

Study on foaming of PMI foam materials

HONG-YAN TANG*, QI-ZHEN CHEN, XIAO-BO RAO

Key laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China

PMI foam materials were prepared using two steps, bulk polymerization through free radical copolymerization and then foaming. Effects of foaming agents, nucleating agents and other additives on the microstructure of PMI foam materials were investigated. Nucleating agents could markedly eliminate air bubbles amalgamation. When the mass ratio of the nucleating and foaming agent was 1:3, foaming multiple was the highest. Addition of other additives could do help to foaming, which induced transparent closed-cellular PMI foam materials with uniform cell diameter and distribution. When foaming time was increased, the microstructure of PMI foam materials remained unchanged, the mechanical properties of PMI foam materials were increased because the content of the imide ring was increased.

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1. Introduction

PMI foam materials are the foam materials with closed cell, unique thermal conductivity, the highest specific strength and specific modulus in the world. PMI foam materials could be used in the field of thermal insulation, package, acoustic attenuation, absorbents, vibration damping and membranes for separation [1-4]. What's more, PMI foam materials have high distortion temperature (180~240°C). Therefore, PMI foam materials are the optimal core material of the sandwich structure with lightweight and high strength, which are already used in the fields of aerospace, high-speed ship, railway, wind power and others [5-7]. Recently there are a few papers on PMI foam materials [8-11], in which Acrylonitrile (AN), MAM / acrylamide (AM) were used as the main reactive monomers, morphology of the foam and mechanical properties were studied. It only mentioned that alcohols were used as foaming agents in the literature about PMI foam materials. No paper aimed at study on foaming. Foaming was the very important step. Foaming is meaningful to preparation of PMI foam materials. The final microstructure of the foam materials is almost totally depended on foaming.

In our research, supertoxic AN was abandoned, atoxic BMA and MAM instead were used as the main reactive monomers [12]. The copolymer was firstly prepared using bulk polymerization through free radical copolymerization, and then PMI foam materials were produced through foaming. Study on foaming of PMI foam materials was investigated in detail in the research. It is expected that it

would lay the foundation of application of PMI foam materials.

2. Experimental

2.1 Materials

Butyl methacrylate (BMA) was obtained from Chengdu Kelong chemicals Co., Ltd (Chengdu, China), with a concentration of 98%. Methacrylamide (MAM) was obtained from Tianjing Kermel chemicals Co., Ltd (Tianjing, China), with a concentration of 99%. Benzoperoxide (BPO) was obtained from Chengdu Kelong chemicals Co., Ltd (Chengdu, China), with a concentration of 99%. Methanamide was obtained from Huipu chemicals and instruments Co., Ltd (Hangzhou, China), with a concentration of 99%. Butyl alcohol, hexyl alcohol, amyl alcohol, urea were obtained from Tianjing Kermel chemicals Co., Ltd (Tianjing, China), with a concentration of 98%. Deionized water and other additives were prepared in the laboratory.

2.2 Preparation of PMI foam materials

PMI foam materials were prepared using bulk polymerization through free radical copolymerization. The whole process could be divided into two steps (shown in Fig. 1):

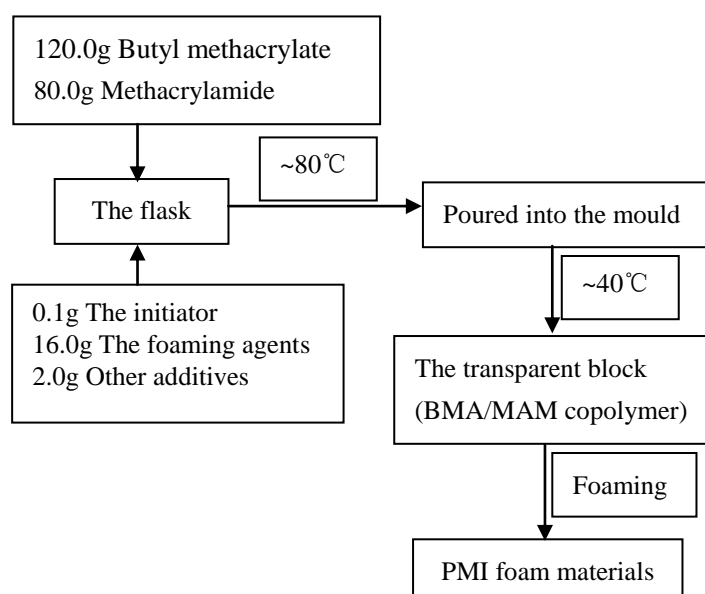


Fig. 1. The synthesis flow chart of PMI foam materials.

At the first step, BMA/MAM copolymer would be prepared. The monomer mixture was obtained by mixing BMA and MAM. A 250ml four-necked flask equipped with a condensation line and nitrogen pipe was evacuated and flushed with nitrogen. The monomer mixture, the foaming agent, the initiator and other additives were introduced into the flask. The reaction batch was flushed with nitrogen for ~1 h, and then stirred in a countercurrent stream of nitrogen under ~80°C. The copolymerization reaction was terminated after some time by cooling in an icy bath, which resulted in the viscous liquid. The viscous liquid was poured into the mould, which was immersed into water under ~40°C for several days. Then the transparent block (BMA/MAM copolymer) was produced.

At the second step, the transparent block would be foamed. The transparent block was placed in the oven and foamed under the following conditions: ~80°C (~2h) → ~180°C (~1h). In the end, PMI foam materials were produced.

2.3 Instrumentation and measurements

Measurement of the density was according to ASTM D1622-98. Measurement of compression strength was according to ASTM D1621-2000. Measurement of tensile strength was according to ASTM D638-1999.

The microstructure of PMI foam materials was characterized by a polarizing microscope (ECLIP SE E400 POL, NIKON).

3. Results and discussion

3.1 Effects of foaming agents on the microstructure of PMI foam materials

According as the foaming process of PMI foam materials, foaming agents need being dissolved in the monomer mixture, and would not separate out and foam during the process of polymerization. In this paper we chose butyl alcohol, hexyl alcohol and amyl alcohol as foaming agents, the microstructure was shown in Fig. 2-Fig. 4. It can be seen that PMI foam materials had closed cellular structure. Besides, no air bubble appeared during the process of polymerization. Foaming multiple of PMI foam materials was relatively low. The cellular diameters were different. Air bubbles easily amalgamated with one another, which resulted in big air bubbles. It showed that only foaming agent was used, gasification of foaming agents would easily gather together, which resulted in big air bubbles and even air bubbles burst.

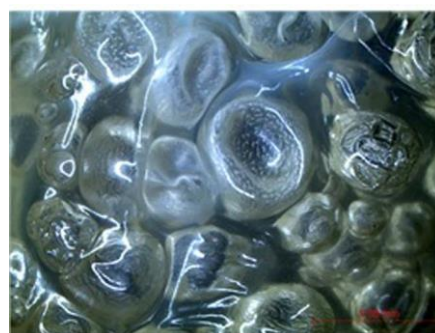


Fig. 2. The microstructure of PMI foam material (butyl alcohol as the foaming agent).



Fig. 3. The microstructure of PMI foam material (hexyl alcohol as the foaming agent).

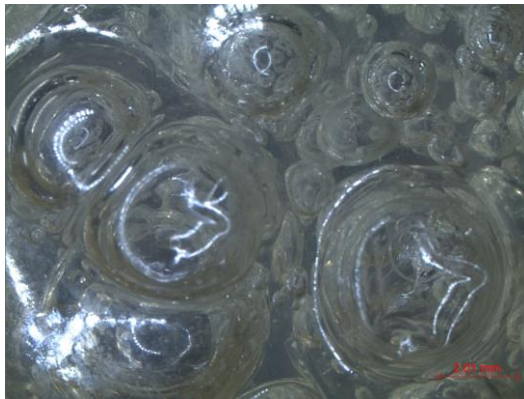


Fig. 4. The microstructure of PMI foam material (amyl alcohol as the foaming agent).

Urea and Methanamide do good to nucleation during the process of foaming [13-16]. Urea is solid at room temperature. The solubility of urea in the monomer mixture is limited. Methanamide is liquid at room temperature, which could dissolve in the monomer mixture and did not separate out. So the addition of methanamide could be freely increased, which induced PMI foam materials with low density. Methanamide was introduced as a nucleating agent in this paper.

In experimenting we found that the mass ratio of the nucleating agent and foaming agent markedly influenced the cellular structure of PMI foam materials, which were shown in Fig. 5-Fig. 7. Comparing with Fig. 2-Fig. 4, when the nucleating agent was introduced, foaming multiple of PMI foam materials was higher, the cellular diameters were relatively identical, air bubbles did not amalgamate with one another, no bigger air bubbles appeared. When the mass ratio was 1:3, foaming multiple was the highest. The cells were crowded together. The difference of the cellular diameters was relatively small.



Fig. 5. The microstructure of PMI foam material (the mass ratio was 1:3).



Fig. 6. The microstructure of PMI foam material (the mass ratio was 1:2).



Fig. 7. The microstructure of PMI foam material (the mass ratio was 1:1).

3.2 Effects of other additives on the microstructure of PMI foam materials

In order to prepare the foam materials with more small and uniform cellular structure, some stabilizer additives should be added to the monomer mixture. Fig. 8 is the microstructure of PMI foam material with siloxane. We could find out the function of the stabilizer additive was powerful. Though the dosage was low, the cellular diameters were smaller, the cellular diameters were almost the same. It was because that siloxane could reduce the surface tension and improve the solubility property of the

components of the raw materials, help to nucleate at the initial stage of foaming and increase the stability of the PMI foam materials [13,17].

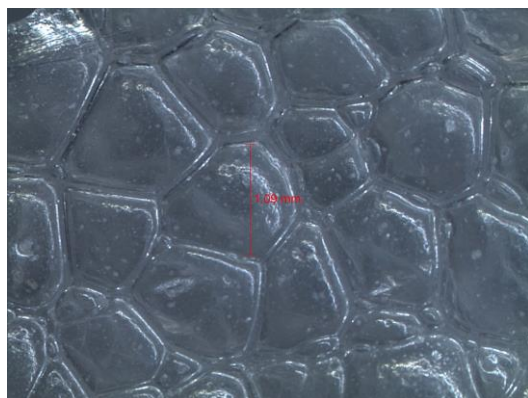


Fig. 8. The microstructure of PMI foam material with siloxane (0.1% weight ratio).

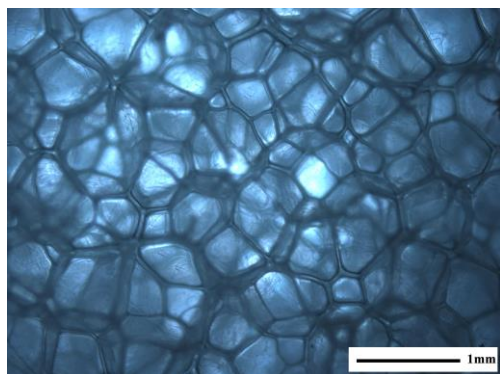


Fig. 9. The microstructure of PMI foam material with siloxane and the inorganic powder.

From Fig. 9 we could find out that PMI foam materials were highly transparent, the second layer, even the third layer could be seen. Foaming multiple of PMI foam materials was the highest. The cellular diameters were further reduced. The cell is composed of polyhedrons, which are constructed by many planar cell walls. The side number of cell wall is between three and seven. Three cell walls intersected as cell aris. The cell wall was smooth and not ruptured, and the cellular diameters were approximately the same, which showed foaming wasn't stunted, air bubbles didn't burst and/or amalgamate with one another to big air bubbles. The closed-cell ratio of was high, which would have many favorable properties and many applications [18,19]. It showed that the inorganic powder could do help to foaming, which induced uniform cell diameters and distribution. The inorganic powder could not dissolve in the monomer mixture. Air bubble would firstly nucleate on the interface between the solid inorganic powder and the liquid monomer mixture, which was called as heterogeneous nucleation. There are some theories on heterogeneous nucleation [14,20].

3.3 Effects of foaming process on the microstructure of PMI foam materials

When foaming time was about 15min, PMI foam materials were fully foamed, which had uniform cell diameters and distribution (shown in Fig. 9). If foaming continued, the microstructure of foam materials remained unchanged. However, the mechanical properties of PMI foam materials were greatly increased, which was shown in Table 1. It was because that the content of the imide ring was increased when the foam time was increased, which showed in Formula (2) of Fig. 10 [12]. The rigid imide ring could remarkably increase the mechanical properties of PMI foam materials. If foaming still continued, the microstructure of foam materials still remained unchanged. However, foaming would do harm to PMI foam materials, which would induce thermal degradation.

Table 1. Effect of foaming time on the mechanical properties of PMI foam materials.

Foaming time	Compression strength /MPa	Tensile strength /MPa
15min	3.53	3.36
30min	3.85	3.71
1h	3.85	3.71

*The density of PMI foam material is $115\text{kg}\cdot\text{m}^{-3}$

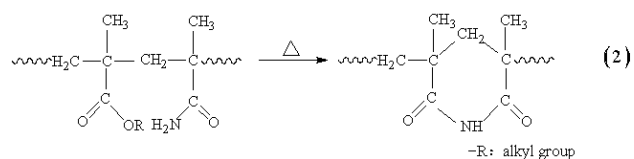
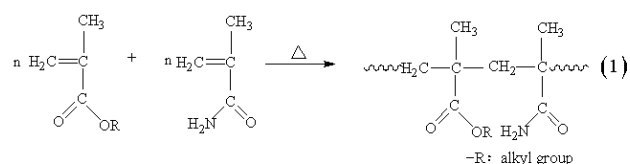


Fig. 10. Polymerization reactions of preparing PMI foam materials.

4. Conclusion

BMA/MAM copolymer was firstly prepared using bulk polymerization through free radical copolymerization, and then PMI foam materials were produced through foaming. Only foaming agents were used, air bubbles easily amalgamated and burst. Nucleating agents could markedly eliminate air bubbles amalgamation. When the mass ratio of the nucleating and foaming agent was 1:3, foaming multiple was the highest. Other additives could do help to foaming, which induces transparent closed-cell

PMI foam materials with uniform cell diameter and distribution. When foaming time was increased, the microstructure of PMI foam materials remained unchanged, the mechanical properties of PMI foam materials were increased because the content of the imide ring was increased.

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*Corresponding author: hytang2004@163.com