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SYNTHESIS OF BISMALEIMIDE-DIAMINEPOLYMER MATRIX IN THE PRESENCE OF DICUMYL PEROXIDE: REACTION, CURING PROFILE AND THERMAL PROPERTIES

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RESEARCH SYNOPSIS

The main aim of this study was to develop an improved method for the preparation of a bismaleimide–diamine (BMI/DDM) polymer matrix, achieving shorter curing time, longer processing time (pot life), and good thermal mechanical properties. A matrix of BMI/DDM thermoset was prepared at optimal conditions and formulation, containing BMI and DDM in a 2:1 mol ratio with 0.1wt% of dicumyl peroxide (DCP) as the curing accelerator. An optimal temperature of 150°C was selected for both melt-mixing and curing processes. The mechanism of matrix preparation was also investigated using differential scanning calorimetry and quantitative Fourier transformed infrared analysis. DCP at the optimal concentration was found to accelerate cross-linking reactions between BMI and DDM without inhibiting the chain-extension reaction of BMI. The specified formulation exhibited longer gel time (208 s/g) and shorter postcuring time (2 h) compared to other formulations. In addition, thermomechanical behavior and thermal stability were analyzed by dynamic mechanical analysis and thermomechanical analysis, and thermogravimetric analysis, respectively. The storage modulus (E′), glass transition temperature (T_g), and decomposition temperature (T_d) of the BMI/DDM thermosets increased with the BMI content of the formulations, while the coefficient of thermal expansion and damping behavior (tan δ) decreased in a similar manner, primarily because of an increase in the degree of crosslinking.

SINOPSIS KAJIAN

Tujuan utama kajian ini adalah untuk mengkaji satu kaedah yang lebih baik dalam penyediaan bismaleimide-diamine (BMI / DDM) matriks polimer yang boleh mencapai masa pengawetan yang lebih pendek, masa memproses ("pot life") yang lebih panjang, dan sifat-sifat haba mekanikal yang baik. Satu matriks BMI / DDM termoset telah disediakan pada keadaan dan formulasi yang optimum, iaitu mengandungi BMI dan DDM dalam nisbah mol 2:1 dengan 0.1wt% peroksida dicumyl (DCP) sebagai pemecut pengawetan. Suhu optimum 150 ° C telah dipilih untuk kedua-dua "melt mixing" dan proses pengawetan. Mekanisme penyediaan matriks juga telah dikaji dengan menggunakan "differential scanning calorimetry" (DCP) and "quantitative Fourier transformed infrared' analisis. DCP pada kepekatan yang optimum didapati mempercepatkan tindak balas silang antara BMI dan DDM tanpa menghalang tindak balas rantai-lanjutan BMI. Formulasi yang digunakan menghasilkan gel dalam masa yang lebih panjang (208 s / g) dan masa "postcuring" lebih pendek (2 h) berbanding dengan formulasi lain. Di samping itu, tingkah laku termomekanikal dan kestabilan terma dianalisis dengan analisis dinamik mekanikal dan analisis termomekanikal, dan analisis Termogravimetri masing-masing. "Storage modulus" (E '), "glass transition temperature" (T_g), dan "decomposition temperature" (T_d) daripada termoset BMI /DDM meningkat dengan kandungan BMI bagi formulasi, manakala "coefficient of thermal expansion and damping behavior" (tan δ) menurun dengan cara yang sama dengan peningkatan tahap silang.

1.0 Pendahuluan (Latarbelakang Masalah, Rujukan Terkini, Objektif Dan Kepentingan Penyelidikan)

Polymeric matrices play an important part in determining the performance of nanocomposite materials. Among matrices, thermosetting plastics (or thermosets) have received considerable attention because of their dimensional stability and their ability to resist viscous flow at elevated temperatures compared to thermoplastics [1]. In addition, thermosets have high thermal stability, high durability and tractability, good water, fire and radiation resistance, and a relatively low cost, making them capable of meeting common engineering needs in high-temperature applications such as those found in the aerospace, defense, and semiconductor packaging industries. In particular, thermosets are often used as matrices for preparation of advanced composite materials [2–7]. Although epoxy resins are also widely used for this purpose and have some advantages such as ease of handling and good processability, they are not appropriate for applications above 250°C because of their low Tg (i.e. 165–240°C) [8,9]. It is therefore necessary to find new classes of polymers capable of withstanding high temperatures and with minimal loss in thermal mechanical properties, as compared to conventional epoxies. Thermosetting polyimide resins such as bismaleimides are currently considered favorably as replacements for epoxy resins in certain commercial and military applications.[10]

Bismaleimide (BMI) systems can serve as thermosetting polymer matrices because of their high performance-to-cost ratio and relatively high-temperature resistance (e.g. high Tg and Td and low coefficient of thermal expansion [CTE]) [11]. In addition, BMI offers superior thermal and oxidative stability, low susceptibility to moisture absorption, and good flame retardance [11]. The main advantage of BMI is that it can withstand high stress at the high temperatures at which typical epoxies, phenolics, and most high-performance plastics become unstable [12]. The main disadvantage of BMI is that it is relatively brittle because of its aromatic nature and its high cross-linking density [3,4]. However, this problem can be solved by co-polymerizing the maleimide double bonds with suitable compounds to reduce brittleness [13,14]. In general, six different methods can be used to toughen BMI resins: (i) linear chain extension using aromatic diamines (DDMs) or aminobenzoic hydroxide to reduce the cross-link density [15–19]. (ii) synthesis of new classes of BMI monomers with flexible segments in the backbone [20,21]; (iii) blending with epoxies [22,23]; (iv) co-polymerization of allyl-type compounds [13,24,25]; (v) incorporation of thermoplastic resins[26]; and (vi) blending with aromatic dicyanate esters [27–29]. Among these methods, co-polymerization with aromatic DDMs by Michael addition is one of the easiest and most cost-effective routes to toughen the BMI resin [30,31].

It is well established that the properties of BMI/DDM thermosets are dependent on the stoichiometric ratio of their components (BMI :DDM mol ratio) as well as their curing temperature [2,3,31–33]. It is beneficial to use BMI-rich stoichiometrics (e.g. 2:1, 3:1, and 4:1), which can yield both chain extension and cross-linking, resulting in a robust polymer structure. As shown in Fig. 1, there are three main reactions that can occur simultaneously in the preparation of a BMI/DDM thermoset: (I) chain-extension reaction between maleimide double bonds and primary amines; (II) crosslinking reaction between maleimide double bonds and secondary amines; and (III) free radical homopolymerization cross-linking reactions of maleimide double bonds [31–33]. It is therefore important to study the kinetics and extent of these reactions at a particular temperature, composition, and time to select the optimal formulation and curing conditions for the BMI/DDM thermoset.

In this study, optimal conditions for the preparation of BMI/DDM thermosets are to be determined as follows. The BMI/DDM is prepared at different stoichiometric ratios in the presence and absence of dicumyl peroxide (DCP) (at optimal concentration) and characterized by differential scanning calorimetry (DSC), and Fourier transformed infrared (FTIR) to understand the mechanism of co-polymerization. Dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and thermogravimetric analysis (TGA) are also used to determine thermal mechanical properties such as storage modulus (E′), damping behavior (tan δ), glass transition temperature (Tg), CTE, and decomposition temperature (Td) at different conditions.

2.0 Tatakaedah/Metodologi Kajian

2.1 Preparation of BMI/DDM polymer matrix

The BMI/DDM polymer matrix was prepared using a melt-mixing procedure. In a typical preparation, mixtures of BMI and DDM prepared at different stoichiometric ratios (2:1, 3:1, and 4:1 BMI : DDM mol ratio) were melt-mixed for 10–15 min at 150°C in an ambient atmosphere. The reaction was conducted in a 25-ml glass vial immersed in a silicon oil bath. The mixture was stirred using a high-speed propeller to ensure homogenous mixing of the components and was followed by degassing to remove air bubbles from the polymer matrix. Degassing was conducted for 5–10 min in a vacuum oven (50mmHg) maintained at 150°C. Thereafter, an appropriate amount of DCP (0.1–1.0wt%) was added to the polymer matrix and mixed homogenously using the propeller for 2–4min. Finally, the prepreg (i.e. partially reacted polymer) was poured into a Teflon mold (dimensions of the cavity: 2mm thick, 10mm wide, and 80mm long) and subjected to a post-curing process at a temperature of 180°C and 200°C.

2.2 Quantitative FTIR analysis

Quantitative FTIR analysis was used to study the progress of the different reactions that occurred in the BMI/DDM system, in relation to time and temperature. This method of analysis was adapted from Hopewell et al.,[32] and the IR spectral assignments follow those of Guilio et al [31]. Concentrations of the primary amine [PA], secondary amine [SA], and maleimide double bonds [MI] were determined by measuring the peak area under 3466, 3373, and 3098 cm^{-1}, respectively, from the normalized FTIR spectra [34]. The aromatic C–C stretching vibration of benzene rings at 1513 cm^{-1} was used as a reference peak. As carbonyl (C=O) harmonic vibrations have been reported to overlap with NH_2 vibration,[34] the contribution of C=O harmonic vibrations was experimentally determined from the cured pure BMI resin and deducted from the peak area measured at 3466 cm^{-1}. The residual concentration of the functional groups (C_t) was calculated using the following equation:

$$C_t = \left(\frac{C_f}{C_i}\right) C_o \qquad (1)$$

in which C_f refers to the peak area of the particular functional group divided by the peak area of the benzene rings at the time of measurement, and C_i refers to the peak area of the functional groups divided by the peak area of the benzene rings before the reaction. Co refers to the initial concentration of the functional groups (in mmol/g) in the BMI/DDM admixture. The concentrations of tertiary amine ([TA]) and maleimide double bonds consumed for homopolymerization cross-linking reactions ([MI] homopolym) were determined using the following mass balance equations [33]:

$$[TA]_t = [PA]_o - [PA]_t - [SA]_t \quad (2)$$

$$[MI]_{homopolym} = ([MI]_o - [MI]_t) - ([SA]_t - [TA]_t) \quad (3)$$

in which $[PA]_o$ and $[MI]_o$ are the initial concentrations of primary amine and maleimide double bonds, respectively, in the reaction mixture; and $[PA]_t$, $[SA]_t$, and $[TA]_t$ are the concentrations ofprimary, secondary, and tertiary amines at the time of measurement. The curing profile was studied at three different temperatures, i.e. 150°C, 180°C, and 200°C. The curing process was taken to be complete when the peak corresponding to the maleimide double bond (3098 cm^{-1}) was completely depleted.

2.3 Determination of gel time

The gel time of the polymer was determined using a method devised by Shah [35]. A clean wooden probe was inserted into the center of the polymer mixture at 15-s intervals, and with temperature held constant at 150°C, the gel point was detected when the reacting material no longer adhered to the end of the probe. The gel time was determined as the time elapsed from the start of the mixing to the gel point.

2.4 Thermal Mechanical Properties

The BMI/DDM thermosets prepared at different stoichiometric ratios and in presence and absence of DCP (at optimal concentration) were characterized using DMA (Dynamic Mechanical Analysis), TMA (Thermomechanical Analysis) and TGA (Thermogravimetric Analysis) to determine its thermal mechanical properties such as storage modulus (E′), damping behavior (tan δ), glass transition temperature (T_g), coefficient of thermal expansion (CTE) and decomposition temperature (T_d) using the conditions as follows.

i) DMA

DMA was carried out on a Perkin-Elmer DMA 7^e to measure the temperature dependence of the storage tensile modulus (E′) and damping behavior (tan δ) of the cured polymer and nanocomposite samples in a three-point-bending mode. The samples were analyzed over a broad temperature range spanning from 30 to 400 °C with a heating rate of 5 °C/min. A fixed oscillation frequency of 1 Hz was used with a strain of approximately 0.1 %. The sample bars were 2 mm thick, 5 mm wide, and 25 mm long. The T_g was determined by a line intercept method. The peak of tan δ was not used to determine the T_g because BMI polymers usually give a very broad tan δ. The experimental error for the E' and tan δ was below 10%.

ii) TMA

TMA was employed for measuring thermal expansion behavior (CTE) and the glass transition temperature (T_g) of the polymer by using TMA Q400 (Polaris Parkway USA). Specimens were prepared in cylindrical form with 5mm diameter and 8mm height. In a typical measurement, the thermal expansion of cured BMI/DDM thermoset was analyzed in a temperature range of 25–350°C at a heating rate of 5°C/min. Specimens were mounted between a quartz platform and probe, and a static load of Fs (0.05 N) was applied. The dimension of each specimen was monitored by a linear variable differential transducer throughout the analysis. T_g of the materials was obtained by the onset deflection point of the two different slopes of the curve. CTE of the polymers (before [α_1] and after [α_2] the T_g) was obtained from the slope of the dimension change versus temperature curve. The experimental error for T_g and CTE was below 10%.

iii) TGA

TGA was conducted to determine the thermal stability of the polymer by using a Mettler Toledo (Polaris Parkway USA) TGA/SDTA 851^{e} at a heating rate of 10°C/min under N2 flow. The TGA results were analyzed using STAR^{e} SW8.10 software (Polaris Parkway USA).

iv) FTIR Spectroscopy

FTIR spectra (using KBr) were recorded using a Perkin-Elmer 2000 FTIR spectrometer for studying the progress of reactions between the BMI and DDM. All the FTIR spectra were normalized prior to the interpretation and quantitative analysis using SPECTRUM 3.02 software (Perkin-Elmer Malaysia).

v) DSC

DSC was used to study the effect of different formulations on the curing profile of the BMI/DDM matrix using a Pyris 1 DSC instrument (Perkin-Elmer, Malaysia) at a heating rate of 10°C/min under N_2 flow in the range of -50°C to 400°C. The resulting thermograms were analyzed using Perkin-Elmer DSC 7 software to obtain the onset temperature (T_{onset}), peak temperature (T_{peak}), and enthalpy (ΔH) of various endothermic/exothermic reactions. The BMI/DDM admixtures were prepared by homogenously mixing specific amounts of BMI and DDM using a pestle and mortar.

3.0 LATAR BELAKANG DAN TEMPAT KAJIAN

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4.0 HASIL PENYELIDIKAN DAN ANALISIS KAJIAN

4.1 Effect of BMI/DDM stoichiometry on the curing profiles: DSC studies

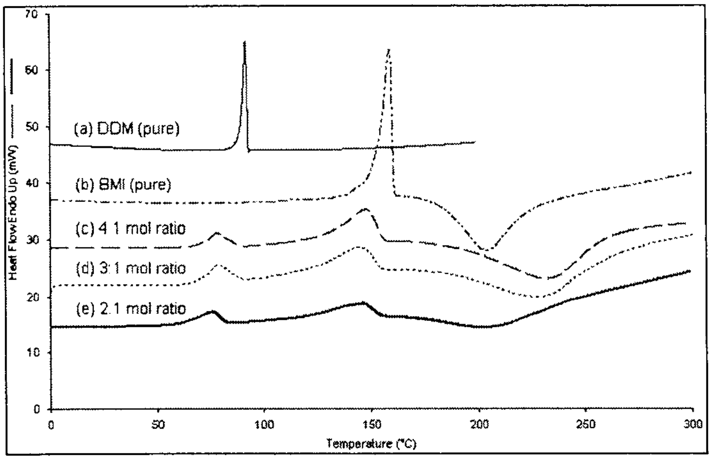

Figure 2. DSC thermograms of pure and admixtures of BMI and DDM at different stoichiometric ratios.

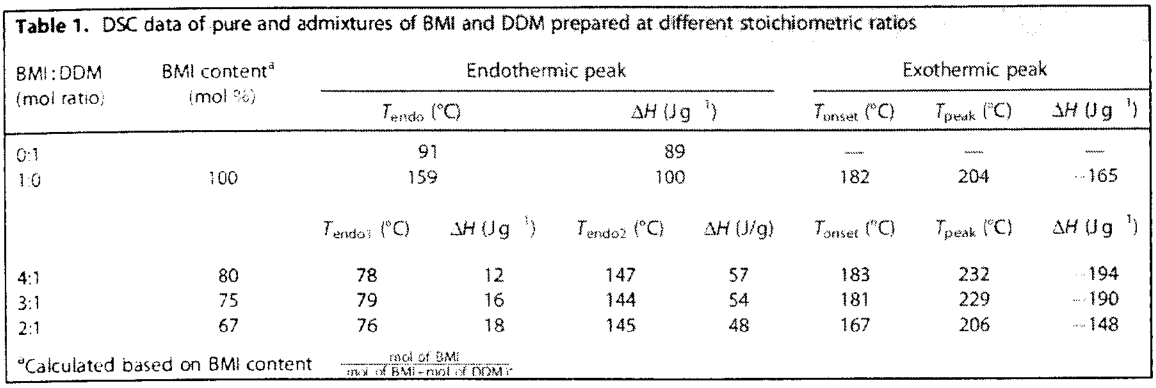

Table 1. DSC data of pure and admixtures of BMI and DDM prepared at different stoichiometric ratios

BMI : DDM (mol ratio)	BMI content[a] (mol %)	Endothermic peak				Exothermic peak		
		T_{endo} (°C)		ΔH (J g^{-1})		T_{onset} (°C)	T_{peak} (°C)	ΔH (J g^{-1})
0:1		91		89		—	—	—
1:0	100	159		100		182	204	-165
		T_{endo1} (°C)	ΔH (J g^{-1})	T_{endo2} (°C)	ΔH (J/g)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J g^{-1})
4:1	80	78	12	147	57	183	232	-194
3:1	75	79	16	144	54	181	229	-190
2:1	67	76	18	145	48	167	206	-148

[a] Calculated based on BMI content $\frac{\text{mol of BMI}}{\text{mol of BMI} + \text{mol of DDM}}$

Figure 2 and Table 1 show the thermograms and data obtained from DSC of pure BMI and DDM as well as their admixtures prepared at different BMI/DDM stoichiometric ratios. As shown in Fig. 2(a, b), the endothermic peaks at ~90°C and ~160°C indicate the melting temperatures of the DDM and BMI monomers, respectively. Additionally, all admixtures (Fig. 2(c–e)) showed two endothermic peaks, which correspond to the melting temperature of DDM and BMI. All systems (formulations), except for pure DDM, showed an exothermic peak indicating one or more polymerization reactions. The pure BMI in Fig. 2(b) demonstrated an exothermic peak starting at ~180°C, which represents reaction III (Fig. 1). As illustrated in Table 1, the addition of DDM has reduced the melting temperature (from 158°C to ~146°C) and the corresponding enthalpy (from 100 to 48 J g^{-1}) of BMI. This could be due to the reaction between the melted DDM and BMI monomers, which leads to rapid depletion of BMI.

The T_{onset} and T_{peak} of the exothermic peaks of the BMI/DDM admixtures decrease with increasing DDM content, and this might be due to the high magnitude of reaction I (Fig. 1). Tungare et al. [33] have reported that reaction I occurs prominently at 125°C, while reaction III is predominant at temperatures above 165°C. It should be noted that the exothermic peak representing reaction I could not be seen clearly from the thermograms (Fig. 2(c–e)) because of possible overlap with the BMI melting peak, which starts at around 130°C. Therefore, the exothermic peak observed for BMI/DDM admixtures mainly represents reaction III. However, the DSC study showed that reaction I starts at a lower temperature, while reaction III occurred at a higher temperature, which is consistent with previous work [32–34,36]. The results also show that the enthalpy of the exothermic reaction increases with BMI content in the admixture, probably because of an increased possibility of reaction III (Table 1).

However, the ΔH of the pure BMI was found to be lower than that of BMI/DDM in 4:1 and 3:1 formulations. This might be due to incomplete conversion of the maleimide double bonds in the pure BMI during the dynamic DSC scan. It has been reported that cessation of polymerization prior to total monomer conversion is typical in the curing of thermosets due to diffusion control [37,38]. Figure 2(c-e) also shows that the exothermic peak becomes broader and shifts to a higher temperature (Tpeak, Table 1) with an increase in BMI content. These phenomena could be related to the increase in viscosity of the BMI/DDM at higher BMI content because of an increase in the degree of cross-linking [1,37]. It is important to note that reaction I will predominantly occur during the melt-mixing process, which was conducted at 150°C in this study; 150°C is the best temperature for the melt-mixing process because the BMI melts at this point in the presence of DDM (Table 1). In addition, the selection of temperatures above this point for the meltmixing process would lead to intense reaction III,[33] which would increase the viscosity of the polymer melt and affect the molding process.

4.2 Effect of DCP on the curing profile of BMI/DDM thermoset

Table 2. DSC data of BMI/DDM prepolymers prepared at different mol ratio and different concentrations of DCP

	Prepolymer	Exothermic peak		
DCP content (wt%)	T_g (°C)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J g^{-1})
0.0[a]	43	163	204	−88
0.1[b]	47	144	163	−152
0.3[b]	45	138	156	−155
0.5[b]	—	146	177	−40
0.1[c]	47	148	166	−174
0.1[d]	53	139	157	−180

[a] Blank.
[b] BMI/DDM 2:1.
[c] BMI/DDM 3:1.
[d] BMI/DDM 4:1.

The use of a curing accelerator or initiator can decrease the curing temperature and shorten processing time. Table 2 shows the data obtained from DSC of BMI/DDM prepolymers prepared in a 2:1 mol ratio with different DCP concentrations. All the prepolymers (except for the 0.5% DCP) showed a T_g in the lower temperature range (i.e. 43–47°C). The low T_g not observed for 0.5% DCP content might be attributed to the rapid cross-linking reaction (III) during the melt-mixing process at 150°C. The introduction of DCP into the BMI/DDM system (up to 0.3%) also decreased the T_{onset} and T_{exo} of the exothermic peak compared to the blank system (Table 2).

The reduction in T_{onset} and T_{exo} of the exothermic peak indicates an acceleration of reaction III in the presence of DCP (free radicals). The presence of DCP will initiate reaction III at a much lower temperature because its molecules will decompose to form peroxide radicals at ~120°C (for pure DCP) compared to the thermal initiation (homolytic cleavage) of maleimide double bonds, which starts at ~180°C (Fig. 2(b)). The peroxide radicals from DCP will react with the BMI monomers to form BMI radicals, which will react with BMI monomers to form the cross-linked structure illustrated in Fig. 1(III). However, it should be noted that the introduction of DCP did not start the reaction at ~120°C but at ~140°C (Tonset, Table 2), which is presumably due to competition between primary amines (of DDM) and peroxide radicals toward the maleimide double bonds.

The results given in Table 2 also show that increasing DCP concentration above 0.3% resulted in increased T_{onset} and T_{exo}, indicating a rapid cross-linking reaction (III) during the meltmixing process at 150°C. The exothermic ΔH values at 0.1% and 0.3% DCP contents are found to be similar to the exothermic ΔH of 2:1 admixture (Table 1). These results indicate that the number of maleimide double bonds available for the polymerization reactions is almost same for the 2:1 stoichiometric ratio. The ΔH value at 0.5% DCP content was found to be the lowest as most of the maleimide double bonds are consumed by reaction III, as manifested by the disappearance of the low T_g. On the other hand, the exothermic ΔH of 2:1 prepolymer mol ratio without DCP was very low (-88 J g^{-1}, Table 2) compared to the admixture (-148 J g^{-1}, Table 1). The low exothermic ΔH is a result of the consumption of maleimide double bonds by reaction I during the melt-mixing process. However, it should be highlighted that the ΔH obtained for the exothermic reaction of various BMI/DDM formulations does not necessarily mixing process at 150°C. The introduction of DCP into the BMI/DDM system (up to 0.3%) also decreased the T_{onset} and T_{exo} of the exothermic peak compared to the blank system (Table 2).

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Table 2 also shows the DSC data obtained for the prepolymers at different stoichiometric ratios containing 0.1% DCP concentration. The formulation demonstrates a decrease in reaction temperature (T_{onset} and T_{exo}) as compared to formulation without DCP (Table 1). Increasing the BMI content at a fixed amount of 0.1% DCP shows that the ΔH of the exothermic reaction increases, similar to the findings obtained for the formulations without DCP. It is important to highlight that the addition of DCP only accelerates reaction III. However, the extent of reactions I and II occurring in the system, especially in the presence of DCP, is still unknown at this point from the DSC studies. Selection of curing temperature will significantly affect the extent of these reactions. Reaction III will be highly favored if the curing temperature is chosen to be above 160°C (as suggested by T_{peak}). Therefore, temperature at 150°C (slightly higher than T_{onset}) was selected as the optimal curing temperature. However, all the proposed reactions (I, II, and III) will occur simultaneously at 150°C [32,33].

4.3 Characterization of BMI/DDM reactions using FTIR studies

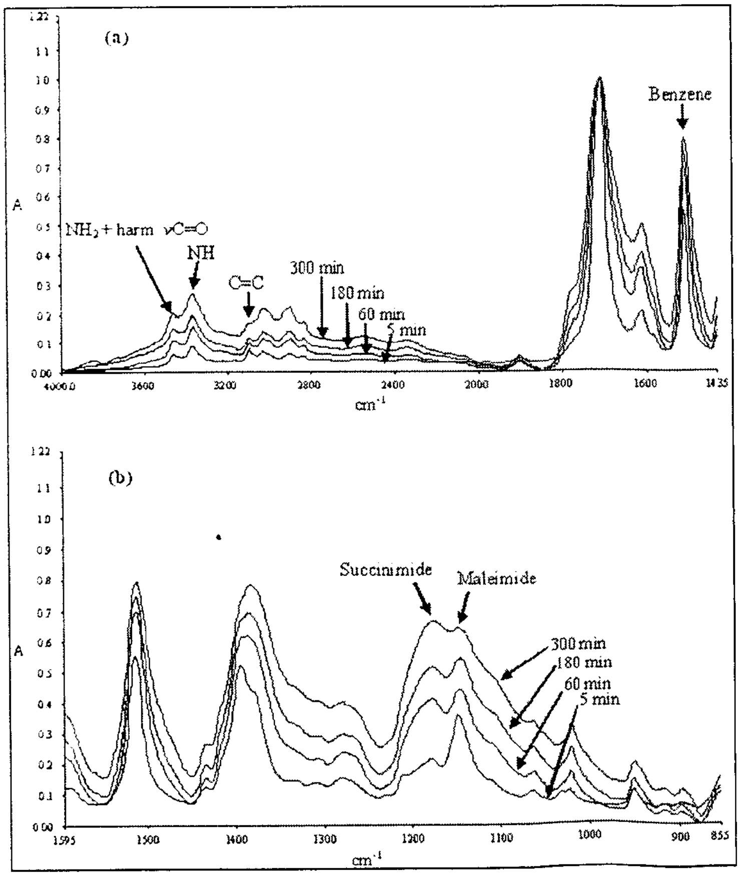

Figure 3. FTIR spectra of 2:1 BMI/DDM prepolymer cured at 150°C as a function of curing time, in the range of (a) 4000–1435cm^{-1} and (b) 1595–855cm^{-1}.

Quantitative FTIR analysis was used to analyze the extent of the polymerization reactions in various formulations of BMI/DDM/DCP. Figure 3 shows the FTIR spectra for the 2:1 stoichiometric ratio of BMI/DDM prepolymers, cured at 150°C (isothermal) as a function of curing time. The peak assignments are given, according to the literature,[31] as follows: 3466 cm^{-1}: harmonic νC=O+NH_2, 3373cm^{-1}: NH, 3100 cm^{-1}: ν=C–H maleimide, 1516 cm^{-1}: benzene, 1717cm^{-1}: νC=O out-of-phase, 1185 cm^{-1}: νCH–CH succinimide, 1145 cm^{-1}: νC–N–C maleimide, 827cm^{-1}: δC=C–H maleimide, 690 cm^{-1}: δC=C–H (cis)maleimide. As the reaction proceeded (increasing reaction time), a decrease in the (normalized) peak intensity was observed for the maleimide (3100 and 1145 cm^{-1}) and primary amine (3466cm^{-1}) peaks. However, the primary amine peak does not completely disappear because of overlap with harmonic C=O vibrations [31]. At the same time, the intensity of secondary amine (3373 cm^{-1}) vibration and succinimide (1185 cm^{-1}) peaks is increased. This observation indicates the progress of reactions I and III with increasing reaction time. However, it is important to quantitatively evaluate these results to obtain information on the progress of various polymerization reactions in the BMI/DDM system [32].

The plot of concentration of various functional groups, i.e. primary amine ([PA]), secondary amine ([SA]), tertiary amine ([TA]), total maleimide groups ([MI]), and maleimide groups consumed for reaction III ([MI]homopolym) as a function of reaction time provides information on the progress of various reactions in the BMI/DDM systems. Figure 4(a–c) shows the concentration of various functional groups as a function of time for different stoichiometric ratios. In general, the trends observed in the figures were consistent with the findings reported by Hopewell et al. [32] [SA] shows the chain-extension reaction I, while [TA] and [MI]homopolym show the cross-linking reactions II and III, respectively.

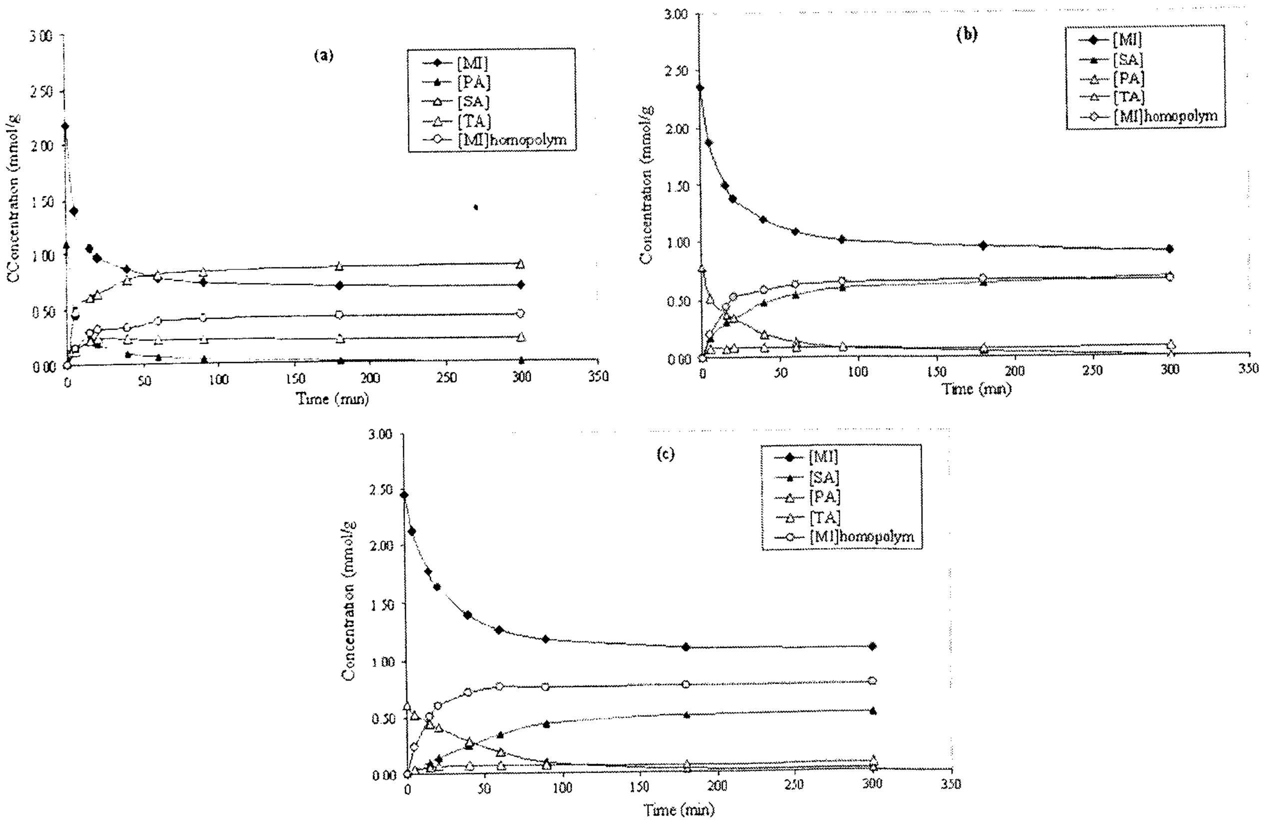

Figure 4. Concentration of various functional groups as a function of time for (a) 2:1, (b) 3:1, and (c) 4:1 BMI/DDM formulations cured at 150°C. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

As shown in Fig. 4(a), for the 2:1 stoichiometric ratio, the formation of secondary amine increased rapidly at earlier stages of the reaction (up to 60min) and then became very slow after 120min. However, for the 3:1 and 4:1 stoichiometric ratios (Fig. 4(b, c)), the formation of secondary amine increased at a slower rate at the beginning of the reaction up to 80 and 100 min, respectively, and then became almost constant after ~120min. These results suggest that with higher concentrations of DDM in the admixture, reaction I proceeds at a faster rate. On the other hand, the decreasing trend of [PA] was found to be consistent with the increasing trend observed for [SA]. Moreover, the rate of consumption of primary amine at the earlier stages of the curing process increased with an increase in the DDM content in the formulations. These results again support the earlier suggestion that the rate of reaction I increases with increasing

DDM content in the formulation. For the 2:1 stoichiometric ratio, the formation of tertiary amine (reaction II) increased up to 5 min of reactions and then became constant.

Similarly, both 3:1 and 4:1 stoichiometric ratios showed an insignificant change in [TA] after 5 min of curing, but the final concentration of the tertiary amine for both stoichiometric ratios was lower than that for the 2:1 stoichiometric ratio. For the 2:1 ratio, the formation of homopolymerization cross-links as indicated by [MI] homopolym (reaction III) increased rapidly at the beginning of the cure reaction (up to 60min) and then became almost constant after ~120min. A similar trend was observed for the other two stoichiometric ratios. However, the final [MI] homopolym increased with increasing BMI content in the formulations because of an increase in the degree of cross-links by reaction III. In addition, the maleimide double bonds (as indicated by [MI]) were not completely consumed even after curing for 5 h at 150°C, independent of stoichiometric ratio. The residual (unreacted) [MI] increased with BMI content in the formulations because the curing temperature used was below the T_{onset} determined from the DSC studies (Table 1). Overall, the FTIR studies revealed the simultaneous occurrence of reactions I, II, and III at 150°C. Furthermore, the presence of the residual maleimide double bonds also verifies the need for a curing accelerator (DCP), which could provide cure completion at 150°C.

4.4 Effect of DCP on the BMI/DDM reactions at 150°C

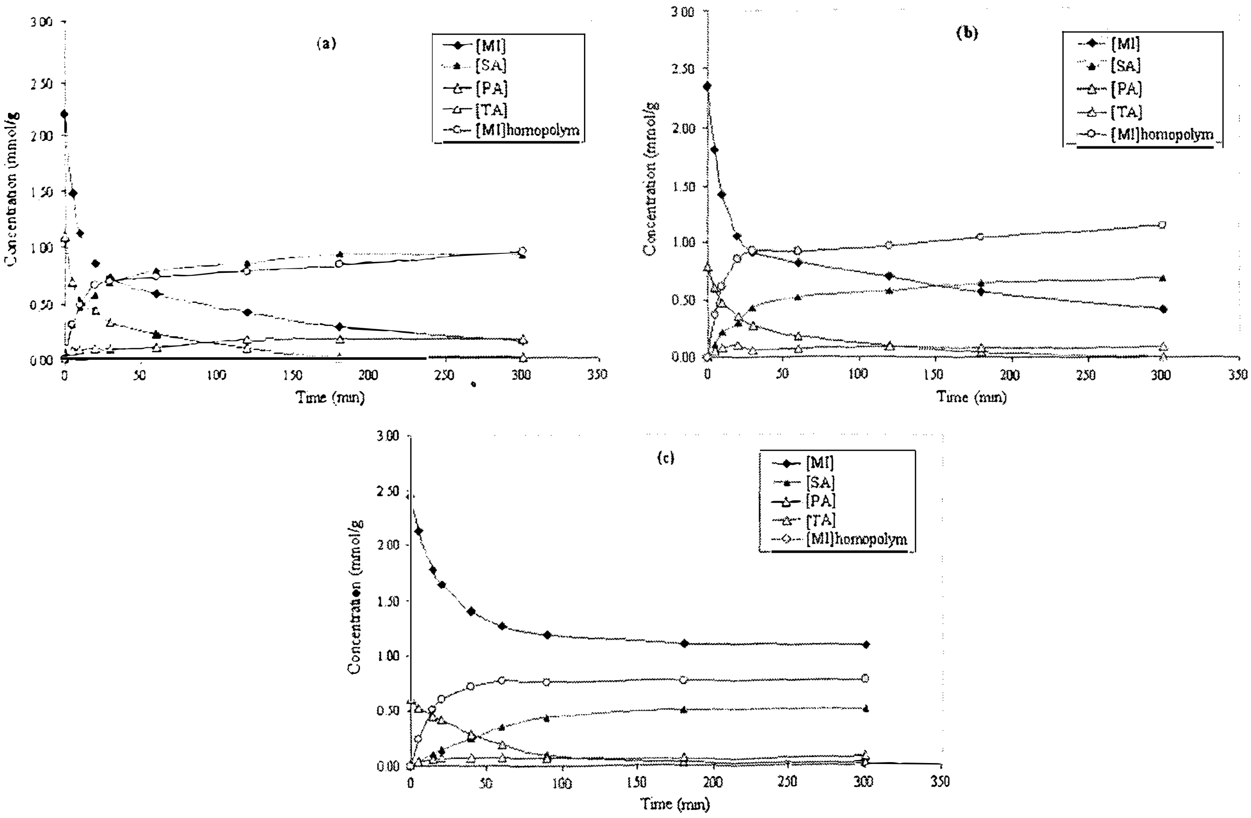

Figure 5. Concentration of various functional groups as a function of time for (a) 2:1, (b) 3:1, and (c) 4:1 BMI/DDM formulations at 0.1% of DCP cured at 150°C. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

The effects of introducing 0.1% DCP in the BMI/DDM formulations on the variation of functional groups at increasing curing time (at 150°C) are shown in Fig. 5(a–c). Essentially, the similar trends are observed as those for the formulations without DCP. For the 2:1 stoichiometric ratio (Fig. 5(a)), [SA] increased rapidly until 60 min and then became almost constant after 180 min. Similar results were observed for [SA] at a 3:1 stoichiometric ratio (Fig. 5(b)). However, for the 4:1 stoichiometric ratio, [SA] increased gradually up to 180min and then becameconstant (Fig. 5 (c)). Correlating with these trends, [PA] decreased accordingly and become almost 0 after 180min, independent of stoichiometric ratio. The trends observed for [TA] were similar to the formulations without DCP, except for the 2:1 stoichiometric ratio, where the formation of tertiary amine was almost constant up to 60min. After that point, [TA] began to increase gradually, becoming constant again after 120min. The suppression of reaction II (as indicated by [TA]) at the beginning of the reaction (up to 60min) could be attributed to the competition between primary and secondary amines toward the maleimide double bonds. As primary amine is more reactive than secondary amine,[34] reaction I was favored at the earlier stage of the curing process, while reaction II becomes prominent after reaction I becomes slower after 60min.

The formation of tertiary amine was found to be less prominent for the 3:1 and 4:1 stoichiometries, which could be due to the low concentration of DDM in the formulations, similar to the formulations without DCP. The [MI]homopolym increased rapidly at the beginning of the curing process, at higher rates than the formulations without DCP (Fig. 4(a–c)). The rate of reaction III, as indicated by the [MI]homopolym curve, also increased with increasing BMI content in the formulations. It was found that the extent of reaction III increases with the addition of DCP and also with the increase in the BMI content in the formulations, consistent with the DSC findings. However, it was found that the rate of reaction III became slower after ~60min (for all formulations), which might be due to the vitrification effect [32]. Interestingly, for the 2:1 stoichiometric ratio, reactions I and III were found to compete at a relatively similar rate. It was found that the result showed that the presence of DCP at low concentrations does not inhibit the amine addition reaction but only slows down its rate, especially for the 2:1 stoichiometric ratio. This is proved by the increase in the completion time for secondary amine formation, i.e. ~180 min (0.1% DCP), compared to ~120 min (without DCP). However, the conversion of maleimide double bonds was not 100%, even in the presence of DCP. It seems that vitrification effect, which restricts the mobility of the molecules, leads slower reaction rates

[32,37,38]. Nonetheless, the conversion of maleimide double bonds achieved in the presence of 0.1% DCP was considerably higher compared to the BMI/DDM systems without DCP. In addition, high conversion was also achieved at a much shorter time (~60 min) compared to the formulations without DCP (~90 min).

Table 3 shows the effect of DCP concentration (0.1–0.5 wt%) on the extent of chain extension (based on [SA]) and on crosslinking reactions (based on [TA] and [MI] homopolym) for various BMI/DM formulations obtained from quantitative FTIR analysis. The results show that the amount of cross-links formed through reaction III (based on [MI] homopolym) increases with increasing DCP content in the formulations. Interestingly, only the formulations with 0.1% DCP showed a similar extent of chain extension (39.4%) to the formulation without DCP (39.9%). The use of DCP above 0.1% resulted in reduced chain extension and enhanced cross-linking, which would increase the brittleness of the BMI/DDM thermoset. In view of this phenomenon, the use of high DCP concentrations will contradict the objective of using DDM to reduce the brittleness of pure BMI resin. Thus, 0.1% is the optimal DCP concentration that could accelerate reaction III without interfering with reaction I; 180 min was selected as the optimal curing time (at 150°C) because the chain-extension reaction (reaction I) was found to be almost complete at this time (based on [SA], Fig. 5). However, it is necessary to conduct post-curing at temperature higher than 150°C to promote total maleimide conversion.