

Mechanical Properties and Morphology of Poly(ethylene glycol)-Side-Chain-Modified Bismaleimide Polymer

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ABSTRACT: Two maleimido-end-capped poly(ethylene glycol) (m-PEG)-modified bismaleimide (BMI) resins [4,4'-bismaleimido diphenylmethane (BDM)] were synthesized from poly(ethylene glycol) (PEG) of two different molecular weights. A series of m-PEGs and unmodified BDM were blended and thermally cured. The effect of incorporating m-PEG side chains on the morphology and mechanical behaviors of BMI polymer were evaluated. The mechanical properties of these m-PEG-modified BMIs that were evaluated included flexural modulus, flexural strength, strain at break, fracture toughness, and fracture energy. The morphology of these blends was studied with scanning electron

microscopy. All the m-PEG-modified BMI polymers showed various degrees of phase separation depending on the molecular weights and concentrations of the m-PEG used. The effects of these morphological changes in the m-PEG-modified BMI polymers were reflected by the improved fracture toughness and strain at break. However, there was a reduction in the flexural moduli in all m-PEG-modified BMI polymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 715–724, 2002

Key words: bismaleimide; phase separation; poly(ethylene glycol); toughness; matrix

INTRODUCTION

Bismaleimide (BMI) resins are increasing being used in aerospace and electronics applications because of their excellent low coefficient of thermal expansion, low dielectricity, and excellent mechanical performance at elevated temperatures. However, BMI resins in general are inherently brittle.^{1,2} Numerous efforts to improve their impact and fracture toughness have been reported, ranging from the incorporation of thermoplastic particles^{3–6} to the addition of elastomeric chain segments to the BMI main chain.^{7,8} In all these cases, the fracture toughness of the BMI resins was improved, with the cured final resins showing multiphase morphologies.⁹

In this study, a different approach for improving the fracture toughness of BMI was adopted. Unlike in other reported methods, in which BMI reacts with elastomers containing multiple reactive end groups, monomaleimido-end-capped poly(ethylene glycol) (m-PEG) was used in this evaluation. The significant difference between these approaches is the location of the elastomeric segment in the cured BMI polymer. When the reactions involve elastomers containing multiple reactive end groups, the elastomeric segments are incorporated into the main chain of the BMI polymer structure; that is, the elastomer serves as a

chain extender. However, in the approach discussed here, when m-PEG is reacted with BMI, the poly(ethylene glycol) (PEG) segment exists as a side chain along the BMI polymer backbone. This approach is believed to offer the advantage of good miscibility between m-PEG and BMI blends and, therefore, improved mixing and dispersion of the reactants during the initial stages of curing. Phase separation was expected to occur after the incorporation of the m-PEG segment into the BMI structure was completed because of the large solubility differences between the BMI matrix and the PEG side chain. In this study, various quantities of two m-PEG oligomers of different molecular weights were blended and cured with commercially available 4,4'-bismaleimido diphenylmethane (BDM). The effect of incorporating these m-PEG oligomers on the mechanical properties and morphology of the BMI polymer were studied and are reported here.

EXPERIMENTAL

Materials

BDM (TCI), 4-aminophenol (Fluka; 98%), maleic anhydride (Fluka; >99%), poly(ethylene glycol) methyl ether (number-average molecular weight = 2000 or 5000 g/mol; Aldrich), tolylene-2,4-diisocyanate (TDI; 80%; TEC Acros), acetone (Baker), and *N,N*-dimethylformamide (DMF; Aldrich) were used. All the chemicals were used as received except for acetone and

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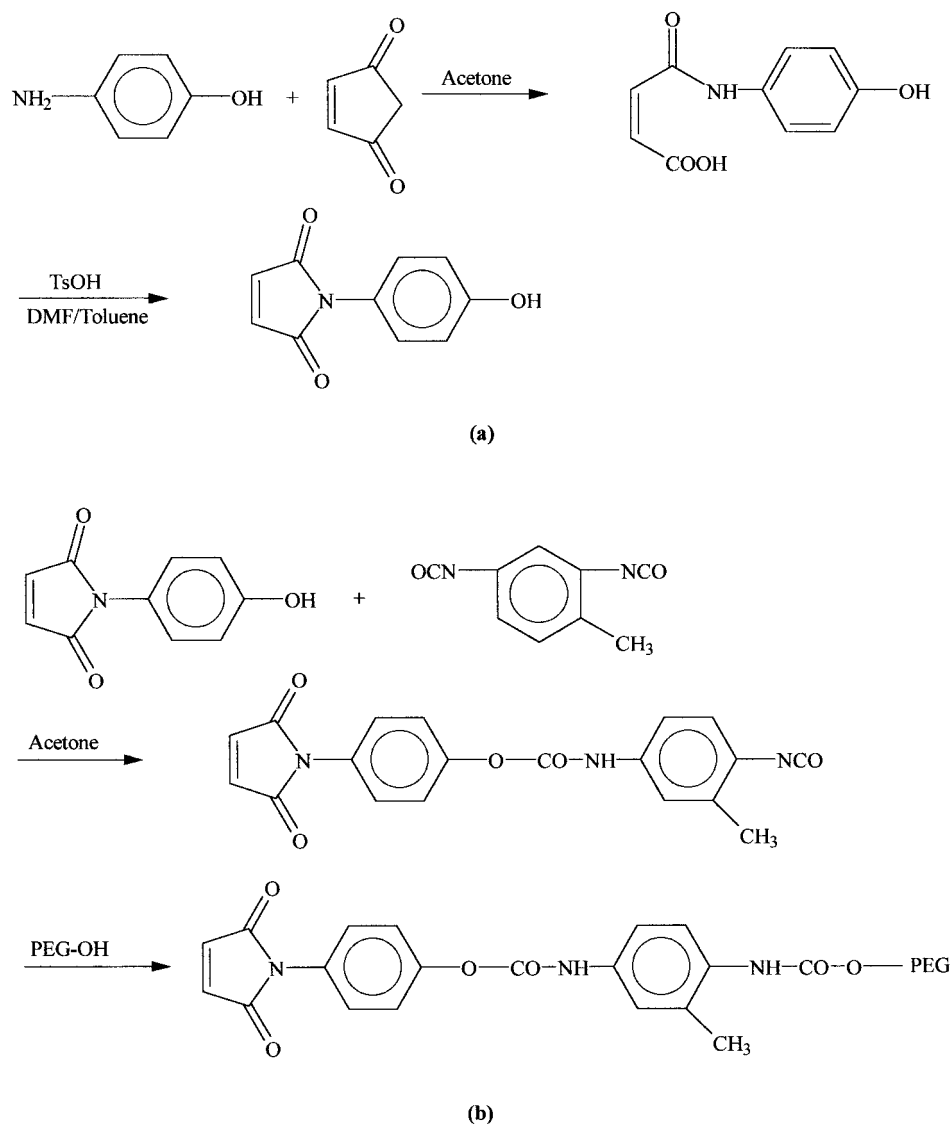


Figure 1 Syntheses of (a) 4-maleimido phenol and (b) m-PEG.

DMF, which were dried by standing over freshly regenerated 4-Å molecular sieves for 24 h before use.

Preparation of 4-maleimido phenol

4-Maleimido phenol was synthesized with the method described by Hao et al.¹⁰ and shown in Figure 1(a). The product was recrystallized from a mixed solvent of water and isopropyl alcohol (1:1 v/v). The yield obtained was approximately 48%. The purified product was characterized and the structure was confirmed with proton nuclear magnetic resonance and Fourier transform infrared (FTIR) spectroscopy.¹¹

Synthesis of m-PEG

A 500-mL, three-necked flask fitted with a mechanical stirrer, a dry nitrogen inlet, and a thermometer was

charged with 2.175 g of TDI (0.01 mol) and 20 mL of acetone. 4-Maleimido phenol (1.89 g, 0.01 mol) dissolved in 70 mL of acetone was then added dropwise into the reaction flask over 2 h at room temperature. The reaction was allowed to continue until the characteristic isocyanate (—NCO) absorption peak at 2270 cm^{-1} showed no further changes with FTIR spectroscopy.

Subsequently, 0.01 mol of poly(ethylene glycol) methyl ether and 100 mL of 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 the —NCO group at 2270 cm^{-1} was undetectable. The solvent in the reaction mixture was then removed in vacuo, and the solid product was collected and washed with 100 mL of hexane.

TABLE I
Summary of Blend Formulations Evaluated

Sample code	m-PEG2K/BDM (w/w)	Sample code	m-PEG5K/BDM (w/w)
m-PEG2K-10	10/90	m-PEG5K-10	10/90
m-PEG2K-15	15/85	m-PEG5K-15	15/85
m-PEG2K-20	20/80	m-PEG5K-20	20/80
m-PEG2K-30	30/70	m-PEG5K-30	30/70
BDM (control)	0/100		

The overall reaction scheme is illustrated in Figure 1(b). Two m-PEGs of different molecular weights (2000 and 5000 g/mol) were synthesized, and they are identified as m-PEG2K and m-PEG5K, respectively.

Preparation of m-PEG-modified BMI polymers

Both m-PEG2K and m-PEG5K oligomers were blended with a commercial BDM resin at different weight ratios and thermally cured. The blend formulations evaluated in this study are summarized in Table I. Fully cured unmodified BMI polymer was chosen as the control.

For each formulation, the appropriate quantities of BDM and m-PEG were weighed and mixed in a glass beaker. The powder mixture was then rapidly melted and mixed at 170°C in a convection oven. The mixture was then transferred to a heated vacuum oven at 155°C and evacuated for 30 min. The degassed liquid mixture was poured into a preheated polytetrafluoroethylene (PTFE) mold at 180°C and cured in a programmable air oven. The curing cycle was 3 h at 180°C, 3 h at 200°C, and 4 h at 250°C. After the curing was complete, the oven was switched off, and the samples were allowed to cool slowly in the oven to room temperature.

Scanning electron microscopy (SEM)

All the samples were immersed in liquid nitrogen and freeze-fractured. The samples were then mounted on an SEM holder with the fractured surfaces exposed. The mounted samples were then gold-sputtered and examined with a JEOL JSM-5600LV SEM system.

Flexural test

In this evaluation, a sample (80 mm × 10 mm × 4 mm) was subjected to a three-point bending test conducted in agreement with ASTM Standard D 790-00. An Instron model 5565 universal tester was used for this evaluation. The test was conducted under ambient conditions (22°C) at a crosshead speed of 0.5 mm/min. Quintuplicate samples were tested, and the average flexural modulus, strain at break, and flexural strength were reported.

Fracture toughness and fracture energy

The sample geometry used in this test was in agreement with the ASTM D 5045-99 single-edge-notch-bending (SENB) specification. The test specimen (80 mm × 10 mm × 4 mm) was sharply notched with a 45° notch cutter. A natural crack was then initiated by the insertion of a fresh razor blade and tapping. The ratio of the crack length a to the specimen width w was chosen to be between 0.2 and 0.5. The notched sample was then subjected to a SENB three-point bending test with an Instron universal tester under ambient conditions (22°C). The fracture toughness and fracture energy for all the samples were determined and compared. For the calculation of the fracture energy, the Poisson ratio (ν) for the BMI resin was assumed to be 0.35.³

RESULTS AND DISCUSSION

Chemical structure

No phase separation of BDM and m-PEG was observed during the melt mixing and initial stages of curing, indicating a good degree of miscibility between the reactants. The good miscibility could be attributed to the end-capped maleimido group on the PEG oligomers. The structural similarity of the end-capped maleimido group with the BDM monomer enhanced the miscibility of the highly hydrophilic PEG polymer with the highly hydrophobic BDM monomer. The good miscibility of the reactants was an important consideration for achieving a randomly and well-dispersed m-PEG in the final BMI polymer. The postulated structure of the modified resin is illustrated in Figure 2.

Morphology

Two samples were found to be optically clear, unmodified BMI and m-PEG2K-10/BDM, whereas the remaining samples were opaque. The optical transparency observed in m-PEG2K-10/BDM indicated two possible morphologies. One possibility was that complete miscibility between m-PEG2K-10 and BDM had occurred and that no heterogeneity was observed. The other possibility was that the domains formed as the

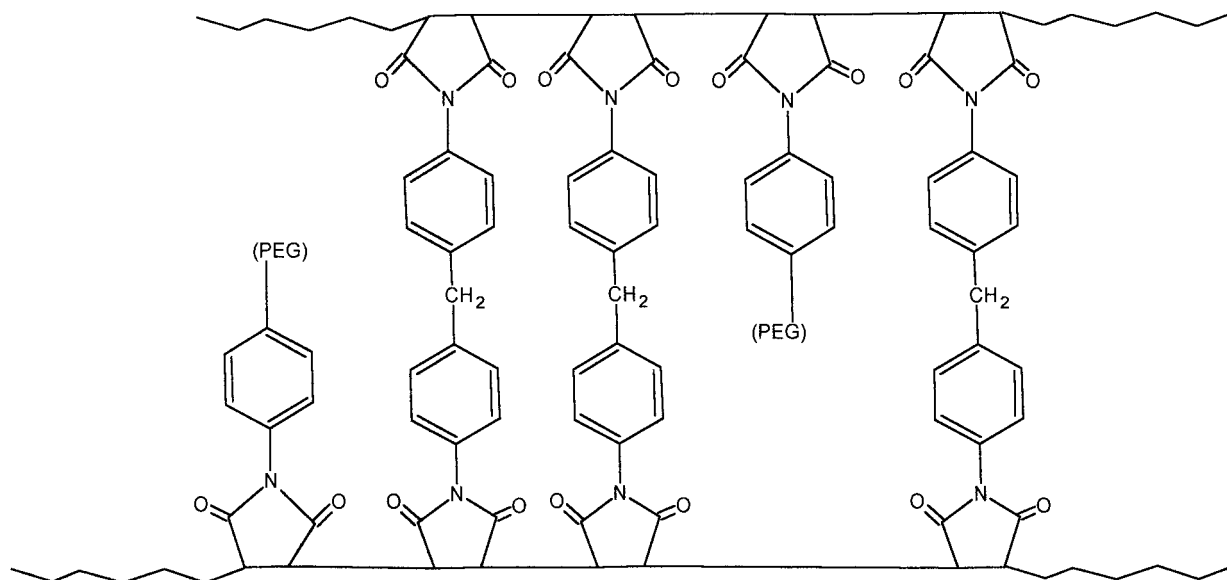


Figure 2 Postulated molecular structure of an m-PEG-modified BMI polymer.

result of phase separation were too small to interfere with the passage of light through the sample. However, it was found under SEM examination that the m-PEG2K-10-modified BMI polymer showed phase-separated domains that were very small and well dispersed in the BMI matrix. The lack of optical transparency in the remaining samples, however, clearly indicated significant phase separations between m-PEG and the BMI matrix.

An SEM micrograph of cured BMI polymer (control) is shown in Figure 3. The fractured surface of the BMI sample was smooth and typical of brittle polymers.¹² In stark contrast, Figures 4 and 5 show SEM photographs of the rough, fractured surfaces of all the m-PEG2K- and m-PEG5K-modified BMI polymers, respectively. The rough, fractured surfaces were due to

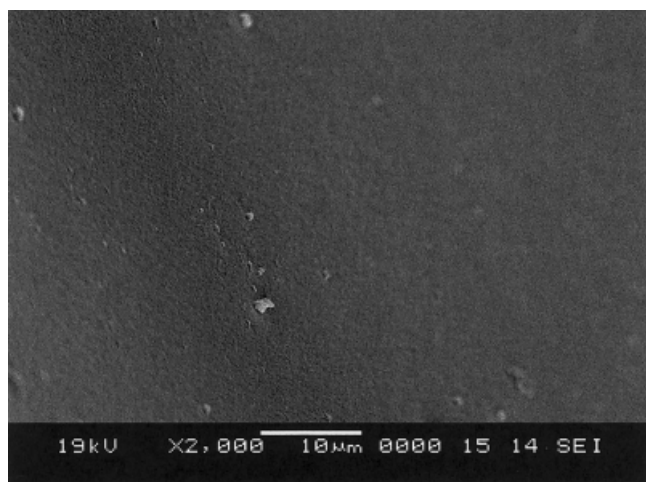


Figure 3 SEM micrograph of a fractured surface of cured BMI polymer.

the various degrees of phase separation of PEG from the BMI matrix. The extent of phase separation was dependent on the molecular weights and amounts of m-PEG incorporated.

The effect of the m-PEG concentration on the degree of phase separation can be seen in Figure 4. At a low concentration of m-PEG, that is, m-PEG2K-10, the phase-separated PEG particles were few and well dispersed [Fig. 4(A)]. The typical size of these particles was less than 1 μm . The combination of low numbers and small sizes of these particles could be the reason for their optical transparency. However, as the concentration of m-PEG increased, the surface roughness increased dramatically because of the greater degree of phase separation in the samples [Fig. 4(B–D)]. The morphological change with increasing m-PEG content is worth noting. The surface morphology in the modified BMI polymer changed from a finely dispersed particulate form at a lower m-PEG concentration to a lamellar structure and eventually formed large agglomerates at higher m-PEG concentrations.

These changes in the morphology could be explained by the effect of the concentration and molecular weight of the m-PEG added. Earlier observations that no phase separation occurred during the mixing and initial stages of curing indicated good initial miscibility between m-PEG and BDM, and this was further confirmed by the good dispersion of PEG in the BMI polymer matrix. However, at a low concentration of m-PEG, with a good dispersion of m-PEG in BMI, the eventually phase-separated PEG particulate that formed remained well separated. In addition, the lower average chain length of the m-PEG2K segment may also be insufficient to allow coalescence of the PEG particles. However, at some minimum concentra-

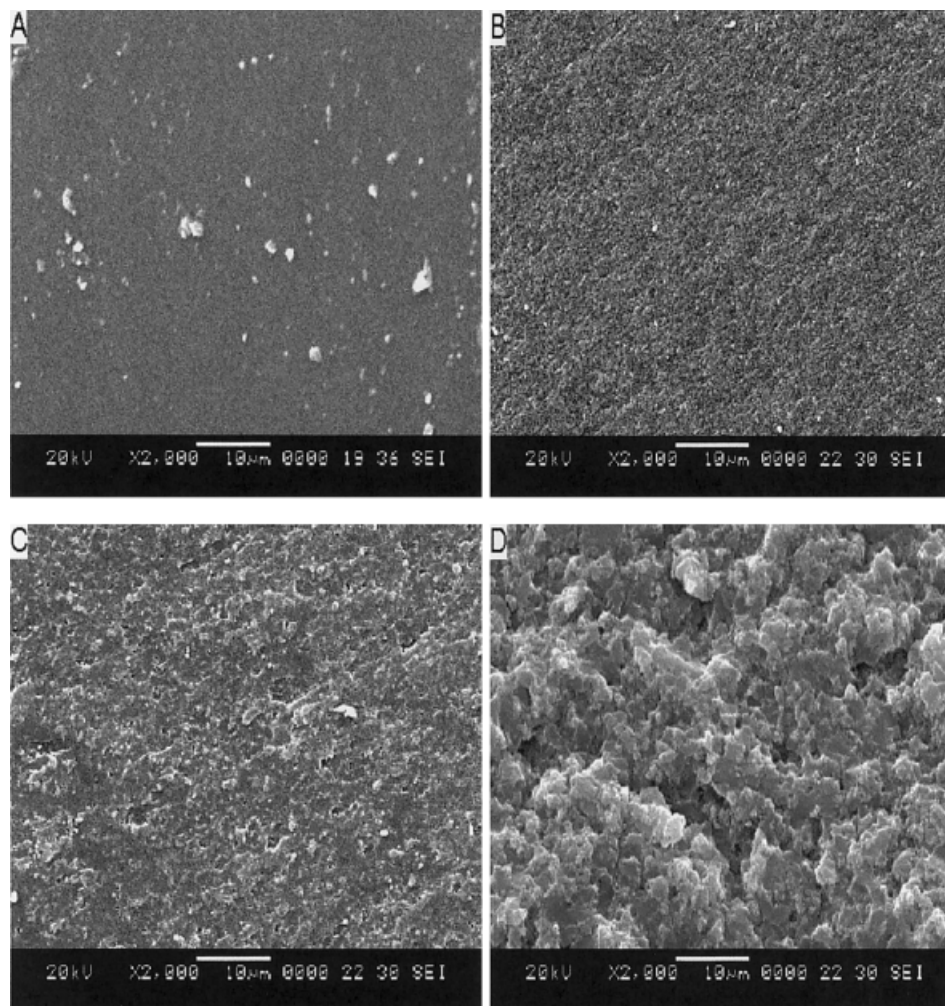


Figure 4 SEM photographs of fractured surfaces of BMI polymers modified with (A) m-PEG2K-10, (B) m-PEG2K-15, (C) m-PEG2K-20, and (D) m-PEG2K-30.

tion of m-PEG, depending on the molecular weight of the m-PEG used, coalescence of the PEG particles started to occur, giving rise to surface roughness [Fig. 4(B)]. Beyond this minimum concentration of m-PEG, the combination of coalescing PEG domains and their incompatibility with the BDM matrix resulted in the formation of the laminate structure shown in Figure 4(C). At a very high concentration of m-PEG (i.e., m-PEG2K-30), the PEG domains formed large nodular agglomerates shown in Figure 4(D).

Similar concentration effects on the morphology of the modified BMI polymer were observed for higher molecular weight m-PEG, that is, m-PEG5K. Because of the higher molecular weight of the m-PEG segment and, therefore, the longer chain length of the PEG side chain, coalescence of the PEG particles occurred at lower concentrations. Figure 5(A) shows that even at a lower m-PEG concentration, that is, m-PEG5K-10, coalescence of the PEG particles occurred. Samples containing higher m-PEG5K concentrations, that is, m-PEG5K-15, m-PEG5K-20, and m-PEG5K-30, showed

similar changes from laminate structures to large nodular agglomerates. The size of the agglomerates increased with the molecular weight of the m-PEG oligomers [Fig. 5(B–D)].

These morphological changes invariably determined the mechanical properties of these m-PEG-modified BMI polymers, which are discussed next.

Mechanical properties

Flexural properties

Three flexural properties were evaluated in this study: flexural modulus, flexural strength, and strain at break. With respect to the unmodified BMI polymer, all the m-PEG-modified BMI polymers exhibited lower flexural moduli, as shown in Figure 6. The flexural moduli of the m-PEG-modified BMI polymers decreased linearly with increasing m-PEG concentration. Although PEG was incorporated as a side chain, its effect on the flexural rigidity of the BDM network

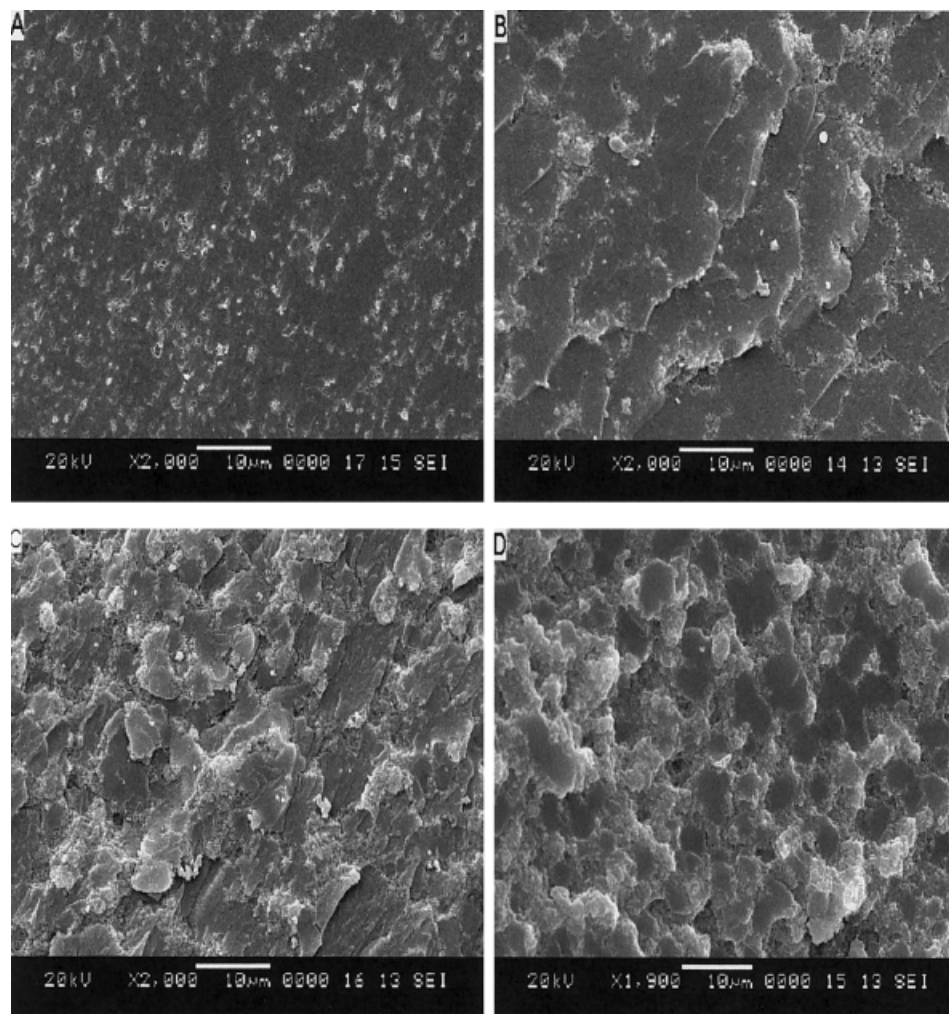


Figure 5 SEM photographs of fractured surfaces of BMI polymers modified with (A) m-PEG5K-10, (B) m-PEG5K-15, (C) m-PEG5K-20, and (D) m-PEG5K-30.

was significant. Even at a low m-PEG concentration, that is, 10 wt %, the reduction in the modulus was approximately 14 and 19% for m-PEG2K and m-PEG5K, respectively. The effect of the m-PEG molecular weight was less significant than the concentration effect, as previously shown.

The flexural strength of the m-PEG-modified BMI polymers showed an initial enhancement at m-PEG concentrations lower than 20 wt % (Fig. 7). The toughening effect of these PEG side chains on the BMI polymer was evident. The combination of the low-modulus side chain, small particulate size, and good distribution of m-PEG in the matrix facilitated the retardation of the failure mechanism of the otherwise brittle BMI polymer. However, at higher concentrations, that is, 30 wt % m-PEG, further embrittlement of the BMI polymer resulted. This embrittlement was probably caused by the presence of stress concentrators formed from these enlarged agglomerates free of PEG side chains. The effect of the particle size on the flexural strengths of highly crosslinked polymers has

been extensively evaluated and reported.¹³⁻¹⁵ In addition, it was observed that increasing the molecular weight of m-PEG reduced the flexural strength of the modified BMI polymer. This observed trend could be attributed to the larger size of the phase-separated PEG domains.

The effect of incorporating m-PEG on the strain at break can be seen in Figure 8. The strain at break of the m-PEG-modified BMI polymers increased with m-PEG concentration, reflecting the lower flexural modulus in the BMI polymer.

Fracture toughness

Both the fracture toughness and fracture energy were determined for the m-PEG-modified BMI polymers. Figure 9 shows the fracture toughness of the m-PEG-modified BMI samples. At m-PEG concentrations up to 20 wt %, the fracture toughness of the blends increased with the m-PEG concentration, reflecting the samples' enhanced ability to withstand fracture. This

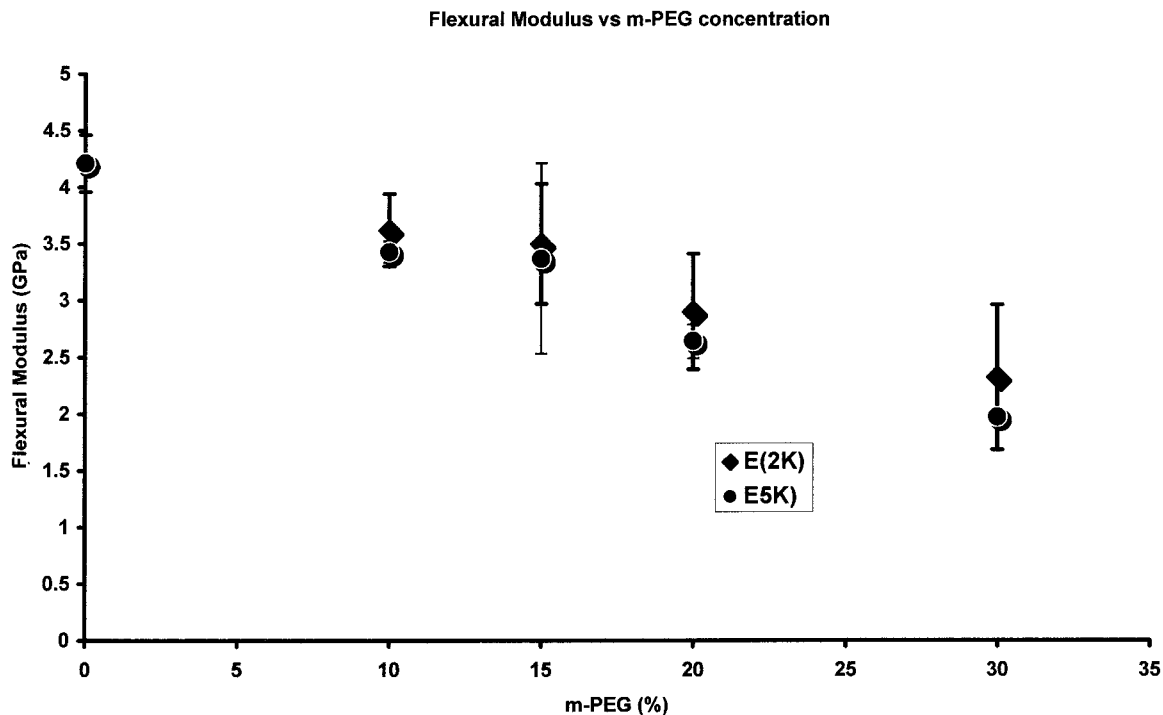


Figure 6 Effect of the m-PEG concentration on the flexural modulus of BMI polymer.

increase in the fracture toughness was relatively independent of the molecular weight of the PEG oligomers. However, at 30 wt % m-PEG, a difference in the fracture toughness of m-PEG2K and m-PEG5K

began to appear. Although m-PEG2K-30-modified BMI showed a continued increase in fracture toughness, the higher molecular weight m-PEG5K-30-modified BMI showed deterioration. The optimal concen-

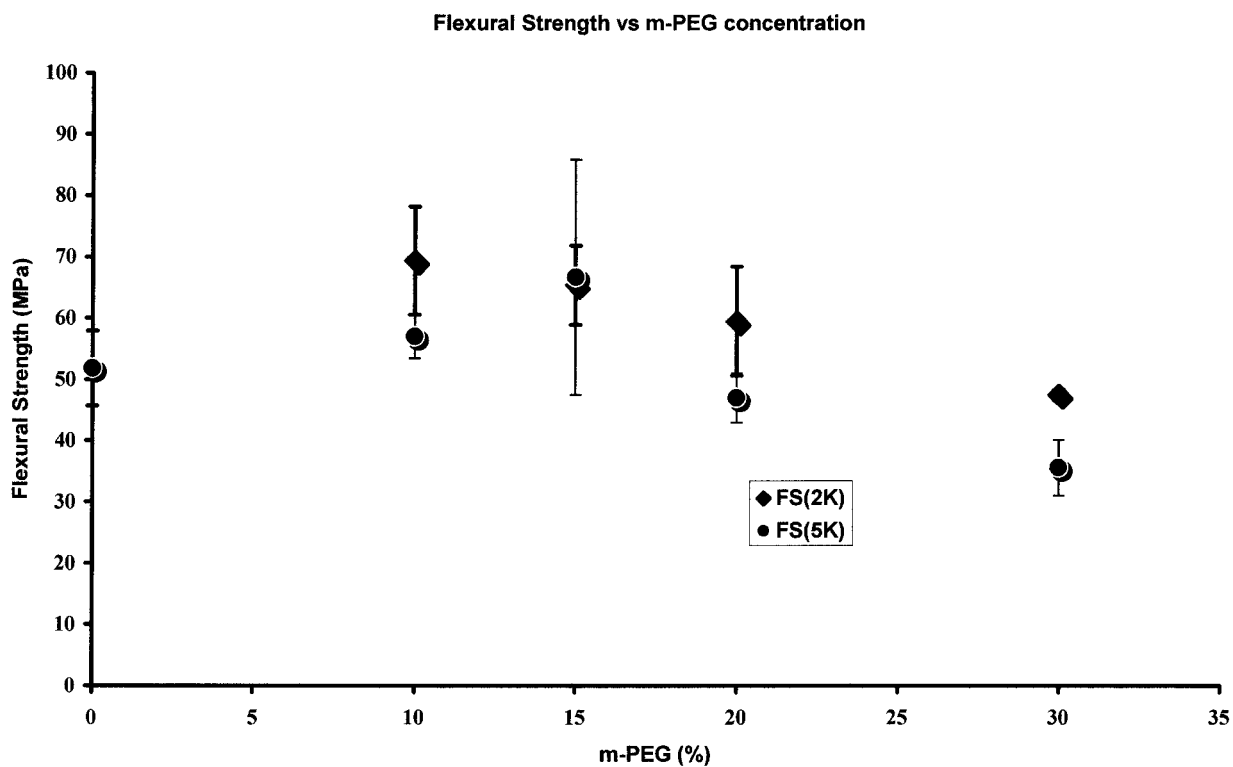


Figure 7 Effect of the m-PEG concentration on the flexural strength of BMI polymer.

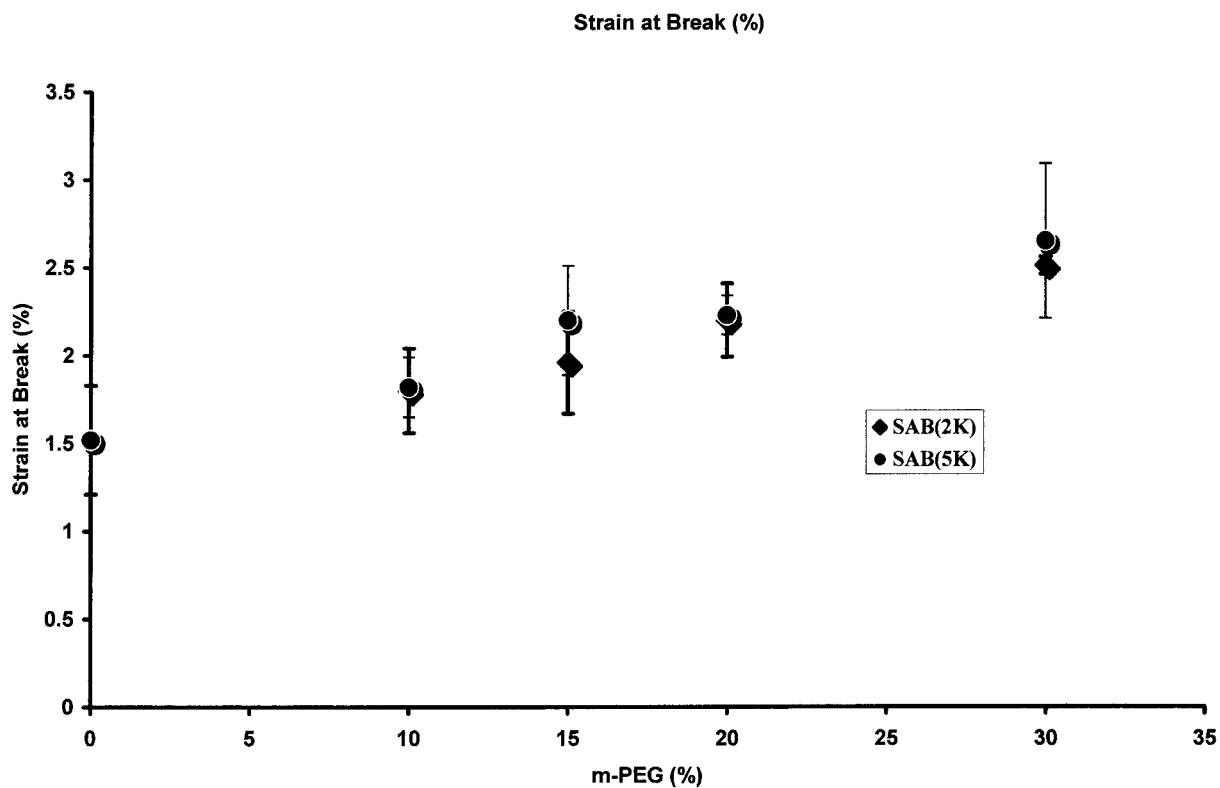


Figure 8 Effect of the m-PEG concentration on the strain at break of BMI polymer.

tration of m-PEG5K for BMI toughening appeared to be approximately 20 wt %. This observed trend in the fracture toughness with the concentration and molec-

ular weight of m-PEG could be related to the morphology of the modified BMI. As the particle size of the PEG domain increased with the m-PEG concentration

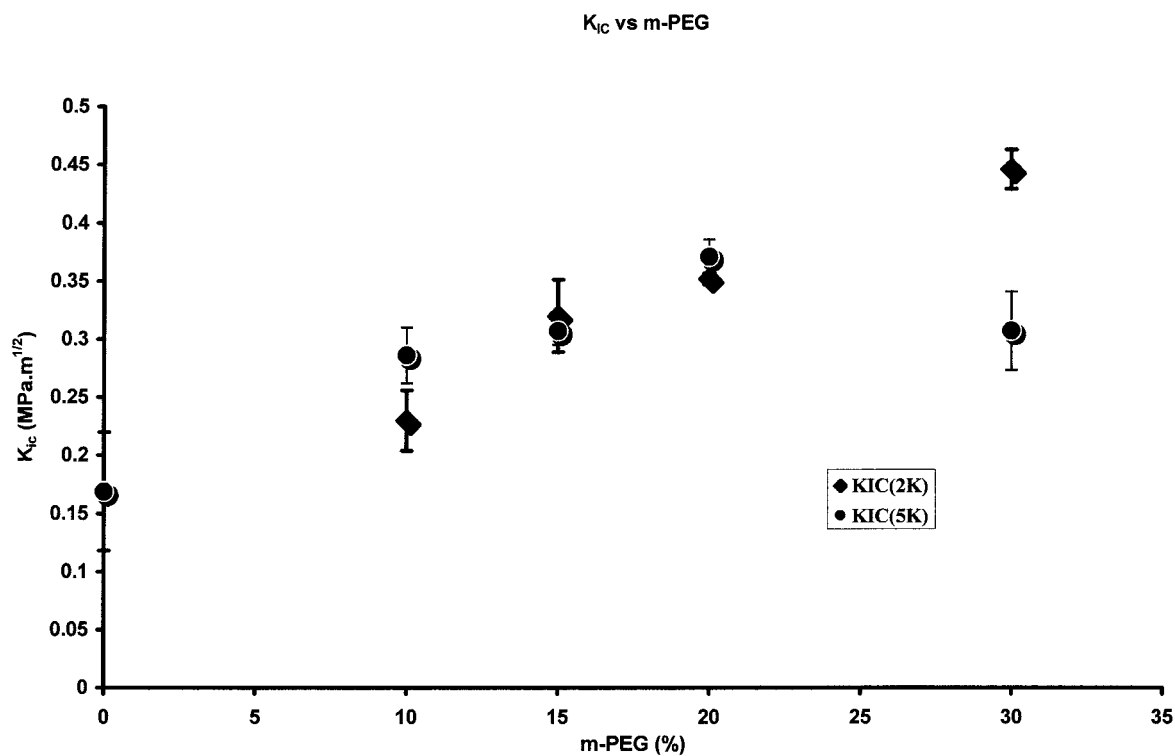


Figure 9 Effect of the m-PEG concentration on the fracture toughness (K_{IC}) of BMI polymer.

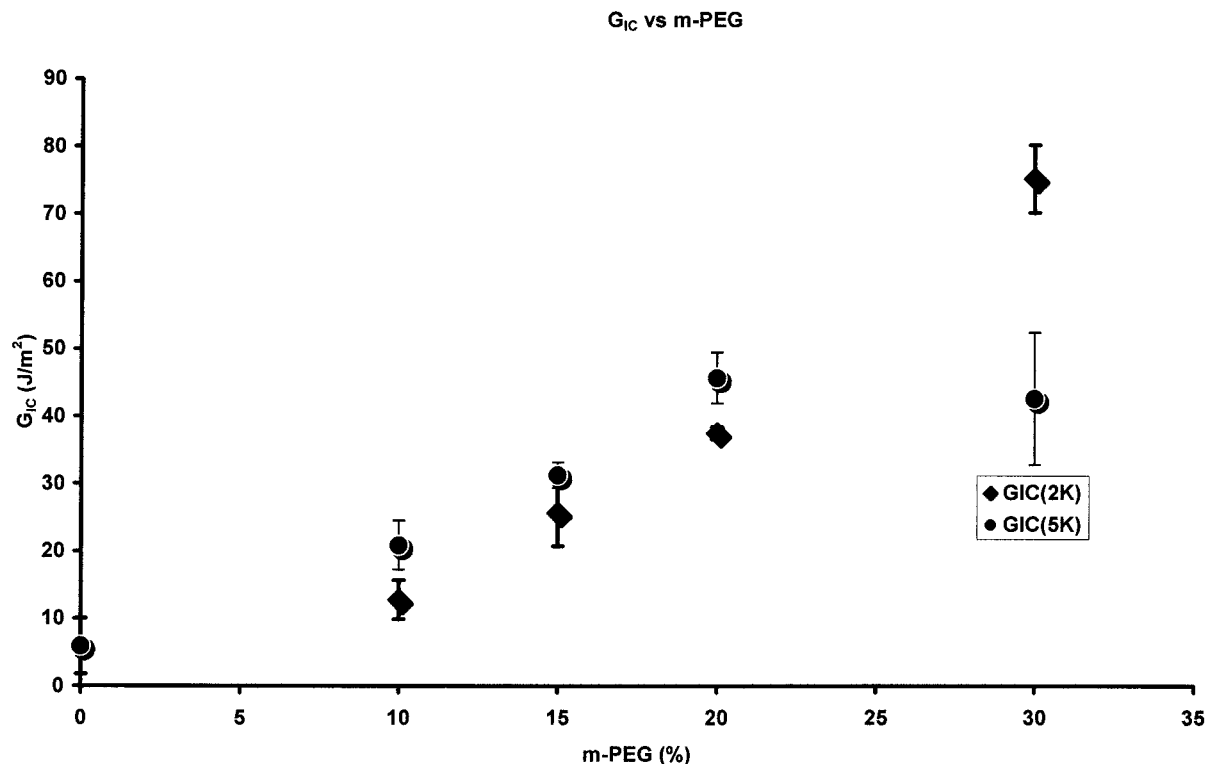


Figure 10 Effect of the m-PEG concentration on the fracture energy (G_{IC}) of BMI polymer.

and molecular weight, a critical point was reached at which these particles became stress concentrators. The dominant effect of the particle size was again reflected in this fracture toughness study.

Fracture energy

Figure 10 shows the influence of incorporating m-PEG on the fracture energy of the modified BMI polymers. Below 20 wt % m-PEG, the fracture energy of the modified BMI polymers increased with the m-PEG concentration and molecular weight. The higher molecular weight m-PEG5K showed a slightly higher fracture energy. However, at 30 wt % m-PEG, although the lower molecular weight m-PEG2K-modified BMI continued to show enhancement in the fracture energy, m-PEG5K-modified BMI showed marked deterioration. The reduction in the fracture energy was probably caused by the presence of large stress concentrators formed from agglomerates of free PEG side chains.

CONCLUSIONS

The curing reaction of m-PEGs of different molecular weights with BDM gave rise to BMI polymer networks containing PEG side chains. These incorporated PEG side chains gave rise to a phase-separated BMI polymer, the morphology of which was dependent on the concentration and molecular weight of the PEG side

chains. At low concentrations of m-PEG, that is, less than 30 wt %, the PEG particles were well dispersed and discrete. However, with the increasing concentration and/or molecular weight of m-PEG, coalescence of the PEG particles occurred, forming lamellar structures. At very high concentrations, agglomeration forming large PEG aggregates occurred, and the size of the aggregates increased with the both molecular weight and concentration of the m-PEG used.

The incorporation of the m-PEG oligomers was very effective in reducing the brittleness of the cured BMI polymer. Even with low levels of m-PEG, significant increases in the flexural strength and fracture toughness could be achieved. The ability to toughen the BMI polymer was highly dependent on the size of the phase-separated PEG particles. As the size of these PEG particles increased with the concentration and molecular weight of m-PEG, the optimal concentration appeared to be around 20 wt % m-PEG. Therefore, by the careful control of the concentration and/or choice of m-PEG of the appropriate molecular weight, one can achieve good fracture properties with minimal loss of polymer rigidity.

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