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*Title:*

HIGH TEMPERATURE, STRUCTURAL, POLYMERIC  
FOAMS FROM HIGH INTERNAL PHASE EMULSION  
POLYMERIZATION

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*Submitted to:*

American Chemical Society  
National Meeting  
New Orleans, LA  
March 24-28, 1996

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Form No. 836 R5  
ST 2629 10/91

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## High Temperature, Structural, Polymeric Foams From High Internal Phase Emulsion Polymerization

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### Introduction

In 1982, a high internal phase emulsion (HIPE) polymerization process to manufacture microcellular, polymeric foam systems was patented by Unilever<sup>1</sup>. 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<sup>2-8</sup>. All the published HIPE polymerized foams have concentrated on materials for low temperature applications.

Los Alamos National Laboratory started working with HIPE polymerized foams in the mid 1980's, and has since developed an extensive knowledge base on HIPE foam technology<sup>9-15</sup>. These efforts focused primarily on variations of a styrene/divinylbenzene (DVB) foam system that produces structural foams with glass transition temperatures ( $T_g$ ) 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 that copolymerizes styrene with maleimide based monomers. Development of high temperature HIPE polymer foam systems could provide significant advantages over existing high temperature foam systems because of their isotropic properties and near-net-shape casting capabilities. Potential applications for these high temperature foam systems include core materials for composite sandwich panels and acoustic/thermal insulation.

Copolymerization of styrene with maleic anhydride and N-substituted maleimides to produce heat resistant thermoplastics has been studied extensively<sup>16-18</sup>. 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 attempting the maleimide styrene copolymerization in a HIPE such as lower polymerization temperatures, maleimide solubility difficulties in both styrene and water, and difficulty 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 DVB isomers was 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.

### **Processing**

The foams were processed by first dissolving the ethylmaleimide and BMI-70 into the styrene/DVB monomers, and then SMO was added to the monomer mixture. In all the foams processed, a total oil weight of 7.5 g was prepared and placed in a 100 ml Qorpak jar. The oil phase was then mechanically stirred at approximately 600-800 rpm while 92.5 g of distilled water containing 1.5 g/L potassium persulfate was added dropwise. After all the water had been added, the emulsion was further stirred for 5 minutes at a speed of approximately 900 rpm and for 5 minutes at a speed of 1000 rpm. 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 hours depending on the morphology of the cells. The dried foams were then postcured at 250°C under vacuum overnight.

### Analysis

Dynamic mechanical analysis (DMA) was performed on a Rheometrics RDA II mechanical spectrometer and the T<sub>g</sub> 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. DMA results will be plotted in this paper for tan delta as a function of temperature.

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 (0.1 in/min).

### **Results and Discussion**

Ethylmaleimide modified foam samples crosslinked with either DVB or BMI-70 were processed and compared to a standard styrene/DVB foam system containing 90% styrene crosslinked with 10% DVB. In all systems 15% by weight SMO was used as the emulsifying agent. Specific sample compositions and identifications are presented in Table 1.

Table 1. Sample Identification and Compositions of Ethylmaleimide Modified Foams with Divinylbenzene Crosslinking Agent

Sample	% by Weight of Each Component			
	Styrene	DVB	BMI-70	Ethylmaleimide
Eth-1	90	10	0	0
Eth-2	80	10	0	10
Eth-3	70	10	0	20
Eth-4	60	10	0	30
Eth-5	50	10	0	40
Eth-6	40	10	0	50
EthBMI-1	70	0	20	10
EthBMI-2	60	0	20	20
EthBMI-3	55	0	20	25
EthBMI-4	50	0	20	30

### 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 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 the maleimide modified foam samples, some compositional processing limitations were determined. However, the majority of the compositions 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.

When BMI-70 was used to crosslink ethylmaleimide/styrene, samples EthBMI-1, EthBMI-2, and EthBMI-3 (Table 1) 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. Processing of the previous samples suggests that the addition of 50% by

weight of a maleimide based modifier appears to be an upper limit in producing a HIPE. Both samples EthBMI-4 and Eth-6 contained a combined concentration of 50% maleimide modifiers by weight and could not be emulsified. The disruptive effect of the ethylmaleimide on the emulsion formation may be due to the partial solubility of ethylmaleimide in water, approximately 5% by weight. Experiments with styrene insoluble or slightly soluble maleimide and BMI modifiers stressed the importance of using styrene soluble maleimide modifiers. However for high concentrations of maleimide modifiers to be used, the maleimide modifiers may also have to be water insoluble.

#### Dynamic Mechanical Analysis

All foam samples were DMA tested after postcure. When ethylmaleimide was incorporated into the standard styrene/DVB system, the beginning of each transition and the tan delta peak increased directly with increasing maleimide concentration, Figure 1. For every 10% increase in the ethylmaleimide concentration, a corresponding increase of 20°C is observed in the foam Tg. A maximum Tg of 204°C was obtained with an addition of 40% ethylmaleimide by weight.

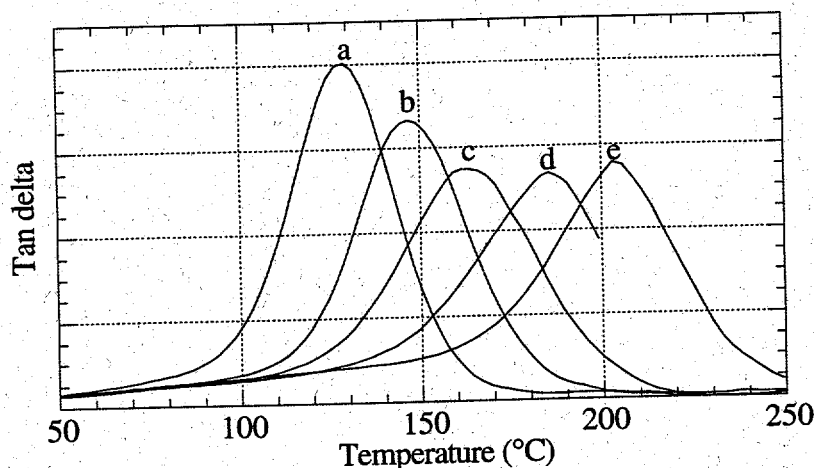


Figure 1. Tan Delta as a Function of Temperature of Ethylmaleimide Modified Foams Crosslinked with Divinylbenzene: (a)Eth-1, 129°C, (b)Eth-2, 144°C, (c)Eth-3, 164°C, (d)Eth-4, 184°C, (e)Eth-5, 204°C

The DMA results of the BMI-70 crosslinked systems show slightly different results, Figure 2. All three samples show very similar behavior with a peak in the tan delta curve at approximately 219°C. The increasing concentration in ethylmaleimide decreases the width of the transition; however, the peak in the tan delta curve is not affected to a major degree.

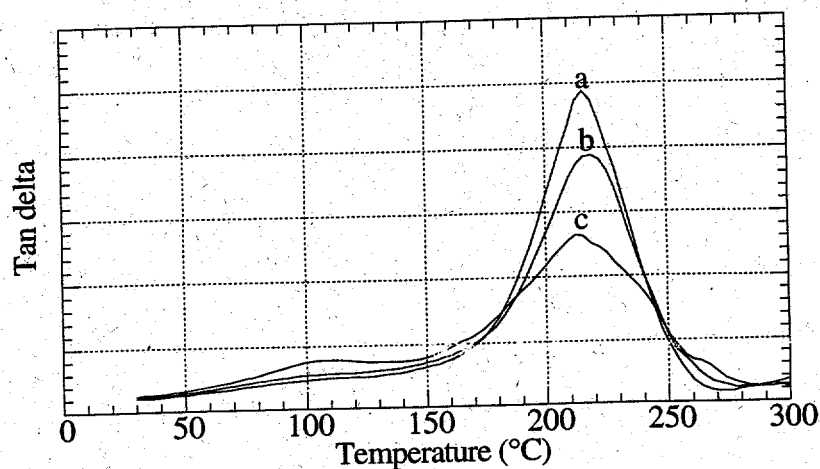


Figure 2. Tan Delta as a Function of Temperature for Ethylmaleimide Modified Foams Crosslinked with BMI-70: (a)EthBMI-1, (b)EthBMI-2, (c)EthBMI-3. All Three Peaks at Approximately 219°C.

In both sets of DMA data, one main transition region is observed indicating that the ethylmaleimide and BMI-70 are being incorporated uniformly into the polystyrene chains. Therefore, the ethylmaleimide and BMI-70 participated in the free radical polymerization reaction, and a copolymer of styrene with ethylmaleimide and BMI-70 is produced.

#### Mechanical Properties

Mechanical properties of the foam samples were evaluated as a compression strength and are presented in Table 2. Foam densities varied slightly due to variations in volume shrinkages during the postcure process. Sample Eth-1 to Eth-4 showed that 10-15% improvements in compression strength are possible with the addition of ethylmaleimide. Therefore, the addition of ethylmaleimide did not have any adverse effects to mechanical properties and may be able to improve the compression strengths. Samples

EthBMI-1 to EthBMI-3 tended to produce slightly lower compression strengths. Optimization of the SMO concentration as a function of the maleimide modifier concentration may improve the final foam mechanical properties by producing a more uniform open cell morphology.

Table 2. Density and Compression Strengths of Foam Samples

Sample	Density, mg/cm <sup>3</sup> (lb/ft <sup>3</sup> )	Compression Strength, kPa (psi)
Eth-1	73.4 (4.58)	721 (105)
Eth-2	76.6 (4.78)	819 (119)
Eth-3	77.9 (4.86)	847 (123)
Eth-4	80.4 (5.02)	718 (104)
Eth-5	a	a
Eth-6	a	a
EthBMI-1	71.9 (4.48)	513 (74.4)
EthBMI-2	72.7 (4.54)	652 (94.6)
EthBMI-3	78.7 (4.91)	773 (112)
EthBMI-4	a	a

<sup>a</sup>Sample did not survive postcure

### Conclusions

Our results have demonstrated that high temperature, structural, polymeric foams can be prepared by copolymerizing styrene with ethylmaleimide and BMI monomers using a HIPE polymerization process. The Ethylmaleimide and BMI-70 were free radically polymerized with styrene and were incorporated uniformly throughout the polymer. A concentration of 50% maleimide modifier by weight appears to be an upper limit in obtaining a HIPE. This process produced polymeric foams with Tg's ranging from 140 - 220°C and compression strengths of 700-850 kPa. Further work is continuing to optimize the emulsion composition effects on the process - structure - property interrelations of these foam systems.

### Acknowledgments

The authors would like to acknowledge the strong support of this work by Ainslie Young in the Department of Defense Program office at Los Alamos National Laboratory. This work was funded under contract W7405-ENG36 for the Department of Energy as part of the Laboratory Directed Research and Development program at Los Alamos National Laboratory.



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