Electron-Beam Curing of Bismaleimide-Reactive Diluent Resins

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ABSTRACT: Electron-beam (E-beam) curing of 4,4'-bis-maleimidodiphenylmethane (BMPM)/BMI-1,3-tolyl/*o,o'*-di-allylbisphenol A (DABPA)–based bismaleimide (BMI) systems and their mixing with various reactive diluents, such as *N*-vinylpyrrolidone (NVP) and styrene, were investigated to elucidate how temperature, electron-beam dosage, and diluent concentration affect the cure extent. The effect of free-radical initiator on the cure reactions was also studied. It was found that low-intensity E-beam exposures cannot cause the polymerization of BMI. High-intensity E-beam exposures give high reaction conversion attributed to a high temperature increase, which induced thermal curing. It was shown that the dilution and activation of NVP in BMI cause a more complete BMI cure reaction under E-beam radiation.

BMI/NVP can be initiated easily by low-intensity E-beam without thermal curing. FTIR studies indicate that about 70% of the reaction is complete for BMI/NVP with 200 kGy dosage exposure at 10 kGy per pass. The sample temperature only reaches about 75°C. The free-radical initiator, dicumyl peroxide, can accelerate the reaction rate at the beginning of E-beam exposure, but does not affect the final reaction conversion. The increase of the concentration of NVP in the BMI/NVP systems increases the reactive conversions almost linearly. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2407–2416, 2004

Key words: electron-beam curing; bismaleimide; reactive diluent; resins; reactive processing

INTRODUCTION

Over the past 20 years, polymer matrix fibrous composites (PMFCs) have been developed for aerospace applications. Structural polymer matrix composites are required to exhibit good high-temperature/high-moisture ("hot–wet") properties, processability, and mechanical performance over a long period of time. Bismaleimide (BMI) resins have been shown to exhibit great potential in aerospace applications because of their high thermal stability, which enables them to bridge the gap between epoxy and high-temperature polyimide resins. BMI also has many advantages such as low moisture absorption and low cost; furthermore, it is nonvolatile and can be easily processed.[1–3]

Thermal cure reactions of BMI systems[4–9] and related resin modifications,[10–17] and structure–property characterization of BMI and BMI composites, have already been widely studied.[17–24] However, conventional thermally cured fabrication has many limitations, such as long curing time, thermal stress and induced shrinkage and microcrack formation, expensive tooling, hazardous chemical volatiles, and size limitations for autoclave processing. Therefore, interest in electron-beam (E-beam) curing of PMFCs has dramatically increased because of its advantages over thermal curing, which include reduced curing times, lower tooling cost, shelf-stable resin systems, low health risks, reduced thermal stresses, and curing at selected temperatures. Moreover, E-beam curing offers the potential to fabricate large integrated structures for cryogenic fuel containments for space vehicles, thus eliminating the need for expensive autoclave processing, which also has size limitations to process such large structures. In addition, the E-beam process could potentially be used to fabricate unique composite hybrids that could not be produced by conventional thermal fabrication processes.[25–29]

E-beam curing is found to be insufficient to cure BMI resin.[30] The addition of reactive diluents into the BMI resin system can increase the reactivity of BMI during E-beam curing. Reactive vinyl diluents, such as *N*-vinylpyrrolidone (NVP), styrene, allylphenol, vinyl

ethers, acrylonitriles, acrylates, and methylacrylates, are widely used to assist BMI curing reactions.[31–33] Grenier-Loustalot et al.[30] made a successful attempt at using NVP as a diluent for E-beam curing of BMI resins. It has been reported that the percentages of residual maleimide functions in BMI/NVP systems are less than 10% and the glass-transition temperatures of the related products are around 240°C after a 400 kGy E-beam dosage at 50 kGy per pass.[30]

E-beam radiation absorption will raise the temperature of the samples together with the resin cure exotherm. The temperature increase ΔT, in samples during E-beam radiation, is proportional to the exposure dosage D and material specific heat C_p, as $\Delta T = D/C_p$. Because the temperature factor plays a critical role in the cure rate and cure mechanisms, processing, and the performance of the final products, the studies of related temperature increases during E-beam curing are important. Unfortunately, there is no report on the temperature–time characteristics of E-beam curing of BMI systems.

In this article we undertook a basic study on E-beam curing of BMI, BMI/styrene, and BMI/NVP systems with *in situ* temperature monitoring to investigate how temperature increases, dosage, diluent concentrations, and catalyst affect cure extent. This will lead to an understanding of the involved reactions and mechanisms, while controlling the optimum processing and performance of final products more easily.

EXPERIMENTAL

Materials

A modified BMI system, CYCOM® 5250-4 resin transfer molding (RTM; Cytec Industries, West Paterson, NJ) was used: it is a tricomponent resin system composed of 4,4'-bismaleimidodiphenylmethane (BMPM), BMI-1,3-tolyl, and *o,o'*-diallylbisphenol A (DABPA) with the molar ratio of 6 : 4 : 5 (Fig. 1). Thus, the overall molar ratio of BMI and DABPA is 2 : 1. This BMI resin is widely used in aerospace composites because of its superior mechanical and thermal properties.[22–24] It will be simply referred to as "BMI" in the following discussion.

N-Vinylpyrrolidone (NVP) and styrene were chosen as the reactive diluents because they have structural units similar to those of BMI and because the crosslinked products with good thermal and mechanical properties can be achieved. Both NVP and styrene were distilled for use. BMI/NVP 20/80, 40/60, 50/50, and 60/40 (wt/wt) and BMI/styrene 50/50 (wt/wt) solutions were prepared for E-beam curing.
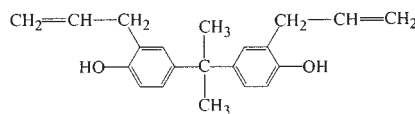
To investigate the effect of catalysts on E-beam curing of BMI systems, dicumyl peroxide was used as a free-radical initiator. After mixing and degassing, the samples of BMI, BMI/NVP, and BMI/styrene, with or
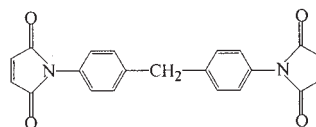
4,4'-Bismaleimidodiphenylmethane (BMPM)
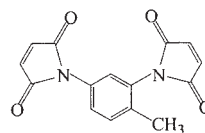
BMI-1,3-tolyl

o,o'-diallylbisphenol A (DABPA)

Figure 1 Chemical structures of the components of BMI 5250-4.

without initiator, were drawn into 1 mL polypropylene syringes for low-intensity E-beam exposures, with an intensity less than 20 kGy per pass. BMI resin was preheated at 75°C in the oven, until molten, to be drawn into the syringes. For high-intensity E-beam exposure with 400 kGy dosage at 40 kGy per pass, samples were stored in small glass vials (diameter: 3 mm) instead for E-beam curing because the plastic syringe will be melted as a result of the high temperature increase from high-intensity E-beam radiation.

E-beam curing

E-beam curing of samples was carried out by a 10 MeV accelerator rated at 4 kW by Acsion Industries, Inc. (Pinawa, Manitoba, Canada). Different dosages and pass increments were applied, and thermocouples were used to monitor the temperature of samples during exposure. A fully cured epoxy sample, provided by Acsion Industries, was used as a reference during temperature monitoring to determine whether the temperature increase arose from exothermal chemical reactions or beam energy absorption only. The resin-filled syringes or vials were placed on a conveyor belt and passed back and forth under the accelerator. The thermocouples were embedded roughly 2 cm into each of the syringes or vials.

The dependency of reaction conversion on accumulated exposure dosage was investigated under E-beam radiation at 10 kGy per pass. All of the samples were treated at the same time. Then, one of samples was removed after the first pass. The rest of the samples were subsequently treated by E-beam and, then, one of samples was removed after each pass. The samples were treated and then removed one by one in this manner, producing samples with different dosage exposures.

Characterizations

Temperature profiles of BMI, BMI/styrene, and BMI/NVP systems during E-beam curing were monitored in a range of experiment sets. To investigate the response of temperature increase on each radiation dose and reaction progress, the samples were cooled to room temperature by applying a fan after each dose of E-beam exposure. In other experiments, the temperature profiles were obtained without a need to use a fan.

The glass-transition temperatures (T_gs) of the cured samples were measured by a Perkin–Elmer DSC Pyris I system (Perkin Elmer Cetus Instruments, Norwalk, CT). Temperature was scanned from -50 to 350°C at 10°C/min.

FTIR analysis was used to measure the reaction conversion of BMI after E-beam curing. A Nicolet Avatar 360 spectrometer (Nicolet Analytical Instruments, Madison, WI) was used in this study. BMI monomer and the cured samples were ground into a powder and then prepared as KBr pellets. For liquid samples, such as NVP and styrene monomers or uncured mixture solutions, a drop of sample was placed between two KBr windows and then measured. The number of accumulations was set at 64 with a resolution of 2 cm^{-1}.

The degree of crosslinking (gel content) was measured by dissolution tests. A sample of approximately 0.1 g (m_1) was ground into a powder and then wrapped in a filter paper with known mass (m_2). The package was placed in a Soxhlet extraction apparatus and extracted by refluxed acetone for 48 h. The package was then removed and dried in a vacuum oven at 80°C for 16 h. The mass of the package (m_3) was then weighed. Degree of crosslinking was measured in terms of the percentage gel content, using the equation.

$$\text{Gel content (\%)} = [(m_3 - m_2)/m_1] \times 100$$

RESULTS AND DISCUSSION

Low-intensity E-beam curing

Temperature profile

During the experiment, the samples were cooled to room temperature after each dose and then treated by the next
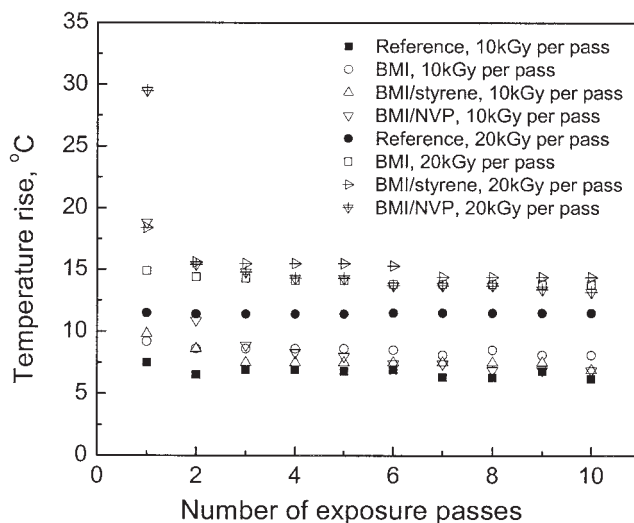

Figure 2 Temperature increase of different systems versus number of E-beam exposure passes.

dose. As shown in Figure 2, the temperature increase of samples is dependent on total applied E-beam exposure dosages and applied dosage per pass. The corresponding rise values at 20 kGy per pass radiation are twice those at 10 kGy per pass, which obeys the relation $\Delta T = D/C_p$. However, the temperature increase ΔT during each pass is quite different during the whole cure processing. For the BMI resin, the temperature increase during each pass did not change significantly. However, for BMI/styrene and BMI/NVP systems, temperature increases of the samples during the first two passes were higher than those during the rest of the passes. The temperature increase during E-beam radiation comes from both beam energy absorption and free-radical–induced exothermal cure reactions. The cure reactions are slowed after the first two passes, as the concentration of unreacted species decreases. The reaction rate was the highest during the first radiation pass and then went smoothly thereafter. The diffusion-control mechanism plays a role as the rising T_g reaches the cure temperature, which means the mobility of free radicals and molecular chains decreases because of the increase of viscosity of the systems, so that the cure reactions are hindered from proceeding easily and smoothly. Therefore, E-beam–induced dissociation of the double bond of NVP or styrene containing BMI occurred more easily than that of BMI itself. Meanwhile, specific heat C_p of the material will increase during the cure reactions, which also reduces the extent of temperature increase. The extent of cure reactions, as monitored by FTIR measurements, substantiates the above explanations.

Cure results of BMI, BMI/NVP, and BMI/styrene systems

A comparison of the FTIR spectra of uncured, thermal-cured, and E-beam–cured BMI samples (Fig. 3) shows
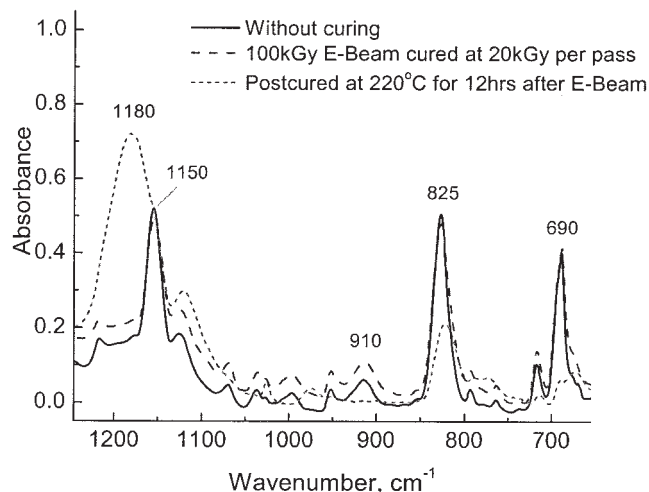
Figure 3 FTIR spectra of BMI systems.

Figure 4 Reaction conversions of BMI cured by different E-beam radiation conditions from FTIR measurements.

that the absorptions around 1150 cm^{-1} ($\nu_{\text{C—N—C}}$ in maleimide ring), 990 and 910 cm^{-1} ($\delta_{\text{C=C—H}}$ of allyl group), 825 cm^{-1} ($\delta_{\text{C=C}}$ of maleimide double bond), and 690 cm^{-1} ($\delta_{\text{C=C—H}_{\text{cis}}}$ cis) decrease significantly after thermal curing. On the other hand, a new strong absorption at 1180 cm^{-1} ($\nu_{\text{C—N—C}}$ in succinimide ring) appears after thermal curing. Therefore, the reaction conversion of BMI can be given by the consumption of double bonds through the calculation of the decreased intensities of the bands at 1150, 825, and 690 cm^{-1}. Because the absorption of 825 cm^{-1} is superimposed on a vibration band of the aromatic =C—H out-of-plane deformation, it never disappeared completely from the spectrum after thermal cure. We can assume that the reaction conversion of thermal-cured BMI reaches 90% and then compare the intensity of 825 cm^{-1} absorption of E-beam–cured samples with that of thermal-cured BMI to obtain the relative reaction conversion. The absorption of benzene rings around 1511 cm^{-1}, inert from the reactions, was used as an internal standard. The reaction conversion can be calculated by relative intensity ratio compared between the intensity of the reaction-involved peaks and that of the internal standard. The quantitative results are shown in Figure 4.

From the results of FTIR, the reaction conversions of the BMI system are low and around 5–15% after E-beam treatment. The reaction conversions are increased with increasing total dosage and applied dosage per pass, as shown in Figure 4. DSC results showed that all the T_gs of the treated BMI samples are around 10–20°C, which are very close to the T_g of uncured BMI at 10°C. Because 5250-4 RTM BMI resin cannot flow below 70°C, together with the cure temperature data (as shown in Fig. 2) from E-beam curing, which shows that the temperature of BMI did not exceed 40°C during the E-beam exposure, the BMI resin will remain in the solid state during E-beam
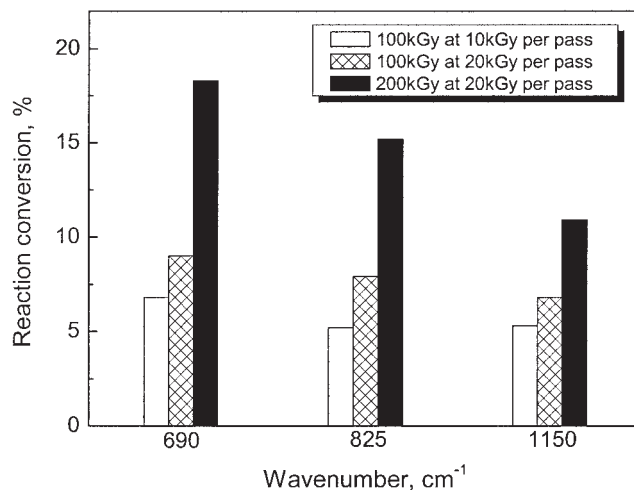
exposure at 10 or 20 kGy per pass. Therefore, even if free radicals are generated by E-beam exposure at low temperatures, chain propagation is still hindered from readily occurring. As a result, the temperature increase of BMI samples, under relatively low E-beam intensity radiation, remains low and is mostly generated from beam energy absorption.

A comparison of the FTIR spectra of uncured and thermal cured BMI/styrene 50/50 samples (Fig. 5) shows that the absorptions around 1150, 990, 910, 825, and 690 cm^{-1} decrease significantly, together with the appearance of 1180 cm^{-1} after thermal curing. Because both BMI and styrene have IR absorption around 990 and 690 cm^{-1}, the total consumption of allyl groups in the BMI/styrene system can be calculated from the
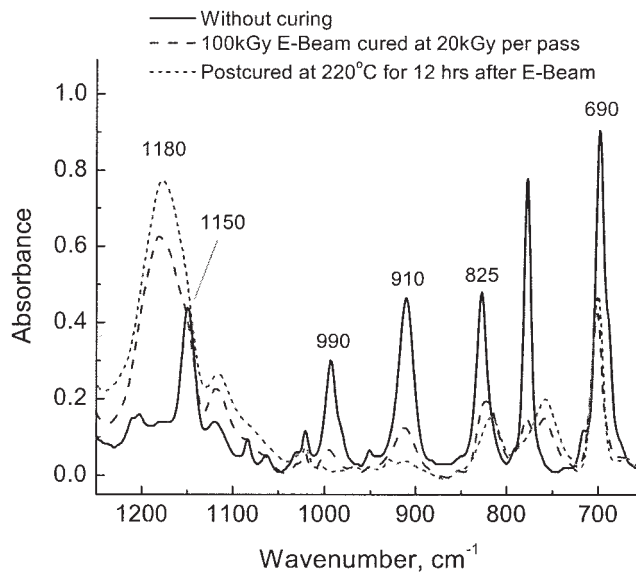

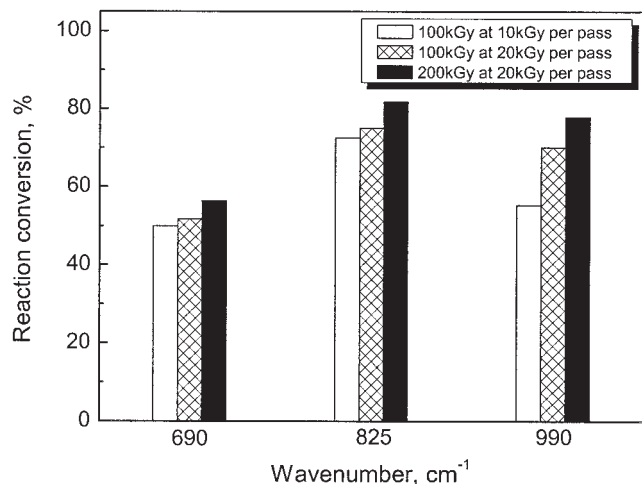**Figure 5** FTIR spectra of BMI/styrene systems.

Figure 6 Reaction conversions of BMI/styrene 50/50 cured by different E-beam radiation conditions from FTIR measurements.

Figure 8 Reaction conversions of BMI/NVP 50/50 cured by different E-beam radiation conditions from FTIR measurements.

decreased intensities of these two bands, with 1511 cm^{-1} as an internal standard. The band at 825 cm^{-1} is attributed to BMI only, so that the reaction conversion of BMI in the system can also be obtained. From these quantitative results, shown in Figure 6, the reaction conversion of the BMI/styrene system reaches above 60% after 200 kGy E-beam radiation. The conversion increases with the increase of applied dosage per pass and total applied dosage. However, the cure products of the BMI/styrene system showed serious phase separation that probably is attributable to the high vapor pressure of styrene and unfavorable variation of the entropy of mixing.[34] As a result of these findings, we chose NVP as the reactive diluent in the following study.

A comparison of the FTIR spectra of uncured and thermal-cured BMI/NVP 50/50 samples (Fig. 7) shows that the absorptions around 1330 cm^{-1} (in-
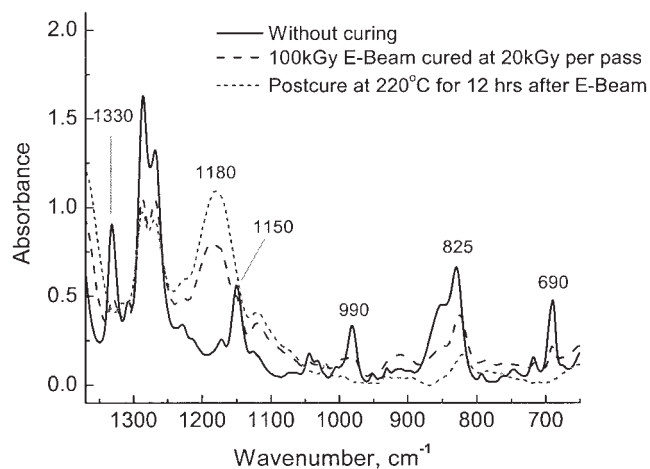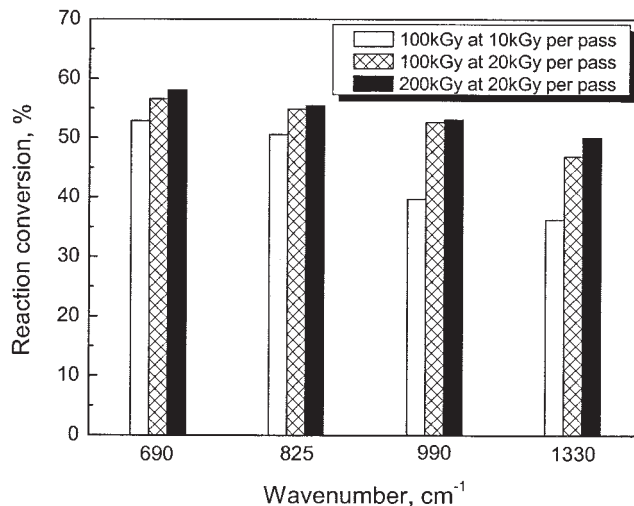
plane CH deformation vibrations of NVP vinyl group), together with 1150, 990, 825, and 690 cm^{-1}, decreases significantly after thermal curing. Meanwhile, 1180 cm^{-1} appears after thermal curing, which is attributed to the structure of the succinimide ring. The band at 990 cm^{-1} is attributed to the double bonds of both BMI and NVP, so that it can be used to calculate the total consumption of allyl groups in the BMI/NVP system. The band at 1330 cm^{-1} is attributed to NVP only and the bands at 825 and 690 cm^{-1} are attributed to BMI only, so that the consumption of BMI and NVP can also be obtained separately. The peak at 1511 cm^{-1} was used as an internal standard. From the quantitative data shown in Figure 8, the conversion results of BMI/NVP are similar to those of BMI/styrene. Above 50% reaction, conversion can be achieved after 200 kGy dosage.

Obviously, the addition of reactive diluents into BMI resin can substantially improve the reactivity of the BMI system. The increases of applied dosage per pass and total applied dosage lead to higher reaction conversion. However, the dependency of the reaction extents of these resin systems on dosage must be investigated further to characterize the diffusion-control mechanism and cure kinetics during E-beam radiation.

Effects of total dosage on reaction conversion of BMI/NVP system

We carried out a cure reaction study of BMI/NVP 50/50 system at 10 kGy per pass without sample cooling to investigate the effects of total applied E-beam exposure dosage on cure reaction conversion. From the temperature profiles, the maximum temper-
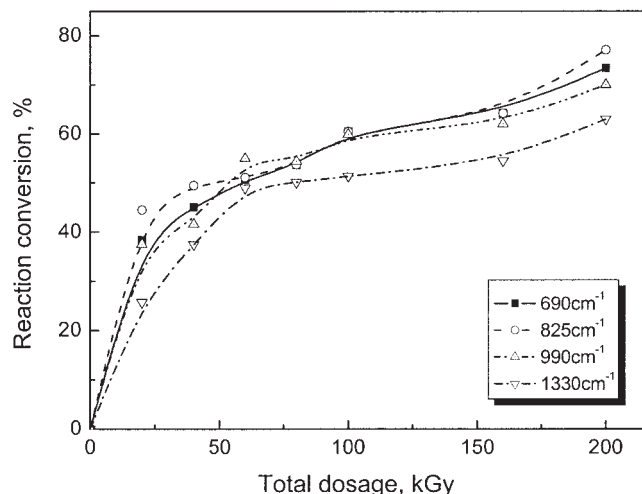

Figure 7 FTIR spectra of BMI/NVP systems.

Figure 9 Dependency of reaction conversion of BMI/NVP 50/50 on applied E-beam dosage (10 kGy per pass).

ature recorded during the whole radiation exposure was 70°C. The intensities of the absorption bands around 690, 825, and 1330 cm^{-1} from FTIR were used to calculate the consumption of BMI and NVP after E-beam exposure. Meanwhile, the consumption of allyl groups was calculated from the 990 cm^{-1} band. From Figure 9, the trends of those curves obtained from the different IR absorptions are similar, which indicates the calculation of reaction conversion is quite reliable. It can be noted that the increase of total E-beam dosage increases the extents of cure reaction. After the first 20 kGy total dosage radiation, a glass-like product was obtained with the reaction conversion of 35% and T_g of 130°C. Subsequently, the reaction rates slowed down and the consumption of double bonds was about 70% after 10 single-pass exposures of 10 kGy. Meanwhile, the T_g of the product increased to 180°C. The degree of crosslinking results, shown in Figure 10, indicate that the sample's degree of crosslinking reached to 40% right after the first 20 kGy total dosage radiation and then finally increased slowly to 65%, similar to the results of reaction conversion obtained from FTIR measurement. Combined with the observation we made earlier from Figure 2, that the temperature increases during the first two passes were much higher and then became stable, we may conclude that vitrification of the BMI/NVP 50/50 system occurred during the first two E-beam radiation passes at 10 kGy per pass. After that, the cure reactions continued more slowly in the glassy state, given that polymerization in the glassy state is diffusion controlled. However, compared to the BMI resin, a much higher solid-state reaction rate of the BMI/NVP system can be achieved under E-beam radiation for similar radiation conditions. NVP substantially increases the activity of BMI as a consequence of charge-transfer effects. Charge-transfer complexes formed be-
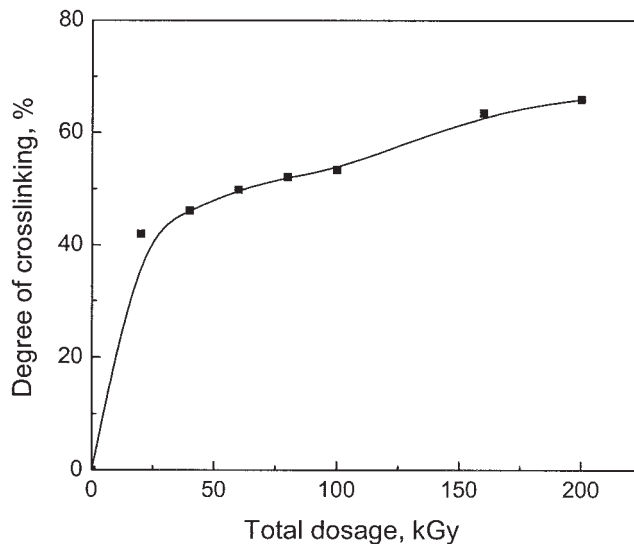
tween NVP and BMI lower the energy required to cure the systems, so that the cure rates and conversions are increased. It has been reported that cyclic amides form charge-transfer complexes that enhance photochemical and free-radical polymerization of maleic anhydride and methyl methacrylate.[35]

The effect of dicumyl peroxide initiator on E-beam curing of BMI/NVP was investigated under the same dosage exposures. Furthermore, the extents of reaction conversions of BMI/NVP 50/50 with those of BMI/NVP 50/50 with 1% dicumyl peroxide (Fig. 11) were compared. The reaction conversions generally increase with increasing applied E-beam radiation dosage, which is similar to the BMI/NVP 50/50 system

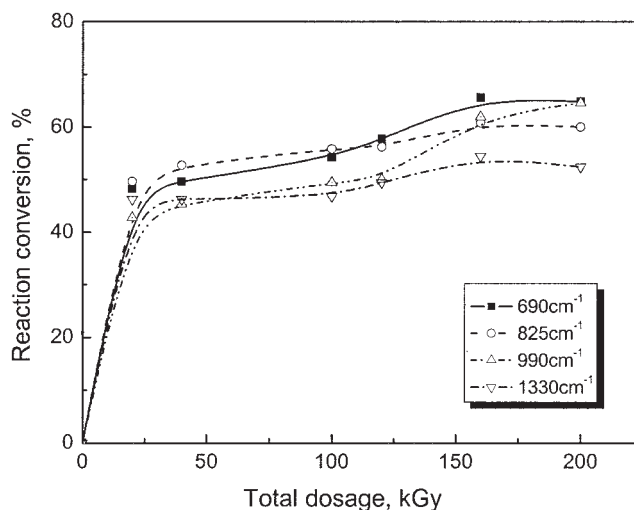**Figure 10** Dependency of degree of crosslinking of BMI/NVP 50/50 on applied E-beam dosage (10 kGy per pass).

Figure 11 Dependency of reaction conversion of BMI/NVP 50/50 with 1% dicumyl peroxide on applied E-beam dosage (10 kGy per pass).
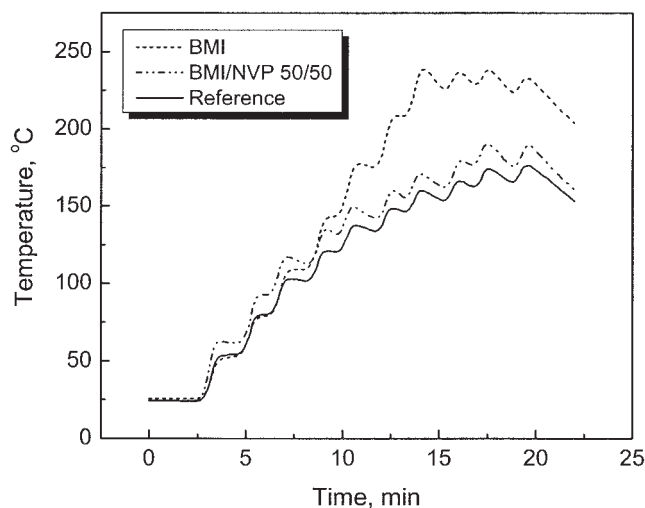
Figure 12 Temperature data of BMI and BMI/NVP 50/50 during E-beam curing at 40 kGy per pass (total 400 kGy dosage).

without peroxide. However, higher reaction conversion of BMI/NVP is observed at the beginning of E-beam exposure in the presence of the initiator. Finally, the consumption of allyl groups in both systems tends to be very close. We can conclude that the initiator can increase the reaction rate at the beginning of E-beam curing of the BMI/NVP system when the viscosity of the materials was still relatively low. After the cure reaction reached a certain level and the vitrification took place, initiators hardly affected the glassy-state reaction rate, nor did they affect the cure conversion to the final products.

High-intensity E-beam curing

To investigate the effects of high-intensity E-beam radiation on BMI and BMI/NVP cure processes, a total 400 kGy E-beam exposure at 40 kGy per pass, without any sample cooling process, was applied for the curing of BMI and BMI/NVP 50/50 systems. The temperature profiles are shown in Figure 12. Each peak in the curve corresponds to the temperature increase during each radiation dose. The whole process took 20 min. We can observe that the high-intensity E-beam radiation caused a significant increase in temperature. The temperature of the BMI/NVP 50/50 sample rose to 62°C after the first 40 kGy dosage and 190°C after 10 passes. The temperature of the BMI sample even reached 230°C after 10 passes. The following reaction types have been proposed to be involved in the thermal-cure process of BMPM/ DABPA-based resin: "ene," Diels–Alder, homopolymerization, copolymerization, rearomatization, and etherification.[6] It is known that these reactions will not take place until the temperature reaches above 100°C.[6]

Therefore, thermal-cure mechanisms will occur in such a high-intensity E-beam radiation process.

As shown earlier, E-beam radiation can initiate the polymerization of BMI/NVP even at low intensity and low temperature. Thus, the initial temperature increase of BMI/NVP was higher than the reference during the E-beam process because of the onset of the cure reactions. However, the increases of temperature in BMI were very close to those of the reference sample during the first two doses, but much higher than those after the third dose, thus indicating that E-beam curing alone cannot propagate the polymerization of BMI even at 40 kGy per pass until the three passes of 40 kGy radiation (total 120 kGy dosage) have been applied. From Figure 12, the temperature of BMI during the third pass of E-beam radiation increased from 77 to 110°C. The original three-component BMI resin can flow above 70°C, and the viscosity of the resin is reduced significantly, which increases the chain mobility and the reactivity of the system. Meanwhile, the "ene" reaction and other thermal-curing mechanisms were induced when the temperature of BMI exceeded 100°C. The heat generated from these reactions further increased the temperature of BMI during E-beam exposure. After three passes of exposure (total 120 kGy dosage), the temperatures of BMI were even much higher than those of BMI/NVP because a significant portion of the BMI/NVP cure already occurred during the initial radiation exposure.

Based on the 690 and 825 cm^{-1} infrared bands from FTIR measurements (Fig. 13), the reaction conversions of BMI and BMI with 1% dicumyl peroxide reach 80% after 400 kGy E-beam exposure at 40 kGy per pass and the T_g of the product is 215°C. Obviously, the high-intensity E-beam process significantly increases the cure conversion. However, the consequent fast tem-
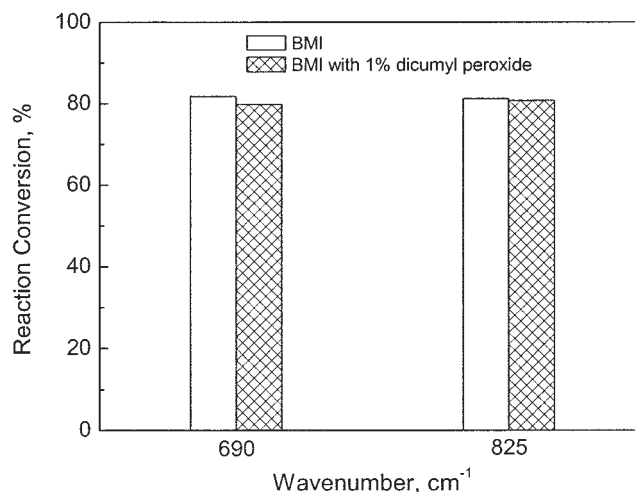

Figure 13 Reaction conversions of BMI systems after high-intensity E-beam radiation (dosage applied: 400 kGy at 40 kGy per pass).
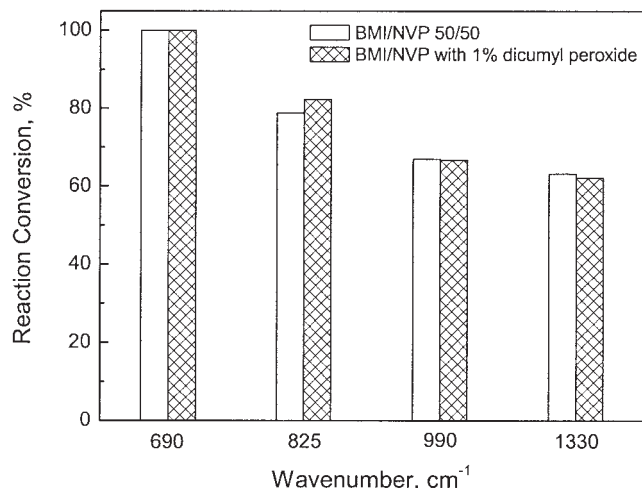
Figure 14 Reaction conversions of BMI/NVP systems after high-intensity E-beam radiation (dosage applied: 400 kGy at 40 kGy per pass).

Figure 15 Temperature data of different BMI/NVP systems during E-beam curing at 10 kGy per pass (total 200 kGy dosage).

perature increase must be considered carefully because thermal stresses and induced shrinkage stresses could affect the final resin properties and diminish the advantages of E-beam curing. Figure 14 shows the reaction conversions of BMI/NVP 50/50 and BMI/NVP 50/50 with 1% dicumyl peroxide systems after 400 kGy of E-beam exposure at 40 kGy per pass. It is shown that the conversion of BMI in the BMI/NVP system is above 80%, but the consumption of NVP and total allyl groups is only about 62 and 67%, respectively. The T_g of the final product is 200°C. The above reaction conversions and T_g of BMI/NVP products are close to those reported by Grenier-Loustalot et al.,[30] who cured the modified BMI/NVP resin by 400 kGy at 50 kGy per step. Also, the conversion results support our earlier conclusion that initiators do not affect the cure conversion of the final products. We note that the effect of higher-intensity E-beam radiation on the BMI system is much more significant than that on the BMI/NVP system, which indicates that thermal curing is the dominant process in the BMI system during high-intensity E-beam exposure. However, for the BMI/NVP system, E-beam–induced cure rather than thermal cure is dominant, which makes low-intensity E-beam curing at low temperature possible.

Effects of diluent concentration

To investigate the effects of diluent concentration on E-beam curing of BMI resins, BMI/NVP systems with different NVP concentrations were irradiated by a total 200 kGy of E-beam exposure at 10 kGy per pass, with the temperature being monitored. The temperature profiles are shown in Figure 15. Each peak in the plots corresponds with temperature increases during each radiation pass. The higher the concentration of
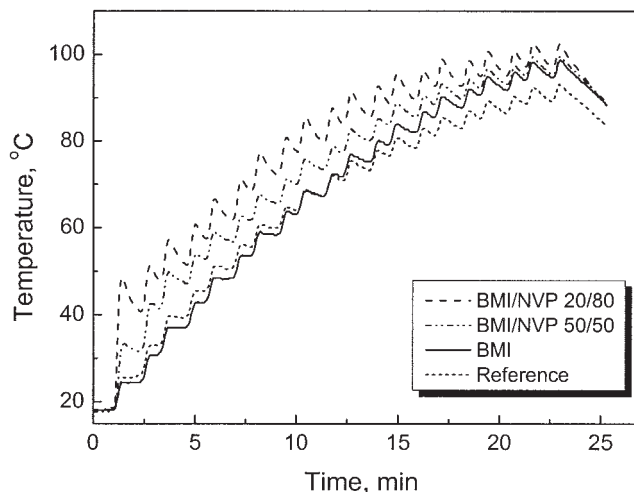
NVP in the BMI/NVP system, the higher the sample temperature found during the E-beam radiation. The higher concentration of reactive diluents in the BMI system, the lower the viscosity, and the greater reactivity of the system together cause a higher temperature increase during the cure reaction. It is also shown that the temperature increase of BMI tends to be close to that of BMI/NVP systems after the temperature of BMI reaches about 95°C, which is consistent with earlier observations from high-intensity E-beam exposure. The temperature increases of BMI are similar to those of the fully cured reference when the sample temperature is below 70°C and much higher than those of the fully cured reference when the sample temperature is above 70°C, which together confirm
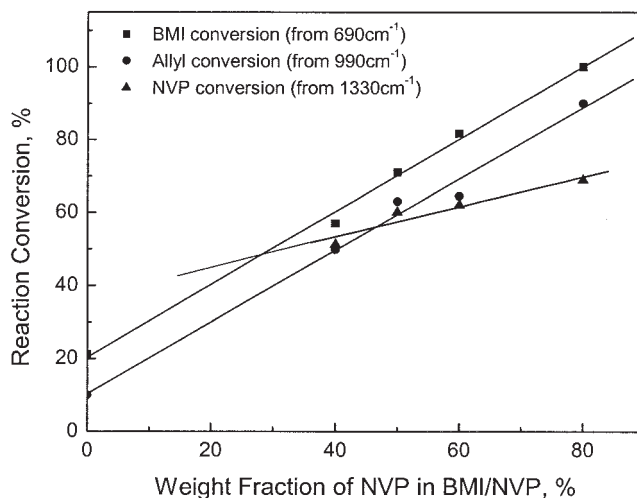

Figure 16 Dependency of reaction conversion of BMI/NVP system on concentration of NVP (dosage applied: 200 kGy at 10 kGy per pass).
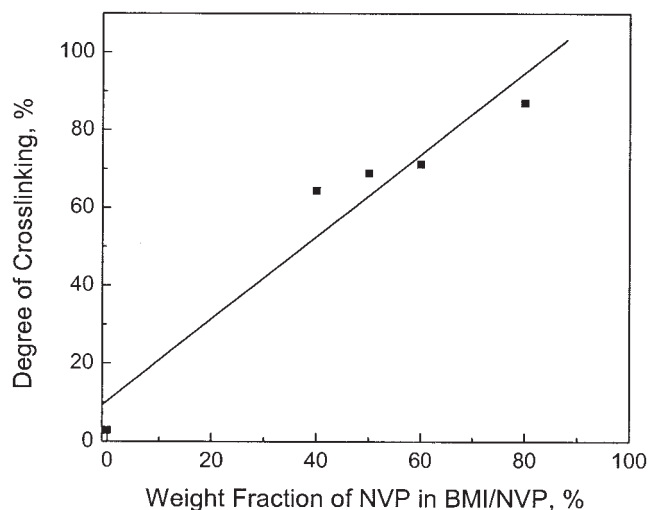
Figure 17 Dependency of degree of crosslinking of BMI/NVP system on concentration of NVP (dosage applied: 200 kGy at 10 kGy per pass).

that the viscosity of the BMI resin plays a critical role in E-beam curing. Based on FTIR measurements, the reaction conversions of the BMI/NVP system increase almost linearly, with increasing concentration of NVP in the system (Fig. 16). The degree of crosslinking of BMI/NVP 20/80 reaches 87% (Fig. 17). The increase of NVP fractions in the BMI/NVP system will decrease the viscosity of the BMI resin and activate the curing so that both the reaction conversion and degree of crosslinking are significantly increased. However, the increase of NVP fractions in the system does not increase the reaction conversion of NVP itself as much as that of BMI. It should be noted that NVP alone does not cure readily with E-beam radiation. Even using NVP alone we can obtain only less than 80% of conversion after E-beam radiation at the same dosage condition. Free-radical homopolymerization of NVP is well known and it is a readily polymerizable monomer. It would appear that the enhanced cure conversion observed with NVP as a diluent monomer is attributable to charge-transfer complexes formed between NVP and BMI, which means the dilution and activation effects of NVP together play the most important role in the interaction between BMI and NVP, and make BMI more reactive upon E-beam radiation.

CONCLUSIONS

According to the results of reaction conversion of BMI cured by different total E-beam radiation dosages at 10, 20, and 40 kGy per pass, E-beam exposure cannot propagate the polymerization of BMI system until the temperature increases to 100°C. However, the solid-state cure reaction of BMI does occur to some extent and small amounts of oligomers may be generated

under low-intensity E-beam radiation, although the reaction conversion is low. A higher-intensity E-beam at 40 kGy per pass can give high reaction conversion of BMI above 75%. However, the temperature of BMI reached 250°C, which induced the normal thermal cure mechanism.

NVP is a good reactive diluent for BMI resin. It decreases the viscosity of BMI resin so that the reactivity of the system is significantly increased. The cure extents of BMI/NVP increase with increasing dosage and applied dosage per pass. The reaction conversion of BMI/NVP is up to 40% after the first two passes of 10 kGy dosage exposure. The reaction rate slows down after that because of diffusion control. According to the results from FTIR, 200 kGy total dosage E-beam exposure, at 10 kGy per pass, can give 70% reaction conversion of BMI/NVP with a temperature increase of no more than 50°C. The product has a T_g of 180°C. The free-radical initiator dicumyl peroxide can accelerate the reaction rate at the beginning of E-beam cure reaction but hardly affects final cure conversion.

The effect of higher-intensity E-beam radiation on the BMI system is much more significant than that on the BMI/NVP system, which indicates that thermal curing is the dominant process in the BMI system during high-intensity E-beam exposure. With respect to the BMI/NVP system, E-beam–induced cure rather than the normal thermal cure is dominant, which makes low-intensity E-beam curing at low temperature possible. The increase of the concentration of NVP in the system increases the reaction conversions almost linearly. The dilution and activation effects of NVP together play the most important role in the interaction between BMI and NVP, causing BMI to have a more active response on E-beam radiation.

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