechanical property deterioration, for over an order of magnitude time difference between available laboratory data and expected service environment exposure times more sophisticated predictive methodologies are being pursued[2,8]. An expression has been developed for the T_g service environment induced increases in terms of chemical cure characteristics and BMI glassy-state diffusion restrictions, equation (3)

$$T_g = k_3 e^{k_4 \int [k_{\mathrm{CHEM}}[\mathrm{A}]^x[\mathrm{B}]^y e^{-(k_1 U_{\mathrm{CHEM}} + k_2 e^{-U_{\mathrm{DIFF}}(T_g - T)/RT})/RT}] \mathrm{d}t} \qquad (3)$$

where: (i) [A] and [B] are the chemical reactant concentrations of the unreacted C=C double bond and OH species in the system; (ii) x and y are the number of reactant groups involved in the cure reaction; (iii) k_{CHEM} is the reaction constant for the cure reactions; (iv) U_{CHEM} is the activation energy of the cure reactions; (v) U_{DIFF} is the activation energy of the glassy-state diffusion restrictions imposed on the cure reactions; (vi) k_1, k_2, k_3 and k_4 are constants.

CONCLUSIONS

Systematic *FT*i.r. isothermal cure studies indicate the BMPM–DABPA BMI composite matrix is not fully

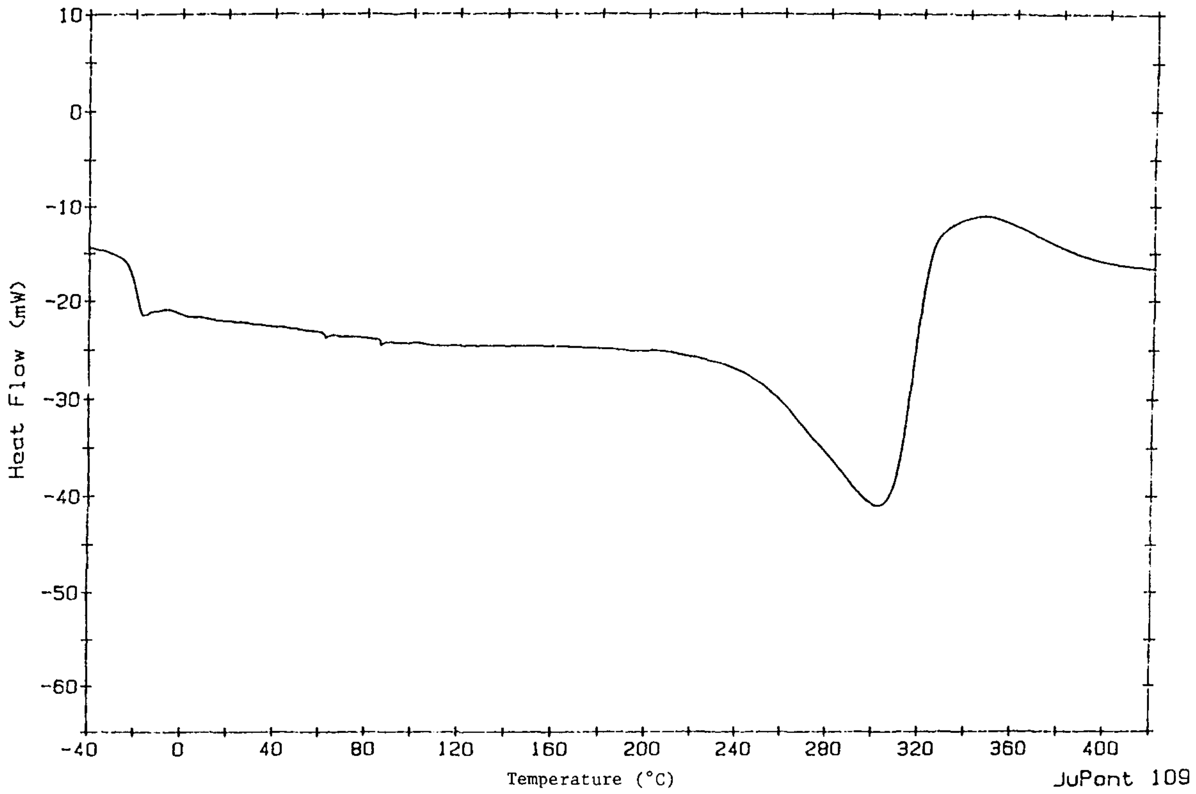


Figure 12 D.s.c. scan of DABPA monomer, 10°C min^{-1} heating rate, N_2 atmosphere

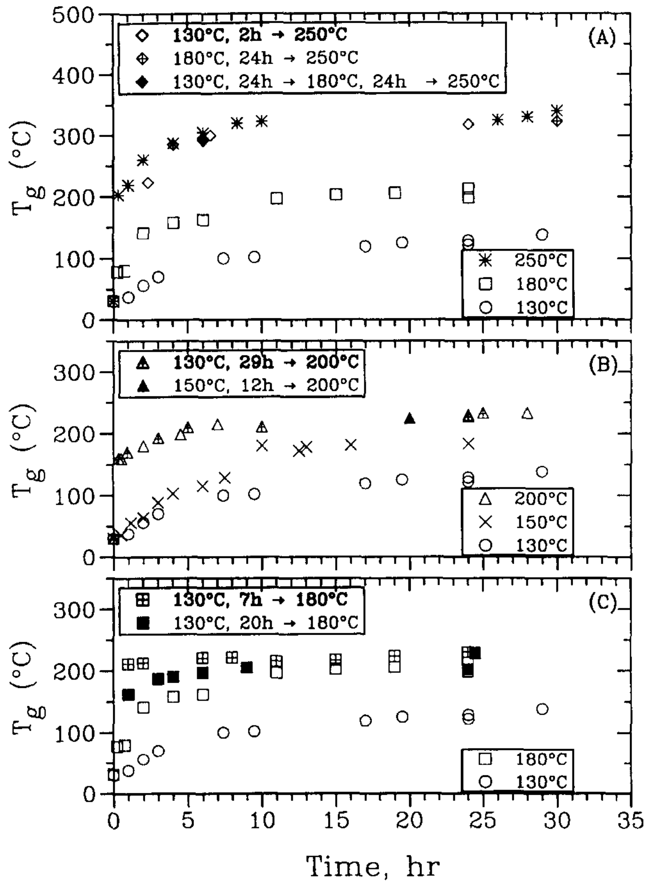


Figure 13 T_g vs cure history path in the 130–250°C temperature range for the BMPM-DABPA (1:1 molar) BMI system

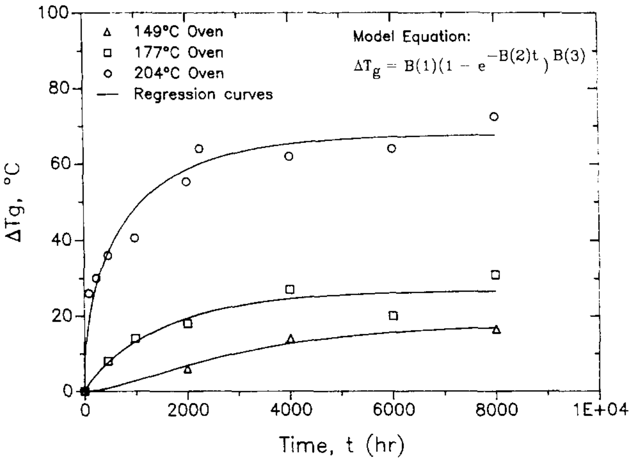


Figure 14 T_g increase vs isothermal exposure time for commercial BMI-carbon fibre composite (BASF 5260); data from Loechet and Rothschild[10], published with permission

cured under standard recommended commercial cure conditions of 6 h at 250°C. All C=C bonds of the BMPM-DABPA 'ene' adduct completely react after 3 h at 250°C. However, only 50% of the hydroxyl groups associated with the dehydration crosslink reaction BMPM-DABPA 'ene' adduct are reacted after 9 h at 250°C. Further cure takes place at higher temperatures of 300°C over periods of hours and at lower temperatures, 150–250°C, over periods of time up to 10^4 h.

Further cure via dehydration results in a higher T_g and a more brittle mechanical response.

The reaction rates of the allyl, maleimide and propenyl C=C bonds of the BMPM-DABPA 'ene' adduct may depend on cure path history sequence with

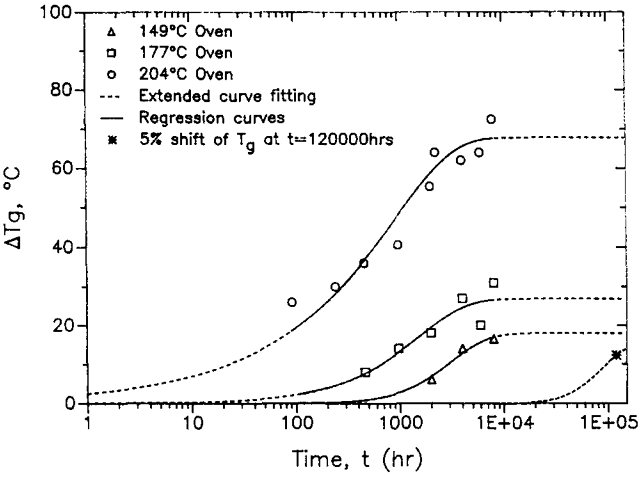


Figure 15 Δt_g *versus* $\log t$ for isothermal exposures for commerical BMI–carbon fibre composite (BASF 5260)

intramolecular reactions, as identified by molecular models, favoured at higher viscosity conditions. Any network structural differences caused by different viscosity–time cure history profiles do not affect the final T_g.

The degree of cure, α, as determined from d.s.c. measurements is less sensitive to the dehydration reaction because of a lower heat of reaction compared to the C=C bond cure reactions.

For a T_g increase of $\leqslant 5\%$ over 120 000 h exposure, as would be required in commercial aircraft applications the service environment exposure temperature could only be 120°C, well below expected HSCT service environment temperatures.

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