

High temperature, polymeric, structural foams from high internal phase emulsion polymerizations

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High temperature, polymeric, structural foams were prepared using a high internal phase emulsion (HIPE) to copolymerize styrene with maleimide based monomers. In this work, *N*-ethylmaleimide and a bismaleimide (BMI) monomer, bis(3-ethyl-5-methyl-4-maleimide-phenyl)methane, were successfully free-radically copolymerized with styrene in a water-in-oil HIPE to produce polymeric foams with glass transition temperatures (T_g s) ranging from 140 to 220°C depending on composition. The ethylmaleimide and BMI were uniformly incorporated throughout the polymer, which allowed the thermal performance of the foams to be tailored by controlling the concentration of ethylmaleimide and BMI modifiers. In addition, the thermal oxidative stability of the foam systems increased with increasing concentration of maleimide based monomers. The resulting polymeric foams contained an open cell morphology with cell sizes of approximately 10 μm in diameter. Compression tests of the high temperature foam systems showed that compression strengths of approximately 700–850 kPa were obtainable at foam densities under 80 mg cm^{-3} (5.0 lb ft^{-3}). © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polymeric foam systems are typically manufactured using blowing techniques, which expand a fluid polymer phase into a cellular morphology and stabilize the foam structure by further polymerization or cooling¹. Blowing agents can take the form of dissolved gases that expand with a reduction in pressure, incorporation of volatile liquids that expand with the application of heat, or gaseous by-products generated by blowing agent decomposition or polymerization reactions. These blown foam systems generally contain a closed cell morphology, possess anisotropic properties in relation to the direction of expansion, and have problems associated with them, such as outgassing of the expansion gases. Open cell foam structures can be obtained from closed cell structures by breaking of the cell walls with either mechanical or chemical methods creating a reticulated polymer foam. Again, however, the resulting foam contains anisotropic morphologies and properties.

In 1982, a high internal phase emulsion (HIPE) polymerization process to manufacture microcellular, polymeric foam systems was patented by Unilever². This patent discloses a polymerization process that occurs in a water-in-oil emulsion in which the water represents at least 76% of the emulsion by volume. The oil phase consists of vinyl monomers such as styrene and acrylates, that are crosslinked by divinyl monomers during polymerization. After polymerization and drying to remove the water phase, the result is a crosslinked

polymer foam with an open cell microstructure that is homogeneous throughout in terms of morphology, density, and mechanical properties. Since 1982, numerous patents have examined various HIPE polymerized foam processing techniques and applications that include absorbents for body fluids, cleaning materials, and ion exchange systems^{3–28}. All of the published HIPE polymerized foams have concentrated on materials for low temperature applications.

Los Alamos National Laboratory started work with HIPE polymerized foams in the mid 1980s, and has since developed an extensive knowledge base on HIPE foam technology^{29–35}. These efforts focused primarily on variations of a styrene/divinylbenzene (DVB) foam system that produces structural foams with glass transition temperatures (T_g s) of approximately 100°C. Recently, we have been working to expand these systems with the development of a high temperature, $T_g > 200^\circ\text{C}$, HIPE polymerized foam system.

The large increase in demand for light weight structural materials, primarily driven by the aerospace industry, has included rigid, polymeric foam systems. Many of these applications require heat resistant materials either during processing (e.g. core for composite sandwich panels) or during use (e.g. engine compartments and exhaust enclosures). Development of high temperature HIPE polymer foam systems could provide significant advantages over commercial blown and extruded heat resistant, structural, polymeric foam systems such as Rohacell[®], a polymethacrylimide closed cell foam. HIPE polymer foams are easily tailorable over a broad range of densities (20–320 mg cm^{-3}), and the

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emulsion produced during processing allows for the near-net-shape casting of isotropic, open celled foams. Blown and extruded commercial foam systems are unable to provide this combination of processing capabilities with isotropic properties.

To develop these high T_g HIPE foams, our work has focused on the copolymerization of styrene with *N*-substituted maleimide and BMI monomers in a high internal phase water-in-oil emulsion. The copolymerization of styrene with maleic anhydride and *N*-substituted maleimides to produce heat resistant thermoplastics has been studied extensively since 1939³⁶⁻⁴². These investigations have shown that styrene will free-radically copolymerize with *N*-substituted maleimides to create an alternating thermoplastic copolymer with a T_g of approximately 200°C. However, there are many difficulties in copolymerizing styrene with maleimides in a HIPE, such as lower polymerization temperatures,

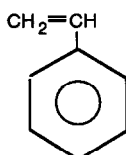
maleimide solubility difficulties in both styrene and water, and difficulty in obtaining a stable HIPE, with a styrene/maleimide oil phase. This work describes the preparation of copolymer foams from *N*-ethylmaleimide and bis(3-ethyl-5-methyl-4-maleimide-phenyl)methane with styrene based monomers and crosslinking agents.

EXPERIMENTAL

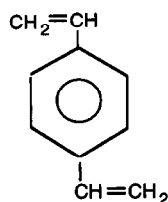
Materials

N-ethylmaleimide was obtained from Aldrich Chemical Corporation and bis(3-ethyl-5-methyl-4-maleimide-phenyl)methane was obtained from the Ihara Chemical Industry Company, with the help of Ken Seika Corporation, under the product name BMI-70. Stabilized styrene was used as received from VWR Scientific, and a 55% mixture of divinylbenzene (DVB) isomers was

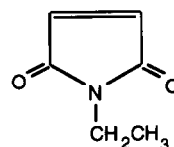
Styrene



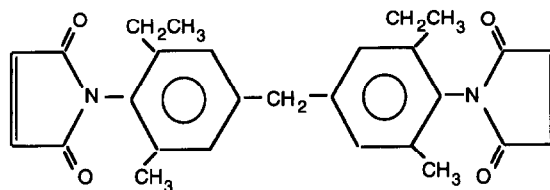
Divinylbenzene (DVB)



N-Ethylmaleimide



BMI-70



Sorbitan Monooleate (SMO)

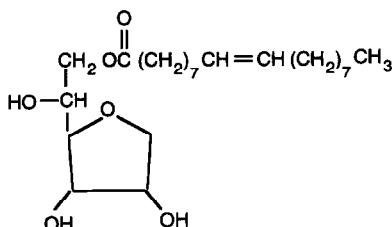


Figure 1 Chemistry of oil phase components

used as received from Polysciences Incorporated. Potassium persulfate was obtained from Aldrich Chemical Corporation and used as the free radical initiator. Sorbitan monooleate (SMO) was used as the emulsifying agent and was obtained from the Henkel Corporation as Emsorb 2500. Chemical structures of the oil phase components are shown in *Figure 1*.

Processing

To process the foam samples, the oil phase was prepared by first dissolving the ethylmaleimide and BMI-70 into the styrene/DVB monomers and then adding the SMO to the monomer mixture. In all the foams processed, a total oil weight of 7.5 g was prepared and placed in a 120 ml wide mouth Qorpak jar. The oil phase was then mechanically stirred with an Arrow Engineering Model 1750 variable speed mixing motor and a 32 mm diameter Stainless Steel Jiffy Mixer obtained from Thomas Scientific. A mixing speed of approximately 600–800 rpm was employed while 92.5 g of distilled water containing 1.5 g l^{-1} potassium persulfate was added dropwise. After all the water had been added, the emulsion was further stirred for 5 min at a speed of approximately 900 rpm and for 5 min at a speed of 1000 rpm. The resulting emulsions were capped and put in a convection oven at 60°C to cure overnight. After polymerization, the foams were removed from the Qorpak jars and returned to the convection oven to dry at 60°C . Drying times varied from several hours to 48 h depending on the morphology of the cells. The dried foams were then postcured at 250°C under vacuum overnight.

Compositions of the oil phase used in processing of the foam samples will be presented using wt%. The SMO concentrations will be reported as wt% of the entire oil phase. Monomer concentrations will be reported as wt% of only the total monomer weight in the oil phase. For example, a 100 g sample of oil containing 15% SMO, 10% DVB, and 90% styrene would contain 15 g SMO, 8.5 g DVB, and 76.5 g styrene. This convention is used because the SMO does not take part in the polymerization reaction and the majority of the SMO volatilizes and is removed during postcure.

Analysis

Dynamic mechanical analysis (d.m.a.) was performed on a Rheometrics RDS II mechanical spectrometer and the T_g of the foam samples was defined as the peak in the $\tan \delta$ curve. A clamping fixture capable of gripping onto the foam samples was machined to fit into the normal Rheometrics adapters. Testing was done at a fixed frequency of 1 Hz, and the temperature was stepped at 5°C increments from 30°C to a maximum temperature of 350°C in a nitrogen environment. D.m.a. results will be plotted in this paper for the shear storage modulus, G' , and $\tan \delta$ as a function of temperature. All G' curves have been normalized to a value of 1 at 30°C by dividing all G' values by the G' value at 30°C for each sample. This normalization eliminates the effects of density and mechanical performance variations between samples and allows for an easier comparison of thermal performance.

Thermogravimetric analysis (t.g.a.) of each foam sample was done on a Polymer Laboratory TGA Model 1500 to examine thermal stability behaviour. Foam samples were dynamically run at $10^\circ\text{C min}^{-1}$ from 10 to 500°C in both air and nitrogen environments.

Foam compression strengths were evaluated on an Instron Model 4483 testing frame. Only one sample of each composition was tested to quickly screen mechanical performance. Samples were cylindrical in shape, approximately 25 mm (1.0 in) high and 45 mm (1.77 in) in diameter, and tested at rate of 0.25 mm min^{-1} (0.1 in min^{-1}).

Morphologies of the foam samples were evaluated by scanning electron microscopy (SEM).

RESULTS

Three series of foam samples were processed and compared to a standard styrene/DVB foam system containing 90% styrene crosslinked with 10% DVB. First, the effect of incorporating increasing concentrations of ethylmaleimide monomer to styrene with a DVB crosslinking agent was investigated. In the second series, BMI-70 was used to crosslink an unmodified styrene system, and the final series combined the use of a BMI crosslinking agent with increasing concentrations of ethylmaleimide. In all systems 15% by weight SMO was used as an emulsifying agent. Specific sample compositions and identifications are presented in *Tables 1–3* for the three series.

Processing of foam samples

The first step in the qualitative characterization of HIPE processing of polymeric foams is to examine the quality of the emulsion produced after mixing and then to evaluate the final foam quality. A high quality emulsion produced after mixing consisted of a smooth

Table 1 Sample identification and compositions of ethylmaleimide modified foams with DVB crosslinking agent

Sample	% By weight of each component		
	Styrene	DVB	Ethylmaleimide
Eth-1	90	10	0
Eth-2	80	10	10
Eth-3	70	10	20
Eth-4	60	10	30
Eth-5	50	10	40
Eth-6	40	10	50

Table 2 Sample identification and compositions of BMI crosslinked styrene foams

Sample	% By weight of each component		
	Styrene	BMI-70	Ethylmaleimide
BMI-1	90	10	0
BMI-2	80	20	0
BMI-3	70	30	0

Table 3 Sample identification and compositions of BMI crosslinked foams modified with ethylmaleimide

Sample	% By weight of each component		
	Styrene	BMI-70	Ethylmaleimide
EthBMI-1	70	20	10
EthBMI-2	60	20	20
EthBMI-3	55	20	25
EthBMI-4	50	20	30

emulsion that flowed easily without water separation. A high quality foam is strong and stiff with a uniformly smooth surface. If water begins to separate out of the emulsion in the mixing process, the final foam will generally contain large pot marks on the foam surface created by the separated water, which leads to a reduction in the final foam mechanical properties. In processing of the maleimide modified foam samples, some compositional limitations were determined. However, the majority of samples produced high quality foams.

Sample Eth-1 (*Table 1*) was a standard styrene/DVB foam system that processed easily producing a smooth white emulsion after mixing and a high quality foam. As ethylmaleimide was added to the styrene/DVB system, samples Eth-2 to Eth-4, no apparent differences were observed in the emulsion or final foam quality. In sample Eth-5, the 40% ethylmaleimide produced a slightly stiffer emulsion during mixing, and the final foam contained pot marks on the surface caused by water separation during emulsification. During postcure, sample Eth-5 shrunk approximately 76% by volume, which produced an unusable foam. When the ethylmaleimide concentration was increased further to 50% in Sample Eth-6, a HIPE could no longer be obtained. A milky white water solution was produced during mixing that polymerized into disconnected polymer particles.

In the BMI-70 modified samples (*Table 2*), BMI-1 to BMI-3 all produced a smooth white emulsion after mixing, however, only sample BMI-1 solidified during polymerization into a foam structure. Samples BMI-2 and BMI-3 produced only disconnected polymer particles. In addition, sample BMI-1 shrunk approximately 91% by volume during postcure, which produced an unusable foam system.

In the final series of samples using BMI-70 to crosslink ethylmaleimide/styrene (*Table 3*), samples EthBMI-1, EthBMI-2, and EthBMI-3 all emulsified easily, but the emulsion viscosity increased as the concentration of ethylmaleimide increased. All three samples produced high quality final foams. Sample EthBMI-4 behaved the same as sample Eth-6. No emulsion was produced during mixing and only disconnected polymer was produced during polymerization.

Ethylmaleimide was chosen for these experiments over other maleimide systems because of a high solubility in styrene, 60% by weight. Experiments with styrene insoluble or slightly soluble maleimide and BMI modifiers produced no improvement in thermal performance. Processing of the ethylmaleimide samples suggest that the addition of 50% by weight of a maleimide based modifier appears to be an upper limit in producing a stable HIPE. Both sample EthBMI-4 and Eth-6 contained a combined concentration of 50% maleimide modifiers by weight and could not be emulsified. This disruptive effect of the ethylmaleimide on the emulsion formation may be due to the partial solubility of ethylmaleimide in water, approximately 5% by weight. Styrene is essentially insoluble in water⁴³. Previous HIPE literature stress the importance of using essentially water insoluble monomers to prevent dissolution of monomers into the water phase and destabilization of the emulsion²⁻³⁵. Additionally, the water phase electrolyte concentration can be used to decrease the solubility of the monomers in the water phase^{11,19}. In order for higher concentrations of maleimide modifiers to be used, the water solubility of the ethylmaleimide may have to be

reduced significantly by increasing the electrolyte concentrations in the water phase.

BMI-70 was also chosen in these experiments because of a high solubility in styrene, 33% by weight, and insolubility in water. The difficulty in producing a BMI-70 crosslinked styrene foam does not appear to be related to an inability of the BMI to free radically polymerize with styrene but indicates that processing conditions have not been optimized. A foam was produced at a low concentration of BMI-70, sample BMI-1, and there was no difficulty in using BMI-70 to crosslink the styrene/ethylmaleimide system. In addition, the BMI crosslinked styrene/ethylmaleimide system survived postcure without melting indicating that the BMI participated in the free radical polymerization reaction and created a crosslinked polymer system. The disconnected polymer particles produced in samples BMI-2 and BMI-3 are indicative of a high emulsifier concentration³⁰. Typically, as the emulsifier concentration is increased in the HIPE process, the foam structure will begin to break down and produce a disconnected polymer system. For styrene/DVB systems, a disconnected polymer system is not generally obtained until emulsifier concentrations larger than 50% by weight are used. With the use of BMI-70 to crosslink styrene, this critical emulsifier concentration to produce a foam may be less than the 15% SMO used during processing.

Morphology

SEM photomicrographs were taken of samples Eth-1 to Eth-4 and of EthBMI-1 to EthBMI-3, shown in *Figures 2* and *3* respectively. Sample Eth-1 shows the typical morphology obtained with a styrene/DVB system when 15% SMO is used during processing. The foam cells tend to be approximately 10 μm in diameter with a very open celled character of interconnecting pores. As the concentration of ethylmaleimide is increased in samples Eth-2 to Eth-4, the basic open celled foam structure remains the same, but the cell structure has a tendency to be composed more of a connected strut configuration with larger interconnecting pores. Addition of the ethylmaleimide appears to be changing the interaction between the oil and water phase during processing, and therefore, the structure of the final foam cellular structure. The SEM of sample Eth-5 shows the collapsed foam morphology that was obtained during postcure.

The effect of the maleimide addition on the foam structure is readily apparent in samples EthBMI-1 to EthBMI-3 (*Figure 3*). In Eth-BMI-1, the basic open cell structure still exists, however, areas of disconnected polymer are observed. As the ethylmaleimide concentration is increased further in samples EthBMI-2 and EthBMI-3, an increase in the quantity of disconnected polymer regions is observed. Therefore, the addition of the maleimide monomers into the foam system appears to have a disruptive effect on the final cell structure formation.

As discussed previously, the partial water solubility of the ethylmaleimide probably plays a large role in the disruption of the cellular structure. Similar changes in the cellular structure can also be achieved by varying the concentration of the emulsifying agent in the oil phase and the concentration of the electrolyte in the water phase. Both of the emulsifying agent and the electrolyte concentrations have large influences on the size of the interconnecting pores between cells^{11,30}. The

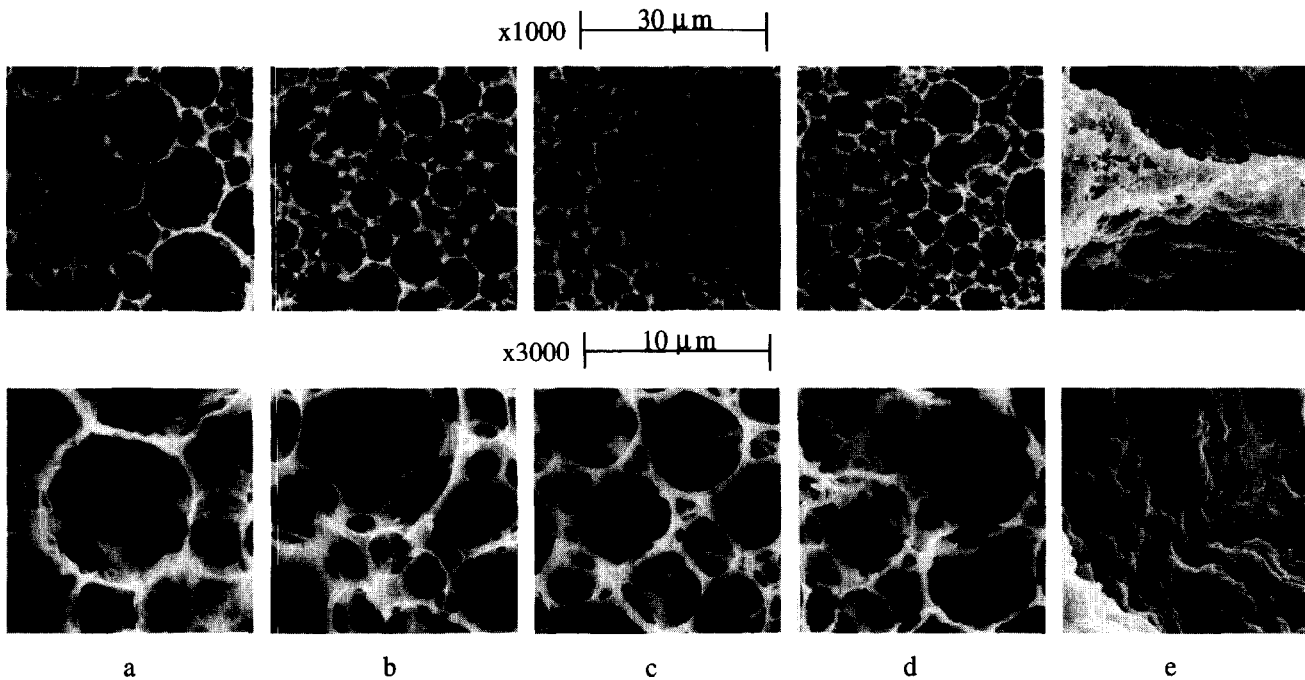


Figure 2 Scanning electron photomicrographs at magnifications of $\times 1000$ and $\times 3000$ of ethylmaleimide modified foams crosslinked with DVB: (a) sample Eth-1; (b) sample Eth-2; (c) sample Eth-3; (d) sample Eth-4; (e) sample Eth-5

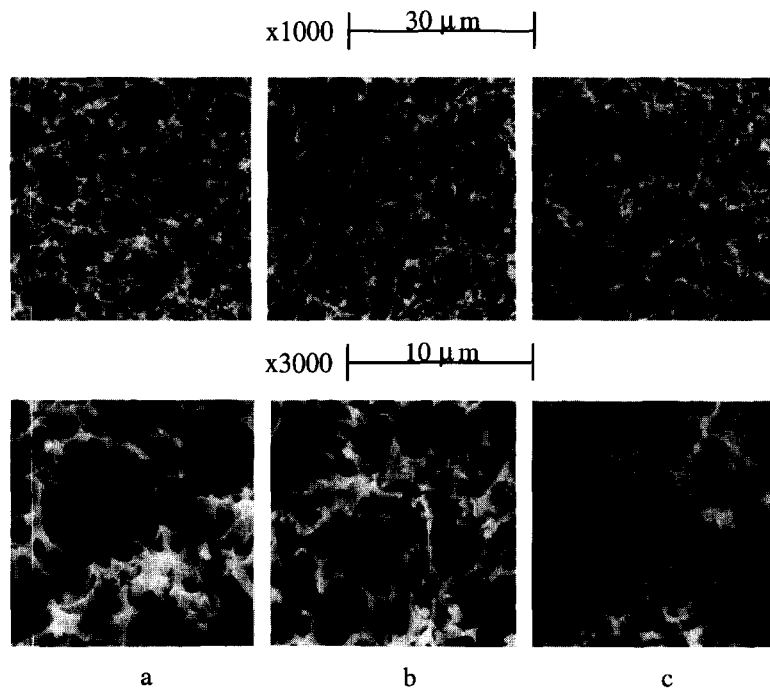


Figure 3 Scanning electron photomicrographs at magnifications of $\times 1000$ and $\times 3000$ of ethylmaleimide modified foams crosslinked with BMI-70: (a) sample EthBMI-1; (b) sample EthBMI-2; (c) sample EthBMI-3

concentrations used in these experiments were based on experience with styrene/DVB systems. With the addition of the maleimide modifiers to the styrene/DVB system, further optimization of the SMO and electrolyte concentrations as well as processing conditions (i.e. shear rates and temperatures during mixing emulsification) is required to produce the desired open cell morphology.

Dynamic mechanical analysis

All foam samples were d.m.a. tested before and after postcure. D.m.a. results for a standard styrene/DVB foam, sample Eth-1 (Table 1), are plotted as a normalized

shear storage modulus, G' , and $\tan \delta$ as a function of temperature in Figures 4 and 5 for foam samples before and after postcure respectively. Before postcure, the foam T_g , as defined by the peak in the $\tan \delta$ curve, is 120°C . However after postcure at 250°C overnight under vacuum, the T_g of the foam increased to 129°C . This increase in T_g is mostly due to the removal of SMO from the foam during postcure. At 250°C under vacuum, the SMO is volatilized and removed by the vacuum. The removed SMO is easily collected in a cold trap placed between the vacuum oven and the vacuum pump. After postcure, the measured weight loss of the

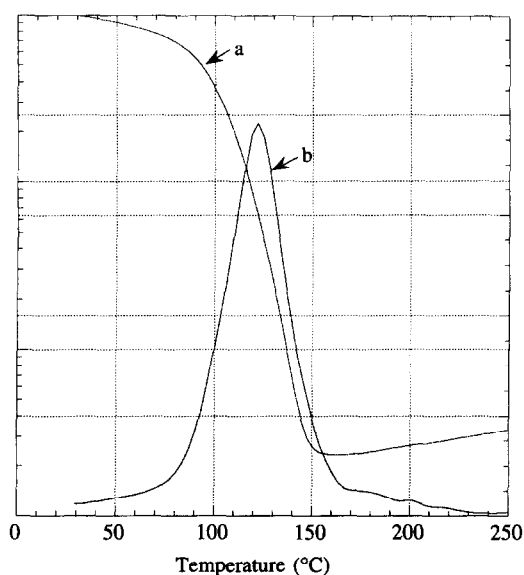


Figure 4 Dynamic mechanical analysis of styrene/DVB foam, sample Eth-1, before postcure: (a) shear storage modulus curve; (b) tan δ curve with peak at 120°C

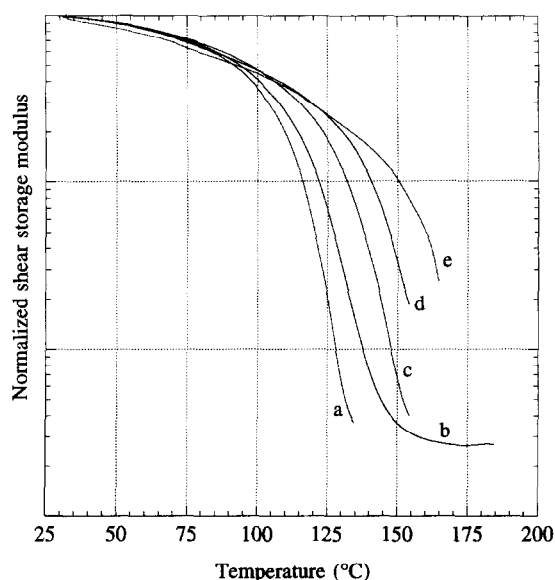


Figure 6 Normalized shear storage modulus curves as functions of temperature for ethylmaleimide modified foams crosslinked with DVB before postcure: (a) sample Eth-1; (b) sample Eth-2; (c) sample Eth-3; (d) sample Eth-4; (e) sample Eth-5

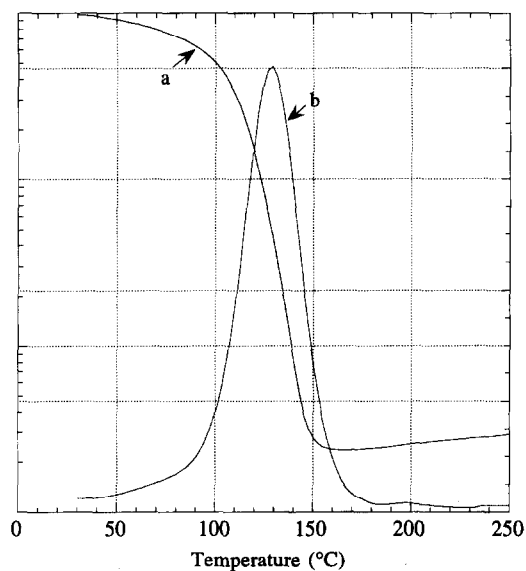


Figure 5 Dynamic mechanical analysis of styrene/DVB foam, sample Eth-1, after postcure: (a) shear storage modulus curve; (b) tan δ curve with peak at 129°C

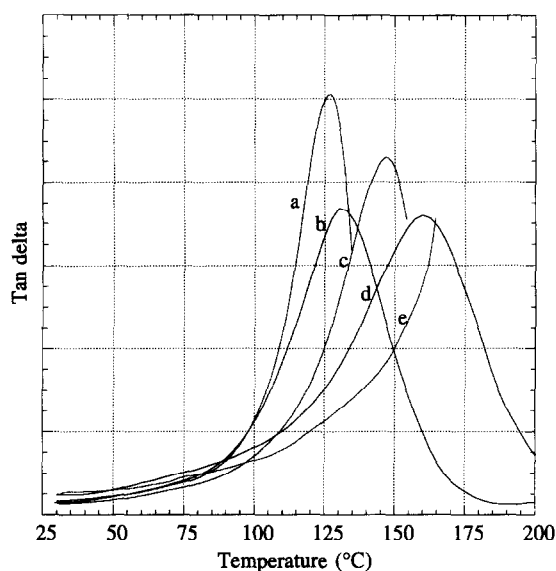


Figure 7 Tan δ curves as functions of temperature for ethylmaleimide modified foams crosslinked with DVB before postcure: (a) Eth-1, peak at 126°C; (b) sample Eth-2, peak at 131°C; (c) sample Eth-3, peak at 146°C; (d) sample Eth-4, peak at 160°C; (e) sample Eth-5, peak at > 165°C

sample was approximately 10%, which represented 67% of the SMO used during processing. Since the SMO acts as a plasticizer in the polymeric foams, the removal of SMO will produce an increase in the postcured foam T_g and mechanical properties³³.

When ethylmaleimide was incorporated into the standard styrene/DVB system, the T_g of the foam samples increased directly with increases in ethylmaleimide concentration. Before postcure, samples Eth-1 to Eth-5 showed increases in T_g with a maximum T_g greater than 165°C for sample Eth-5, shown in *Figures 6* and *7*. The incomplete d.m.a. curves were due to the foam samples softening and slipping out of the testing fixture as they passed through their T_g . As the concentration of ethylmaleimide increased, the peak in the tan δ curve shifted to higher temperatures, and the width of the transition region increased. The beginning of the

transition region is at approximately 100°C for all samples due to the influence of polystyrene blocks within the copolymer. Styrene-ethylmaleimide copolymer regions within the foam cause the peak in the tan δ to increase in temperature with increasing ethylmaleimide concentration. After the samples were postcured, the T_g of each foam sample increased by 25–40°C with a maximum T_g of 204°C, and a decrease in the transition width was observed, shown in *Figures 8* and *9*. Therefore, additional reaction appears to be occurring during postcure. The beginning of each transition and the tan δ peak increased directly with increasing maleimide concentration. For every 10% increase in the ethylmaleimide concentration, a corresponding increase of 20°C is observed in the foam T_g .

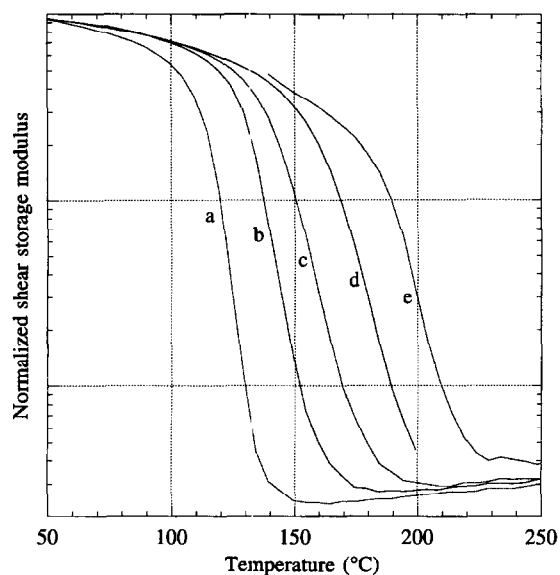


Figure 8 Normalized shear storage modulus curves as functions of temperature for ethylmaleimide modified foams crosslinked with DVB after postcure: (a) sample Eth-1; (b) sample Eth-2; (c) sample Eth-3; (d) sample Eth-4; (e) sample Eth-5

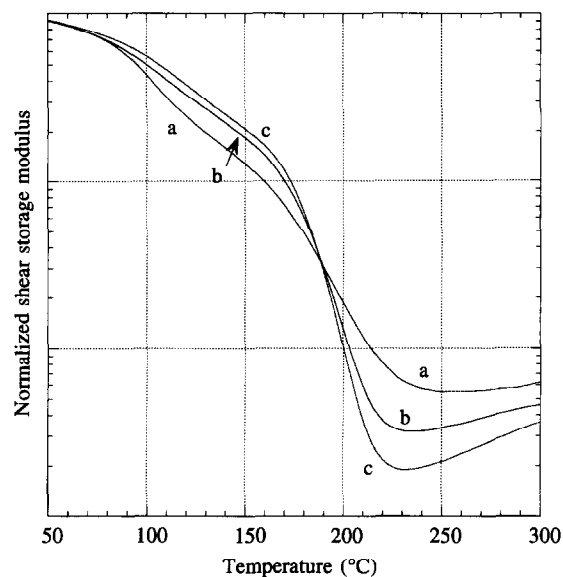


Figure 10 Normalized shear storage modulus curves as functions of temperature for ethylmaleimide modified foams crosslinked with BMI-70 before postcure: (a) sample EthBMI-1; (b) sample EthBMI-2; (c) sample EthBMI-3

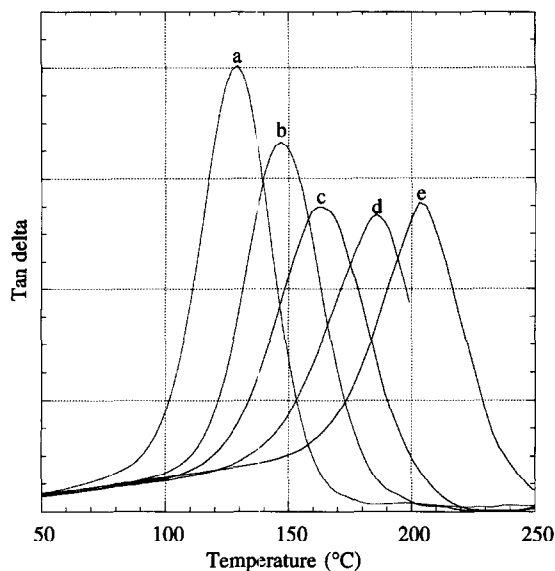


Figure 9 Tan δ curves as functions of temperature for ethylmaleimide modified foams crosslinked with DVB after postcure: (a) sample Eth-1, peak at 129°C; (b) sample Eth-2, peak at 144°C; (c) sample Eth-3, peak at 164°C; (d) sample Eth-4, peak at 184°C; (e) sample Eth-5, peak at 204°C

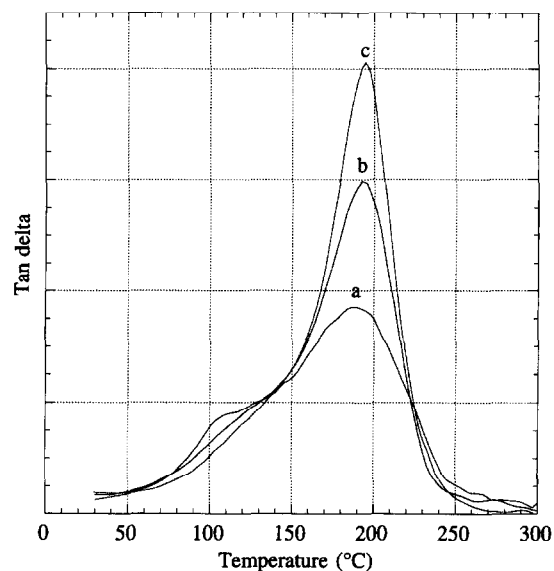


Figure 11 Tan δ curves as functions of temperature for ethylmaleimide modified foams crosslinked with BMI-70 before postcure: (a) sample EthBMI-1; (b) sample EthBMI-2; (c) sample EthBMI-3. All three samples exhibit a tan δ peak of approximately 195°C

In both of sets of d.m.a. data, before and after postcure, one main transition region is observed indicating that the maleimide is being incorporated uniformly into the polystyrene chains. At the lower concentrations of ethylmaleimide modifier, there should still be large regions within the polymer chains containing only polystyrene blocks. These polystyrene regions tend to increase the width of the transition region and skew the curve towards 100°C, the polystyrene T_g . Ideally, a 1/1 molar ratio between the ethylmaleimide and the styrene would be used to obtain an alternating copolymer throughout the polymer foam. However, these data demonstrate that styrene will copolymerize with ethylmaleimide in HIPE processing to provide a heat resistant foam system.

The d.m.a. results of the BMI-70 cross-linked systems exhibit different trends than the DVB crosslinked samples. *Figures 10 and 11* show the d.m.a. results of samples EthBMI-1 to EthBMI-3 (*Table 3*) before postcure. All three samples show very similar behaviour with a wide transition region, and a peak in the tan δ curve at the same temperature. The transitions all begin at 100°C and continue to 250°C, and the peak in the tan δ curve occurs at approximately 195°C for all samples. When the samples are postcured, shown in *Figures 12 and 13*, a much narrower transition region is obtained for all samples, but again all samples exhibit the same T_g as defined by the peak in the tan δ curve. This T_g increased from 195 to 219°C by postcuring the samples. *Figure 12* demonstrates the effect of the increasing ethylmaleimide concentration. As the ethylmaleimide

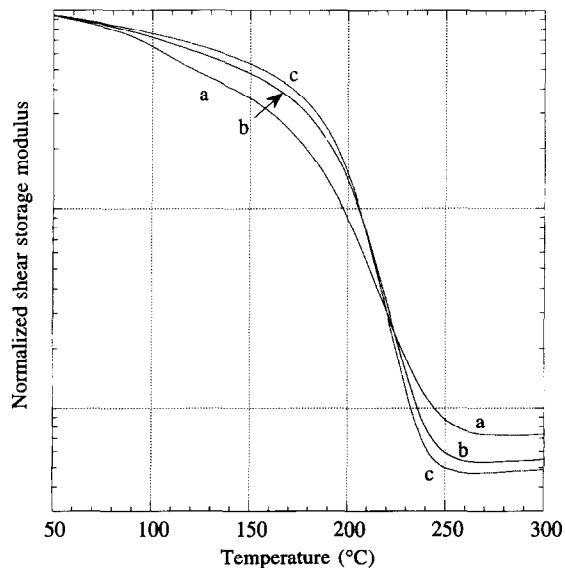


Figure 12 Normalized shear storage modulus curves as functions of temperature for ethylmaleimide modified foams crosslinked with BMI-70 after postcure: (a) sample EthBMI-1; (b) sample EthBMI-2; (c) sample EthBMI-3

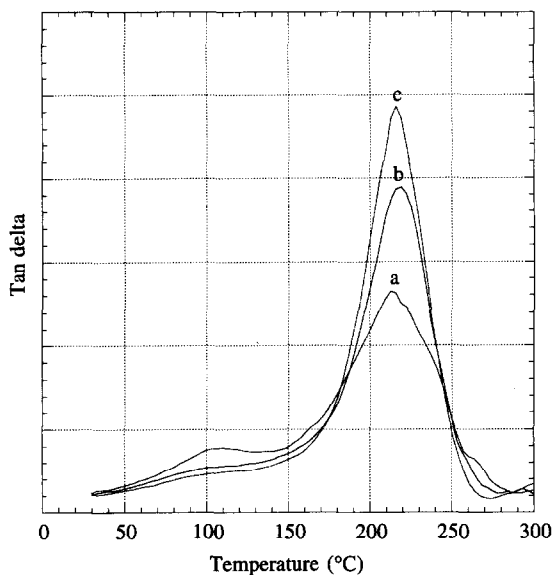


Figure 13 $\tan \delta$ curves as functions of temperature for ethylmaleimide modified foams crosslinked with BMI-70 after postcure: (a) sample EthBMI-1; (b) sample EthBMI-2; (c) sample EthBMI-3. All three samples exhibit a $\tan \delta$ peak of approximately 219°C

concentration is increased, the thermal dependence of G' , or the slope of G' , decreases prior to the main transition. This increase in thermal stability is due to the ethylmaleimide being incorporated into the polystyrene chains between crosslinks creating large blocks of styrene/ethylmaleimide copolymer.

The d.m.a. results of samples EthBMI-1 to EthBMI-3 demonstrate that BMI can be used as a crosslinking agent in a free radical HIPE polymerization reaction. Before postcure, the d.m.a. results indicate that the BMI participated in the free radical polymerization reaction, but postcure of the samples is required to complete the processing of the high temperature foam systems. The concentration of BMI crosslinker used during processing controls the peak temperature of the $\tan \delta$ curve, and the

ethylmaleimide concentration controls the thermal dependence of G' prior to T_g .

Thermal stability

The thermal stability of the foam samples was examined by t.g.a. in order evaluate if the thermal stability of the foam samples increased as the foam T_g increased. T.g.a. plots for samples Eth-1 to Eth-5 (Table 1) in air and nitrogen environments are shown in Figures 14 and 15 respectively. In air, the t.g.a. shows that a styrene/DVB foam, sample Eth-1, is not thermally oxidatively stable above 275°C. A two-step degradation process appears to be occurring with the first step beginning at approximately 275°C, and the second step beginning at approximately 350°C. This oxidative degradation of styrene systems in the 250°C temperature region has been shown by previous researchers⁴⁴. In the open-celled HIPE foam systems, the large surface area of the foams increase their oxygen sensitivity and the rate of oxidative degradation increases in this temperature range. When the ethylmaleimide modifier is added, a decrease in the size of the first degradation step and a shift to the higher temperatures in the overall curve is observed. Therefore, the ethylmaleimide inhibits the first degradation step and improves the overall thermal oxidative stability of the foam systems.

When the thermal stability in nitrogen is examined, shown in Figure 15, a one-step degradation process is observed with an increase in thermal stability with increasing ethylmaleimide concentration. The standard styrene/DVB system, sample Eth-1, exhibits stable thermal behaviour in excess of 300°C in an inert nitrogen environment. With the addition of ethylmaleimide, thermal degradation does not occur until temperatures exceed 350°C.

Similar results are obtained when the BMI crosslinked foam systems are examined for thermal stability, shown in Figures 16 and 17. With increasing ethylmaleimide concentration, there is an increase in thermal stability in both oxygen and nitrogen environments. However, the

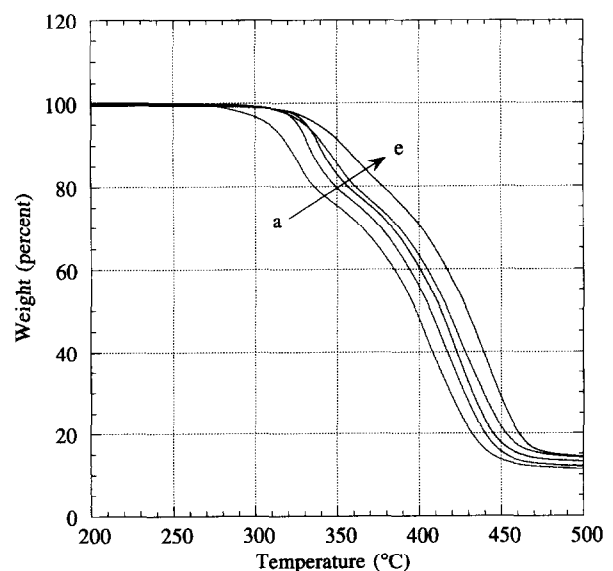


Figure 14 Thermogravimetric analysis in air of ethylmaleimide modified foams crosslinked with DVB after postcure showing increasing thermal stability with increasing ethylmaleimide concentration from (a) sample Eth-1 to (e) sample Eth-5

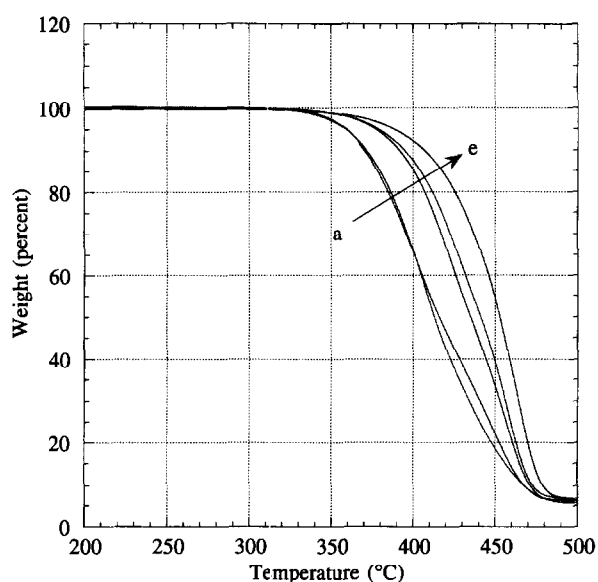


Figure 15 Thermogravimetric analysis in nitrogen of ethylmaleimide modified foams crosslinked with DVB after postcure showing increasing thermal stability with increasing ethylmaleimide concentration from (a) sample Eth-1 to (e) sample Eth-5

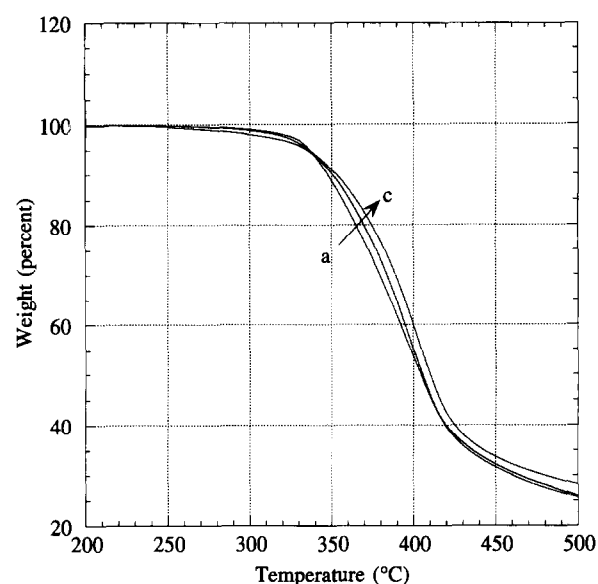


Figure 16 Thermogravimetric analysis in air of ethylmaleimide modified foams crosslinked with BMI-70 after postcure showing increasing thermal stability with increasing ethylmaleimide concentration from (a) sample EthBMI-1 to (c) sample EthBMI-3

majority of the improvement is due to the use of the BMI crosslinking agent. The t.g.a.s in air of samples EthBMI-1 to EthBMI-3 show only a one-step degradation in contrast to the two-step degradations observed in the DVB crosslinked samples. This suggests that the first step in the oxidative degradation in the DVB crosslinked samples is oxidative chain scission on both ends of the DVB crosslink, which allows the DVB block to volatilize. In the BMI crosslinked systems and as ethylmaleimide is incorporated into the DVB crosslinked foams the isolation of the crosslinking molecule is prevented by the higher thermal oxidative stability of the maleimide-DVB and of the styrene-maleimide bonds at both ends of the crosslinks. Therefore, the first weight loss step is eliminated with the incorporation of maleimide modifiers.

This t.g.a. analysis demonstrates improved thermal stability of the styrene/maleimide foam systems. In addition, these data corroborate the single transition in d.m.a. tests and suggests that the ethylmaleimide and BMI are copolymerizing uniformly throughout the polymer system.

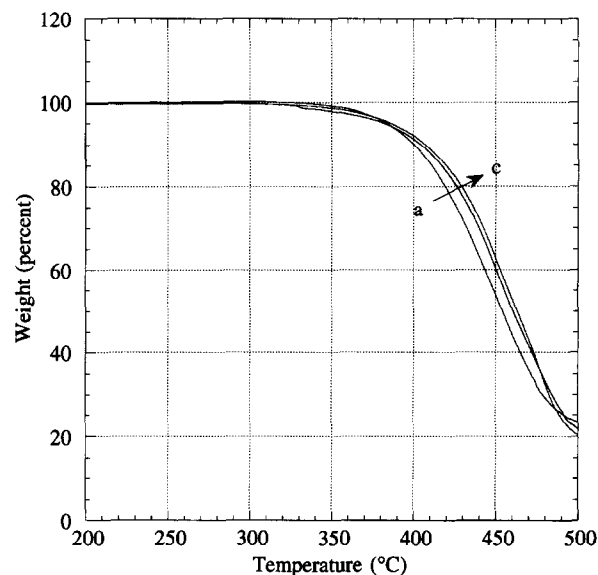


Figure 17 Thermogravimetric analysis in nitrogen of ethylmaleimide modified foams crosslinked with BMI-70 after postcure showing increasing thermal stability with increasing ethylmaleimide concentration from (a) sample EthBMI-1 to (c) sample EthBMI-3

Table 4 Density and compression strengths of foam samples

Sample	Density (mg cm^{-3} (lb ft^{-3}))	Compression strength (kPa (psi))	Specific compression strength ($\text{kPa cm}^3 \text{mg}^{-1}$) ($\text{psi ft}^3 \text{lb}^{-1}$)
Eth-1	73.4 (4.58)	721 (105)	9.82 (22.9)
Eth-2	76.6 (4.78)	819 (119)	10.7 (24.9)
Eth-3	77.9 (4.86)	847 (123)	10.9 (25.3)
Eth-4	80.4 (5.02)	718 (104)	8.93 (20.7)
Eth-5	^a	^a	^a
Eth-6	^a	^a	^a
EthBMI-1	71.9 (4.48)	513 (74.4)	7.13 (16.6)
EthBMI-2	72.7 (4.54)	652 (94.6)	8.97 (20.8)
EthBMI-3	78.7 (4.91)	773 (112)	9.82 (22.8)
EthBMI-4	^a	^a	^a

^a Sample did not survive postcure

Mechanical properties

The mechanical properties of the foam samples were evaluated as a compression strength. Table 4 presents the compression strength results and includes the foam densities and a specific compression strength value. The foam sample densities varied slightly due to variations in volume shrinkages during the postcure process. Therefore, to obtain a more accurate comparison of the foam performance, a specific compression strength was calculated by dividing the compression strength with the foam density.

When ethylmaleimide was used to modify the styrene/DVB foams, samples Eth-1 to Eth-4 show that improvements of 10–15% in compression strengths are obtainable. For the BMI crosslinked foam samples, samples EthBMI-1 to EthBMI-3 possessed slightly lower compression strengths. Specific compression strengths of 7–10 kPa cm³ mg⁻¹ (16–23 psi ft³ lb⁻¹) were measured for sample EthBMI-1 to EthBMI-3 in comparison to the 9–11 kPa cm³ mg⁻¹ (20–25 psi ft³ lb⁻¹) for sample Eth-1 to Eth-4. These compression strength trends can be explained by examining the SEM photomicrographs. Samples Eth-1 to Eth-4 possess a more uniform open celled structure than samples EthBMI-1 to EthBMI-3, and therefore, samples Eth-1 to Eth-4 produced higher compression strength values. Maximum compression strengths can only be obtained by creating the correct cellular morphology during processing.

The optimization of the mechanical performance of these maleimide modified foam systems will require the optimization of the composition and processing conditions to produce a uniform cellular structure. Comparison of the SEM photomicrographs with the compression strength values demonstrates that generating the correct morphology during processing will produce compression strengths of 700–850 kPa (100–125 psi) at densities under 80 mg cm⁻³ (5.0 lb ft⁻³).

CONCLUSIONS

Our results have demonstrated that high temperature, structural, polymer foams can be prepared by copolymerizing styrene with ethylmaleimide and BMI monomers using a HIPE polymerization process. The ethylmaleimide and BMI-70 free radically polymerized with styrene and were incorporated uniformly throughout the polymer. This process produced open-celled polymeric foams with T_g s ranging from 140 to 220°C, that also possessed improved thermal oxidative stability over a styrene/DVB foam system. In addition, these maleimide modified foam systems demonstrated the ability to achieve compression strengths of 700–850 kPa (100–125 psi) at densities under 80 mg cm⁻³ (5.0 lb ft⁻³).

The incorporation of ethylmaleimide and BMI into the HIPE process does have destabilizing influences on the interaction between the oil and water phases in comparison to styrene/DVB systems. SEM results indicate that the addition of maleimide modifiers initially leads to an increase in size of interconnecting pores between cells and eventually a total break down in cellular structure. High internal phase emulsions were unable to be obtained at maleimide modifier concentration of 50% by weight or higher. A significant reason for this breakdown in cellular structure is most likely due to the partial solubility of ethylmaleimide in water, 5% by weight. With the use of a more hydrophilic monomer,

in comparison to styrene, optimization of composition and processing conditions must be examined. This includes emulsifier and electrolyte concentrations as well as the shear rates and temperatures used during emulsification. Further work is continuing to optimize the process–structure–property interrelations of these foam systems.

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