

Synthesis of Bismaleimide Resin Containing the Poly(ethylene glycol) Side Chain: Curing Behavior and Thermal Properties

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ABSTRACT: Two maleimido end-capped poly(ethylene glycol) (m-PEG) of different molecular weights were synthesized and blended at various proportions with bismaleimide resin (4,4'-bismaleimido diphenylmethane) (BDM). The curing behavior and the thermal properties of the m-PEG/BDM blends were studied and presented here. It was found that the addition of m-PEG enhanced the processability of the BDM resin significantly. The processing window of the BDM resin was increased from approximately 20 to 80°C. The addition of m-PEG modified resins, however, resulted not only in the reduction in the thermal stability of the blended BDM resin but also elevation of the coefficients of thermal expansion. The changes in thermal/mechanical properties of the blends were found to be proportional to the amounts of m-PEG incorporated. It was observed that the curing behavior, and thermal and mechanical properties, of the blends were independent of the molecular weight of the PEG segment. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2935–2945, 2002

Key words: bismaleimide; poly(ethylene glycol); graft; thermal properties

INTRODUCTION

Bismaleimide (BMI) resins are widely used in applications where good mechanical and thermal stability are prerequisites such as the aerospace and microelectronics applications. These excellent thermal and mechanical properties found in fully cured BMI are due to their highly crosslinked structures. Other benefits of the high crosslink density in BMI include high glass transition temperature (T_g) and low coefficient of thermal expansion (CTE). Despite the advantages mentioned earlier, BMI suffers from poor mechanical toughness, i.e., extreme brittleness.^{1,2} This brit-

tleness has severely limited the application of BMI resins.

Various attempts to improve the impact and fracture toughness of BMI have been reported and they are generally based on the introduction of an incompatible phase into the highly crosslinked network.³ It has been shown that the presence of these incompatible phases improves the fracture toughness of highly crosslinked thermosets by forming crazes and stopping cracks propagation during deformation. Two common methods of introducing second incompatible phase into thermosets are (1) physical blending of thermoplastics with the thermosetting resins^{4–15} and (2) chemically by copolymerising the thermosetting resins with suitable oligomers that form phase-separated structures during curing.^{16–28}

In the case of BMI resins, it was found that the degree of phase separation in the modified resin

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depended on the amount of modifier used, the modifier structure and their molecular weights.¹⁰ The toughness of the modified resins was strongly influenced by the morphology and compatibility between the thermoplastic used and the BMI network. Resins with co-continue phase structure and good compatibility have better fracture toughness.^{6,11} Generally, the copolymerization route of incorporating a second incompatible phase showed better toughness compared to physical blending route. The reason can be attributed to better compatibility between oligomers and BMI resin forming a morphology with improved co-continue phase.¹⁸ However, copolymerization with thermoplastic oligomers greatly reduced the crosslinking density of BMI resins, resulting in the lowering of the thermal stability, glass transition temperature, and modulus of the final polymers.^{21–27} The crosslink density was greatly reduced because the thermoplastic oligomer when reacted with the BMI resin forms part of the backbone structure of the thermoset. Depending on the length, i.e., molecular weight, of the thermoplastic oligomer chain, the crosslink density of the thermoset will vary accordingly. Using this approach, the crosslink density invariably increases as the oligomer served as a molecular chain spacer between the crosslink sites.

In this paper, a different method of incorporating thermoplastic oligomers was investigated. Unlike previously reported approach, a mono-maleimido terminated thermoplastic oligomer was synthesized and used to modify the BMI resin. In this way, only the reactive mono-maleimido end group would react with the BMI resin while the pendent thermoplastic chain became a side chain in the final structure. The length of the side chain would depend on the molecular weight of the oligomer. Using this approach reduction in the crosslink density would be minimized and at the same time achieve improved toughness.

Two mono-maleimido-terminated poly(ethylene glycols) (m-PEGs) of different molecular weights (2000 and 5000 g/mol) were synthesized and used to copolymerize with a commercial BMI monomer, 4,4'-bismaleimido diphenylmethane (BDM) to obtain PEG "grafted" BMI resins. The curing behavior and thermal properties of the modified resins were evaluated. The effects of the m-PEG side chains and their contents on the thermal properties of modified BMI resin were also studied.

EXPERIMENTAL

Materials

The chemicals used: BDM (TCI), 4-aminophenol (Fluka, 98%), maleic anhydride (Fluka, >99%), poly(ethylene glycol) methyl ether ($M_n = 2000$ and 5000 g/mol, Aldrich), tolylene-2,4-diisocyanate (TDI 80%, TEC Acros), acetone (Baker), and N,N-dimethyl formamide (DMF, Aldrich). All the chemicals were used as received except for acetone and DMF, which were dried by standing over freshly, regenerated type 4 Å molecular sieve for 24 h before use.

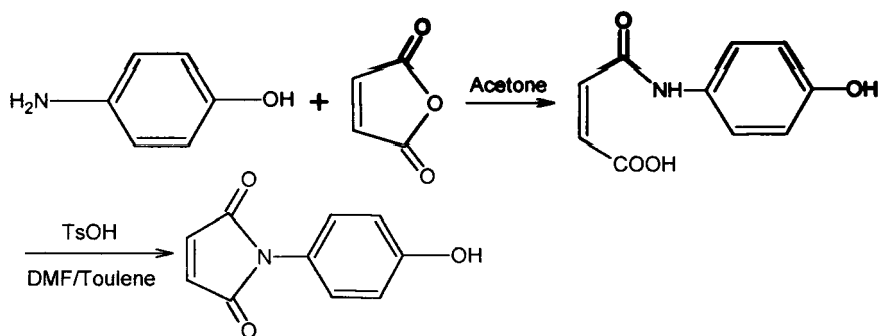
Preparation of 4-Maleimido Phenol

4-Maleimido phenol was synthesized using a method described by Hao and Jiang.²⁸ The reaction scheme is shown in Figure 1(a). The product was recrystallized from a mixed solvent of water-isopropyl alcohol (1:1 v/v). The yield obtained was approximately 48%. The purified product was characterized and the structure confirmed using proton nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy.

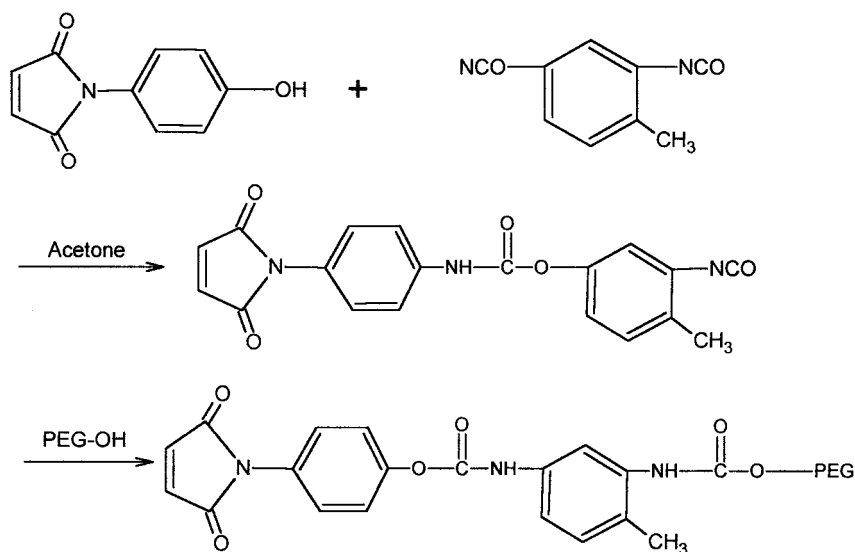
Synthesis of m-PEG

A 500 mL three-neck flask, fitted with a mechanical stirrer, dry nitrogen inlet, and thermometer, was charged with 2.175 g of 2,4-TDI (0.01 mol) and 20 mL acetone. 1.89 g of 4-maleimido phenol (0.01 mol) dissolved in 70 mL acetone was then added dropwise into the reaction flask over 2 h at room temperature. Small amounts of reaction mixtures were periodically removed for FTIR analyses. The reaction was allowed to continue until the characteristic isocyanate (—NCO) absorption peak at 2270 cm^{-1} showed no further changes.

Subsequently, 0.01 mol poly(ethylene glycol) methyl ether and 100 mL acetone were added to the reaction mixture. The reaction temperature was then raised to 40°C to ensure complete dissolution of the poly(ethylene glycol) methyl ether in the reaction mixture. The progress of the reaction was monitored by FTIR and was terminated when the absorption peak of —NCO group at 2270 cm^{-1} was undetectable. The solvent in the reaction mixture was then removed under vacuum and the solid product was collected and washed with 100 mL hexane. The overall reaction scheme was illustrated in Figure 1(b). Two different molecular weight (2000 and 5000 g/mol) m-PEGs were synthesized here and were identified as m-PEG2K and m-PEG5K, respectively.



a Synthesis of 4-maleimido phenol



b. Synthesis of maleimido end-capped PEG

Figure 1 Two-stage synthesis of maleimido end-capped poly(ethylene glycol).

Both m-PEG2K and m-PEG5K were characterized using a FTIR and a differential scanning calorimeter (DSC). The samples were subjected to two heating cycles using the DSC, first to polymerize the oligomer and second to characterize the thermal transition of these polymers, particularly the melting endotherm.

Preparation of m-PEG Modified BDM Resins

Both m-PEG2K and m-PEG5K oligomers were used to blend with a commercial BDM resin and thermally cured. The blend formulations evaluated in this study are summarized in Table I. Pure BDM was chosen as the control.

For each formulation the appropriate quantities of BDM and m-PEG were weighed and man-

ually stirred in a glass beaker. The powder mixture was then rapidly melted at 170°C in a convection oven. Some samples were retained and rapidly cooled in air at this point for subsequent DSC analysis. The remaining mixture was then degassed in a vacuum oven at 155°C for 30 min. The degassed liquid was then poured into a preheated PTFE mold at 180°C and cured in a programmable air oven. The curing cycle used was 180°C/3 h + 200°C/3 h + 250°C/4 h. After curing, the oven was switched off and the samples were allowed to cool slowly in the oven to room temperature.

FTIR Analysis

FTIR analysis was performed on a Nicolet-560 FTIR spectrometer. For solids, the sample was

Table I Summary of Blend Formulations Evaluated

Sample Code	m-PEG2K/BDM wt Ratio	Sample Code	m-PEG5K/BDM wt Ratio
2K-10	10/90	5K-10	10/90
2K-15	15/85	5K-15	15/85
2K-20	20/80	5K-20	20/80
2K-30	30/70	5K-30	30/70
BDM (control)	0/100		

mixed and ground with anhydrous KBr powder before being pressed into a disc for analysis. Where the sample is a liquid, an attenuated total reflectance (ATR) diamond accessory was used. All the samples were scanned 40 times at a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1} .

Proton NMR Analysis

Proton NMR spectra were collected on a 300 MHz Bruker ACF 300 spectrometer. Tetramethylsilane and DMSO- d_6 were used as the internal standard and solvent, respectively.

Differential scanning calorimetry (DSC)

Two different categories of samples were evaluated using the DSC. The first category involved the characterization of the m-PEG oligomers and the second group was the m-PEG modified BMI samples. The m-PEG2K and m-PEG5K samples were polymerized in the DSC heating cell and subsequently characterized for their thermal transitions—in particular, the melting endotherm. This presence of the melting endotherm was used to verify that the polymerized samples of m-PEG2K and m-PEG5K were thermoplastics. In the case of the m-PEG modified BMI samples, the DSC was used to characterize their curing behaviors such as curing exotherm and processing window.

DSC was carried out on a TA Instruments-DSC 2920. All the samples were heated from 30 to 350°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen purge. The melting temperature (T_m), extrapolated onset-curing temperature (T_o), peak curing temperature (T_p), cure exotherm (ΔH), and processing window were obtained from the thermogram. In addition, the processing window of the samples was also determined. In this paper, the processing window (T_{pw}) was defined as the temperature difference between the melting temper-

ature of the BMI resin (T_{m2}) and the onset curing temperature (T_o). Thus:

$$T_{pw} = T_o - T_{m2}$$

Higher T_{pw} value indicates better resin processability.

Thermogravimetric analysis (TGA)

TGA was carried out on a TA Instruments Hi-Res TGA 2950. The analyses were carried out in both dry air and purified nitrogen environments at a heating rate of $20^\circ\text{C}/\text{min}$. The extrapolated onset degradation temperature (T_o), temperatures at 50% sample weight loss (T_{50}), char yield (%), and the complete degradation temperature (T_d) were obtained from the thermogram.

Thermomechanical analysis (TMA)

A TA Instruments TMA-2940 was used to determine the linear coefficient of thermal expansion (CTE) of the samples. Specimens ($5 \times 5 \times 4\text{ mm}$) were tested in the expansion (contact) mode with a static load of 0.050 N at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 environment. The CTE value was calculated from the gradient of the slope between temperature range of 50 and 150°C .

RESULTS AND DISCUSSION

NMR and FTIR Analyses of 4-Maleimido Phenol

The purified 4-maleimido phenol was verified from the proton NMR and FTIR spectrum. $^1\text{H-NMR}$ (DMSO- d_6): 7.42 and 6.72 ppm (4H aromatic ring), 6.28 and 6.47 ppm (2H C=C), 9.34 ppm (1H—OH). FTIR: 3406 cm^{-1} (—OH), 1776, 1702, 1147, and 717 cm^{-1} (maleimido group).

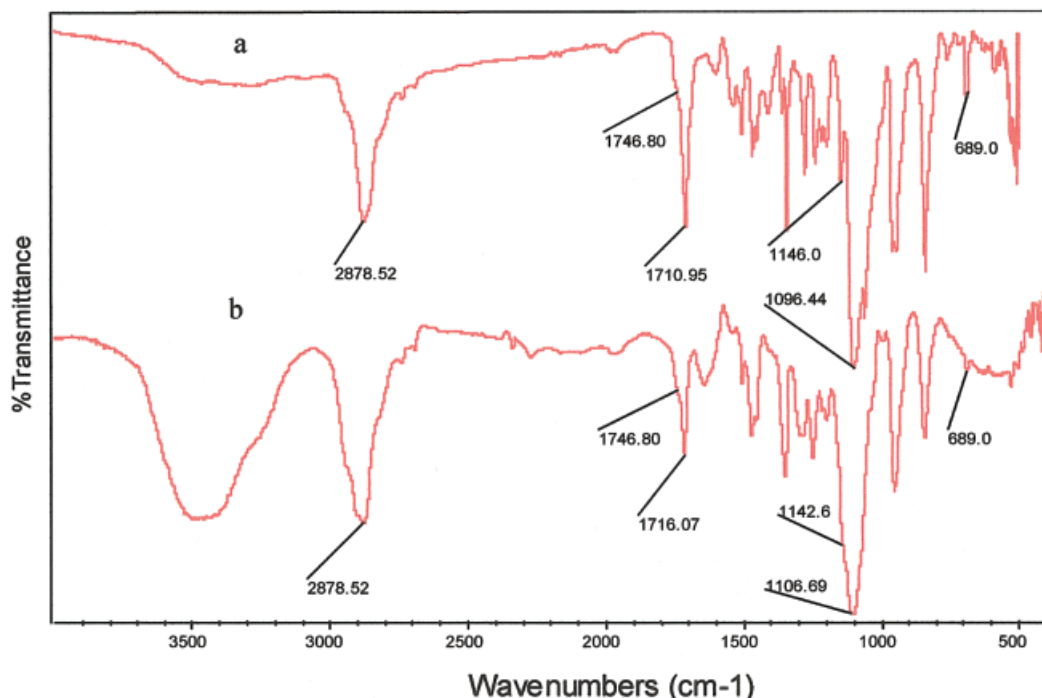


Figure 2 FTIR spectra of (a) m-PEG2K and (b) m-PEG5K oligomers.

Characteristics of the m-PEG Oligomers

The FTIR spectra of m-PEG2K and m-PEG5K are shown in Figure 2. Table II shows the characteristic FTIR absorption peaks of these samples. The two characteristic peaks commonly used to identify the maleimide structure at 689 and 1146 cm^{-1} were observed in m-PEG2K and m-PEG5K.^{28,29} It was observed that these absorption peaks for m-PEG2K were slightly higher than the m-PEG5K sample. This reduction in the absorption peaks could be attributed to a combination of the strong adsorption of ether bond at 1100 cm^{-1} and the corresponding decrease in the maleimido end group due to the higher molecular weight m-PEG5K. In addition, the characteristic

Table II Characteristic FTIR Absorption Peaks of m-PEG²⁷

Wave Number (cm^{-1})	Functional Group
2878	—CH ₂ —
1746	C=O in urethane
1713	C=O in imide ring
1146	Maleimide ring
1110	C—O—C in PEG
689	Imide ring

urethane absorption peak for both samples were also present. Like the maleimido absorption, the relative absorption of the urethane was also found to be slightly dependent on the molecular weight of the oligomer.

Structure of the m-PEG Modified BDM

Based on the structures of the mono-maleimido end-capped m-PEG and BMD, and the known reactivity of these end groups, the postulated structure of the modified resin is illustrated in Figure 3.

DSC of m-PEG Oligomers

The DSC curves of the m-PEG2K and m-PEG5K oligomers and polymers (i.e., re-run samples) are shown in Figure 4. The m-PEG5K sample showed a slightly higher melting point (T_m) than the lower molecular weight analogue, m-PEG2K. This slight increase in T_m could be attributed to higher crystallinity of oligomer associated with fewer end groups due to the increased molecular weight. A small exotherm between 200 to 300°C was observed in the first DSC run for both oligomers, indicating the reactivity of the terminal maleimido end groups. The m-PEG2K sample had a lower onset reaction temperature but

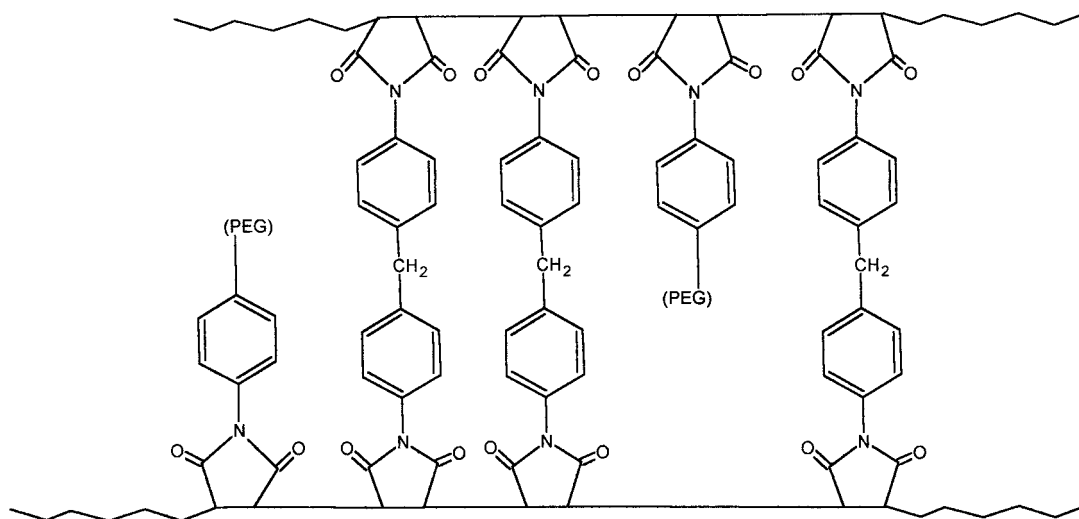


Figure 3 Postulated chemical structure of the m-PEG modified BMI resin.

slightly higher reaction exotherm compared with m-PEG5K. The observed difference was due to the combination of the lower melting temperature and relatively higher concentration of the maleimido end group in m-PEG2K. However, on the second DSC run, both samples did not show any exotherm, indicating that the addition polymerization reaction was completed after the first heating cycle. The presence of the melting endo-

therm on the DSC re-run clearly indicated that the resultant m-PEG polymers formed were thermoplastics.

DSC of m-PEG/BDM Samples

BDM is known to homopolymerize in the molten state via a thermally initiated radical polyaddition mechanism.^{1,2} This addition reaction occurs

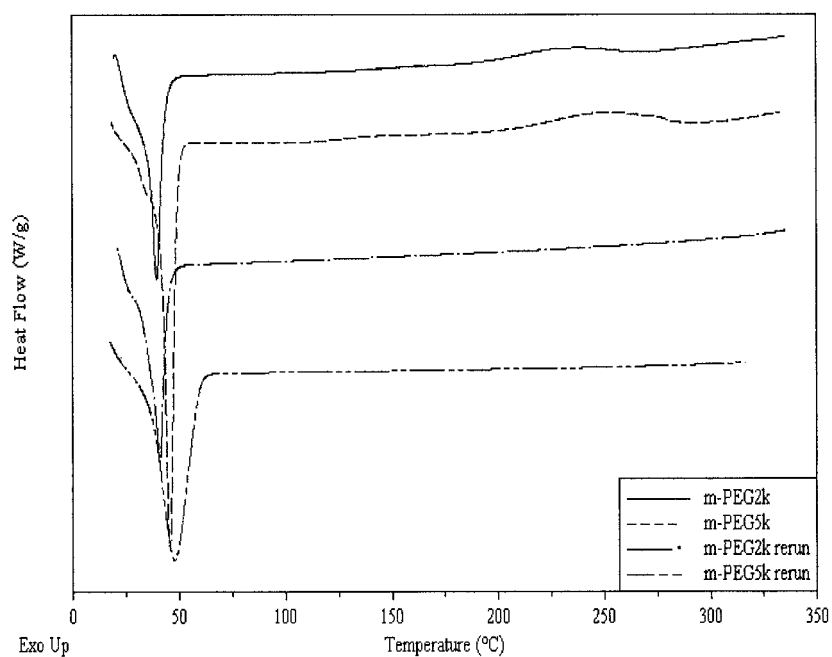


Figure 4 DSC thermographs of m-PEG oligomers during and after polymerization (re-run).

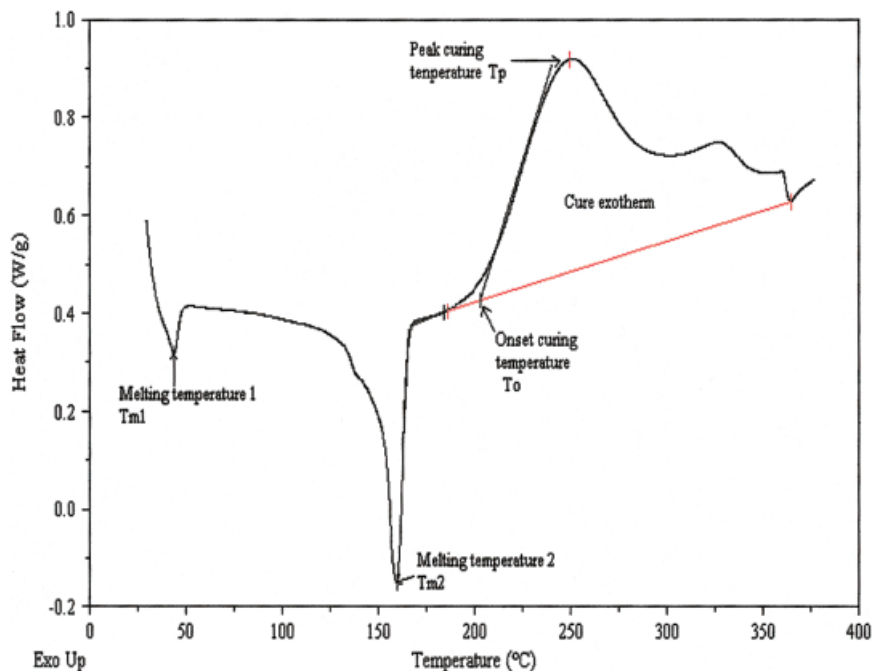


Figure 5 DSC curing thermogram of sample 2K-10.

immediately after the monomer crystalline melt temperature. This narrow temperature between the melting and the onset curing temperature, i.e., processing window, however, gives rise to a

potential processing problem. With a narrow processing window, coupled with the high curing rate of the resin, problems associated with mold filling emerged. As filling of the mold could only take

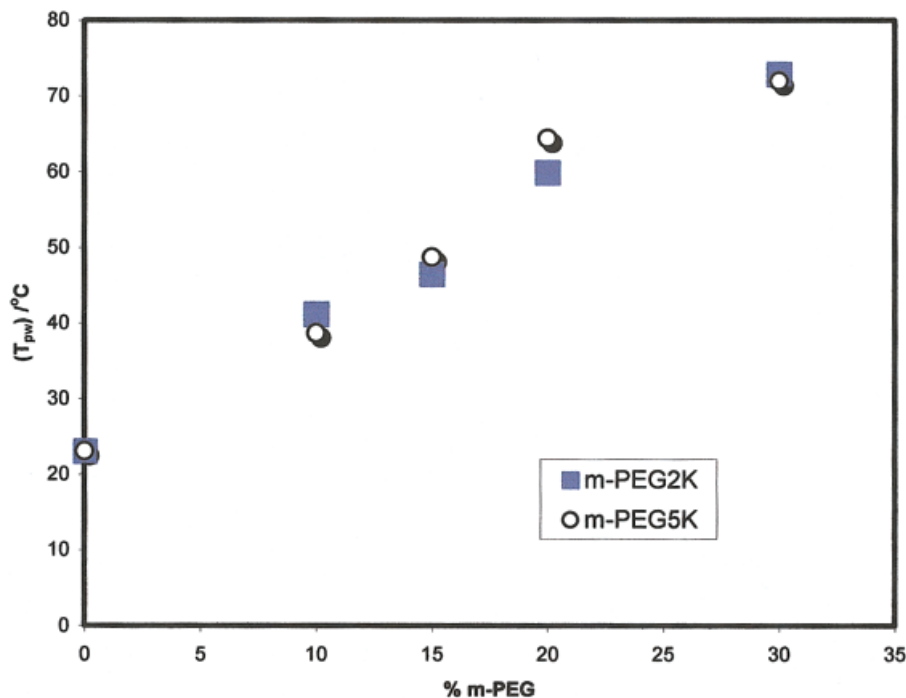


Figure 6 Effect of m-PEG on the processing window (T_{pw}) vs added m-PEG.

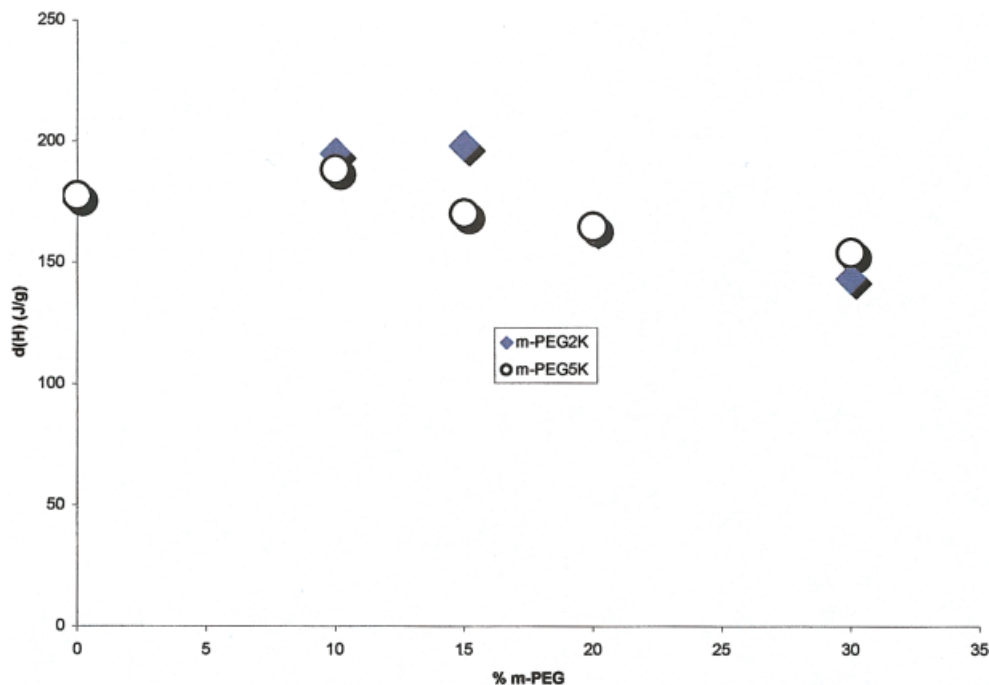


Figure 7 Plot of curing exotherm, $d(H)$, vs added m-PEG.

place with the resin in the molten state, the maximum mold allowable filling time would be determined by the gel time of the curing resin. The shorter the gel time, i.e., faster curing time, the

shorter time would be required to fill the mold. When samples cured in the DSC system were removed, boundary lines were observed on the sample surfaces. These flow lines were formed as

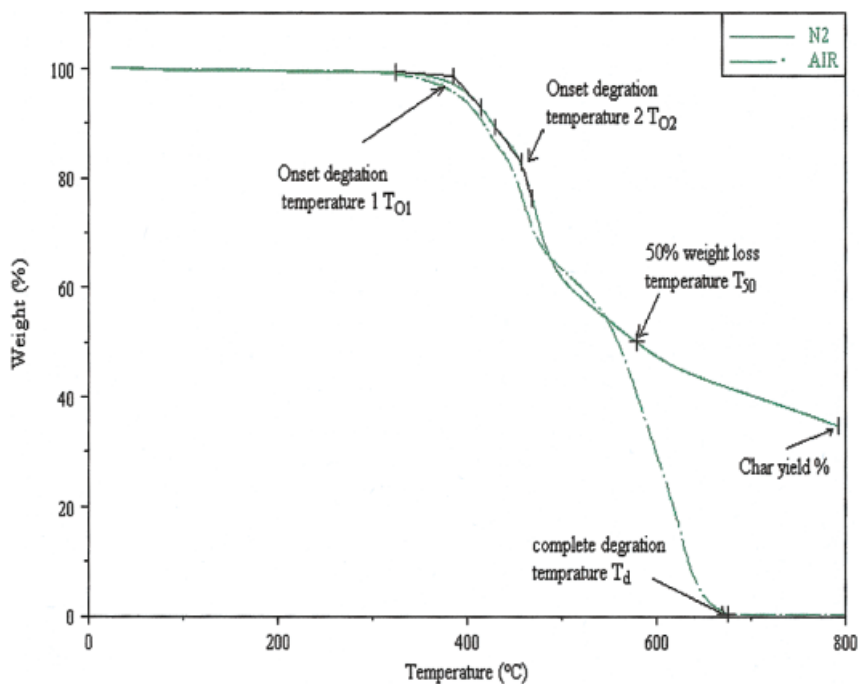


Figure 8 TGA thermograms of sample 5K-10 in air and nitrogen atmospheres.

the direct consequence of a very rapid curing process that impeded the full merging of the molten fronts from various melting polymer granules.

Typical DSC thermogram of curing BDM/m-PEG mixtures was shown in Figure 5. The effect of blending m-PEG oligomers on the processing behavior of BDM is shown in Figure 6, where the processing window (i.e., T_{pw}) the percentage amount of m-PEG was plotted. The results showed that the processing window of BDM increased with amounts of m-PEG added and relatively independent on the molecular weight of the oligomer. The extent of improvement observed was very significant, ranging from 23° (control) to 72°C (for example, sample 5K-30). This improved processing window was also reflected by the absence of flow lines on all the cured m-PEG–BDM blended samples.

The DSC results also showed that the curing exotherm, shown in Figure 7, generally decreased with increasing amounts of m-PEG incorporated. This lowering of the curing exotherm was due to the reduction in the total number of reactive maleimido end groups present since these oligomers were mono-maleimido terminated. Similar trends were also observed on the effect of the molecular weights of the oligomer, i.e., lower molecular weight m-PEG2K oligomer showed a slightly higher curing exotherm than m-PEG5K. This again could be attributed to the lower concentration of the reactive maleimido end groups associated with the molecular weight of the oligomer. In addition, no melt endotherms were observed on the fully cured samples of m-PEG/BMD, unlike the neat samples of m-PEG previously discussed.

Thermal Stability

The typical TGA thermogram of a m-PEG modified BMI is shown in Figure 8. The effect of incorporating m-PEG on the thermal stability of modified BMI resins in both air and nitrogen environments could be observed in Table III(a) and (b). In general, the incorporation of the m-PEG oligomers lowers the thermal stability of BMI in both air and nitrogen atmosphere. The gradual decrease in the T50 (thermal half-life) values of the blends increase with the amounts of added m-PEG oligomers. The effect of molecular weight of the m-PEG oligomers, however, did not have any significance on the relative thermal stability of the blends. The stability of the blend was clearly shown to be dependent solely on the percentage amounts of BMI formed. See Table III(a).

Table III Summary of Results for TGA and TMA Experiments

(a) TGA T50 Results		
Sample	T50 (°C) (Nitrogen)	T50 (°C) (Air)
2K-10	593.8	592.9
2K-15	585.7	584.7
2K-20	564.3	558.0
2K-30	555.8	536.2
5K-10	597.1	581.5
5K-15	579.5	568.3
5K-20	563.0	552.0
5K-30	531.5	517.2
Control (BDM)	698.6	639.4

(b) TGA Residue Results		
Sample	Predicted Residue (Nitrogen)	Actual Residue (Nitrogen)
2K-10	0.4182	0.4276
2K-15	0.3950	0.401
2K-20	0.3718	0.361
2K-30	0.3253	0.3304
5K-10	0.4182	0.4054
5K-15	0.3950	0.3689
5K-20	0.3718	0.3565
5K-30	0.3253	0.3296
Control (BDM)	0.4647	0.4647

(c) TMA Results	
Sample	CTE (ppm)
2K-10	65.4
2K-15	66.5
2K-20	67.3
2K-30	78.5
5K-10	62.5
5K-15	67.6
5K-20	69.4
5K-30	78.7
Control (BDM)	43.3

The predicted residue in nitrogen atmosphere, based on the proportion of BDM in the blends, was found to agree closely with the experimental results. See Table III(b). As the amount of m-PEG in the blends increased, the thermal stability of the cured resin decreased proportionally. The reduction in the thermal stability with m-PEG blended resins were not surprising due to the

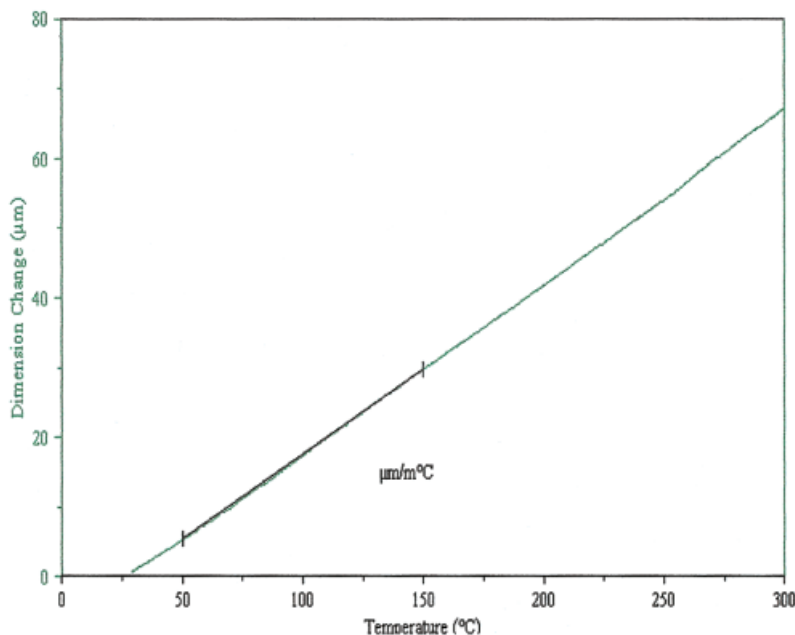


Figure 9 Determination of the coefficient of expansion of sample 5K-15.

lower thermal stability of the aliphatic ether bond in the PEG chain.

Coefficient of Thermal Expansion

All the samples showed a linear plot in the TMA experiment in the temperature range from 30 to 300°C typically shown by sample 2K-15 in Figure 9. None of the thermograms showed any point of inflexion that could indicate the glass transition temperature, T_g , of the samples up to 300°C. The T_g of the samples would likely be higher than 300°C. The CTE values obtained, however, clearly showed a dependence on the amounts of added m-PEG in the blend. Table III(c) showed that the CTE of the samples increased with the amount of m-PEG added. It was also interesting to note that between 10 and 20% of added m-PEG, i.e., samples 2K-10 and 2K-20 or samples 5K-10 and 5K-20, the CTE increase between samples were minimal, but beyond 20wt% of either m-PEG2K or m-PEG5K, the CTE increased significantly. The reason for the observed phenomenon is unknown at this stage but might be indicative of the optimal amounts of m-PEG that could be added in the current system. Once again, the effect of the molecular weight of m-PEG on the CTE of the samples was insignificant. The increase in the CTE could be attributed to an overall increase in the free volume of the sample as the direct consequence of these flexible side chains. As the free

volume is expected to increase with the amounts of added m-PEG oligomers, the CTE of the m-PEG/BDM blends must correspondingly increase, as demonstrated in these samples.

CONCLUSIONS

In conclusion, two m-PEGs of different molecular weight ranges were end-capped with a maleimido group and blended at various amounts with 4,4'-bismaleimido diphenylmethane. The blends were thermally cured and the effect of these oligomers on the processability, curing behaviors, and thermal properties were evaluated. It was found that the blending of the m-PEG with BDM significantly improved the processability of the BMI resins. The increased processing window reduced flow defects caused by very rapid curing. However, the incorporation of the m-PEG oligomers resulted in an overall reduction in the thermal stability of the modified BMI system. This reduction in the thermal stability, as determined by T50, was found to be dependent on the amount of m-PEG added. Similarly, the coefficient of thermal expansion of the modified resins was increased by the addition of the m-PEG component. The long-range segmental mobility of the long m-PEG side chain was found to have profound influence on the CTE of the blended samples. It

was, however, interesting to note that both the thermal stability and CTE were independent on the molecular weights of the m-PEG used. In conclusion, the incorporation of the m-PEG segment provides a feasible mean of improving the processability of BDM systems.

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