

Application of Photo Initiation Copolymerization During the Preparation of Polymethacrylimide Copolymer Foam

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ABSTRACT: Using methacrylic acid (MAA), acrylonitrile (AN), and acryl amide (AM) as monomers, a new high-performance PMI copolymer foam was prepared via radical bulk copolymerization and free heat foaming; afterward, the effects of photo initiation polymerization technology on the foam mechanical and craft performances were further researched. The results showed that photo initiation technology was only fit to be used as the prepolymerization reaction during the preparation of PMI copolymer foam, and it was faster and more easily controlled than thermal

initiation prepolymerization. Photo initiation prepolymerization could eliminate not only the foam inner flaws, but also the size nonuniformity of the foam cells effectively. Accordingly, photo initiation prepolymerization is able to make the foam uniform, transparent, stable, and isotropy, and moreover improve the foam tensile strength. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3041–3047, 2009

Key words: photo initiation polymerization; high performance polymers; foams

INTRODUCTION

When the densities are identical, PMI copolymer foams possess the highest strength and rigidity among all existing structural foams in the world. At the same time, they have excellent heat resistance and creep resistance too. The successful development of PMI copolymer foams by Degussa Co., Ltd. (Germany) in 1972 resulted in many product series with different properties and purposes in American, Japan, and European countries and regions.^{1–11} So they are extensively used as the high-performance sandwich composites in the high-technology realm, such as aviation and space flight.

Using a different recipe (acrylonitrile and acrylamide were used as the second as well as third monomers) and craft (photo-initiation pre-copolymerization) from those of Degussa Co., Ltd. (Germany), the author prepared such a new high-performance PMI copolymer foam that its properties had achieved and surpassed the ones of Degussa Co.Ltd Germany products partly.^{12–25} After the new PMI copolymer foam was developed successfully,

some conclusions were reached: (1) the expandable copolymer preparation was the most important craft procedure, and (2) as the main load-supporting part, the expandable copolymer properties, for example whether the copolymer was uniform, transparent, stable, and isotropy or not, would affect the corresponding copolymer foam product properties directly. However in the industry field, the expandable copolymer preparation is usually based on radical bulk copolymerization, whose drawbacks are that the polymerization system is so ropy that the polymerization heat is difficult to be released from the system because of the absence of solvent or dispersion medium (water), then the reaction temperature is also difficult to be control, and the volume shrinkage is huge, and the reaction extent is not uniform in all reaction system, accordingly, (3) the copolymer usually presented a lot of undesired phenomena such as air bubble, crack, wrinkle, and implosion.

On the basis of these above considerations, it is imaginable that all these copolymer flaws will introduce a lot of the negative influences into the corresponding foam products.^{24–26} So the main objective of this article is to resolve the questions of the heat release and volume shrinkage via photo initiation prepolymerization partly, and further improve the PMI copolymer foam mechanical properties and preparation craft operability.

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EXPERIMENTAL

Instruments and equipments

A water bath (TC-102, Shanghai Cany Precision Instrument Co., Ltd, Shanghai, China) was used to control any sudden heat production and keep the reactor temperature at set-point value. An ultraviolet instrument (NWPU/PHILIP-400, Northwestern Polytechnical University, Xi'an, China) was used to initiate polymerization reaction. A bake Oven (101A-2, Medical Appliance Plant of Peking, Peking, China) was used to make the copolymer boards foam freely and carry out the heat treatment for the copolymer boards or foams.

An electron all-purpose test-bed (CMT 6303 and CMT 7204, Shenzhen Sans Testing Machine Co., Ltd., Shenzhen, China) was used to test the copolymer boards or foams mechanical properties. An optical microscope (ECLIP SE E400 POL, Nikon, Japan) was used to observe the foam cell aperture distribution characteristics.

Materials

MAA (technical grade), AN (technical grade), and AM (technical grade) were all used as copolymerization monomers. Azobisisobutyronitrile (AIBN; technical grade) was used as either the photo initiator-sensitive or the thermal-sensitive initiator. 1-Amyl alcohol (technical grade) was used as the foaming agent.

Preparation of the expandable copolymer board via entire thermal initiation polymerization

The expandable copolymer boards were prepared via entire thermal initiation radical bulk copolymerization and cast-molding. After all supplied materials were blended according to the mixture ratio given in Table I, the uniform and transparent compound was poured into a vitreous mold; afterward, the mold was sunk in the water bath at 50°C for 48 h.

Preparation of the expandable copolymer board via thermal initiation pre-polymerization

After all supplied materials were blended according to the mixture ratio given in Table I, the compound carried out thermal initiation prepolymerization in a biggish container, which was easy to release polymerization heat, in the water bath at 60°C for 6 h; afterward, prepolymer, which had possessed a certain degree of viscosity, was poured into a vitreous mold, then the mold was cooled to room-temperature and ready to be used; at last, the mold was sunk in the water bath at 50°C for 40 h.

TABLE I
Expandable Copolymer Preparation Recipe

Material	Role	Recipe (mass shares)
AN	Monomer 1	60
MAA	Monomer 2	40
AM	Monomer 3	2
AIBN	Initiator	1
1-Amyl alcohol	Foaming agent	4

Preparation of the expandable copolymer board via photo initiation prepolymerization

After all supplied materials were blended according to the mixture ratio given in Table I, the compound carried out photo initiation prepolymerization in a biggish and transparent container, which was easy to release polymerization heat, in the ultraviolet instrument for 5 min; Afterward, prepolymer, which had possessed a certain degree of viscosity, was poured into a vitreous mold, then the mold was cooled to room-temperature and ready to be used; at last, the mold was sunk in the water bath at 50°C for 40 h.

Preparation of PMI copolymer foam

The prepared expandable copolymer board was foamed freely and turned into isotropy foam at 180°C for 30 min, and heat treated at 160°C for 6 h in the bake oven; afterward, the foam board was cooled and shaped at room-temperature.

Preparation of foam tensile property test specimens

The strip (160 mm × 20 mm) cut from the foam board was made into the dumbbell specimen with the all-purpose making specimen machine (ZYJ1000, Shenzhen Sans Testing Machine Co., Ltd., Shenzhen, China). The size of the specimen gauge length segment was 50 mm × 10 mm (The reinforce slip was stuck on the foam segment clip).

Mechanical property test means

Tensile properties of PMI copolymer foam were tested according to ASTM D 638 M. The load speed was set at 5 mm/min. The deformation of the specimen gauge length segment was measured with an elongation instrument.

RESULTS AND DISCUSSION

Photo initiation prepolymerization necessity

Here we discuss the necessity of photo-initiation prepolymerization first.

As a rule, the prepolymerization is used to resolve the bulk polymerization questions such as heat

release and volume shrinkage partly in order to make the polymer more uniform and stable in industry field.^{25–27} From the craft perspective, either thermal or photo initiation prepolymerization is able to be used; however, photo initiation prepolymerization possesses more superiority than thermal initiation during PMI copolymer foam preparation, from the thermodynamics perspective.

The experiment results showed that the copolymerization process of MAA, AN, and AM belongs to the heteropolymerization reaction. The formed polymers were separated from the monomers mixture continuously because they could not be dissolved by the monomers very well, and then two-phase system formed in the reaction system. It is a truth that there are different refractive indexes between two phases; the ray will cause refraction and reflection at the interface between two phases, and cannot penetrate completely, and so the reaction system gradually turned into opaque from transparent. When the polymerization finished, all reaction system turned into a single-phase system on the whole, and turned into the solid state from the liquid state, and so the reaction system turned into transparent from opaque again. If there are any opaque parts in the final copolymer board here, it can be revealed that the polymerization extents of all reaction system are not uniform. These polymerization extent differences will lead the difference of intermolecular forces among the different parts in the all system. Accordingly, when the copolymer board is foamed, the foaming extents of the different parts are also different, and when the undesired stress will be introduced into the corresponding foam product, even stress cracking will occur.

As a rule, if all reaction system is expected to reach a consistent polymerization extent, the thermodynamics condition must be met that the change of reaction system free energy is ought to be less than zero,²⁸ that is $\Delta G = \Delta H - T\Delta S < 0$, where ΔG is the system free energy change. ΔH is the copolymerization heat effect, and the experiment results revealed that the ternary copolymerization reaction of MAA, AN, and AM was an exothermic reaction, so the ΔH is less than zero. ΔS is the system entropy change. It is a truth that the molecules mobility sharp declined when the copolymerization system changed from liquid state to solid state, at the same time the monomer

micromolecules mobility sharp declined after they were linked to a macromolecule chain, and then the entire system confusion extent declined consequently, so ΔS is less than zero. Accordingly, if the condition is expected to be met that ΔG is less than zero, the other condition ($|\Delta H| > T|\Delta S|$) must be met too. But it can be concluded that the above condition is very difficult to be met when the system entropy change is rather large, and the reaction temperature is rather high, and heat release quantity is rather low, such as the prepolymerization stage.

The prepolymerization reaction uses it as the limit that the polymerization system does not appear automatic speedup generally. Here, if thermal initiation is used for the prepolymerization, the condition ($|\Delta H| > T|\Delta S|$) is difficult to be met because the heat release quantity of the polymerization is rather low, while the reaction temperature is rather high. Accordingly, it will be very easy for the system to introduce the polymerization extent difference as soon as the polymerization begins, and the positive role of prepolymerization will be weakened sharply. Whereas photo initiation prepolymerization can be used at a low temperature, so the T decline is very important for the above thermodynamics condition to be met.

Photo initiation effects on pre-polymerization time and process control

The prepolymerization reaction uses it as the limit that the polymerization system does not appear the automatic speedup phenomenon generally, because the viscosity of polymerization system is not so high that heat can be released easily here.

Here the prepolymerization extent was limited to 20% (the extent can be easily determined via the intensity change of C=C double bond FTIR characteristic absorption peak), or else the automatic speedup phenomenon would occur.

Photo initiation effects on the prepolymerization time and process control were researched, and the results are given in Table II. Table II clearly shows that photo initiation craft made the prepolymerization time reduce and the prepolymerization extent easy to be controlled.

Then since thermal initiation is also able to be used as the prepolymerization craft, why was it

TABLE II
Effects Contrast Between Photo Initiation and Thermal Initiation Pre-polymerization

Prepolymerization mode	Prepolymerization time	Prepolymerization extent control operability
Thermal initiation	6 h	Difficult, the reaction did not stopped until it exceeded the desired viscosity much
Photo initiation	5 min	easy, the reaction stopped rapidly as soon as the desired viscosity arrived

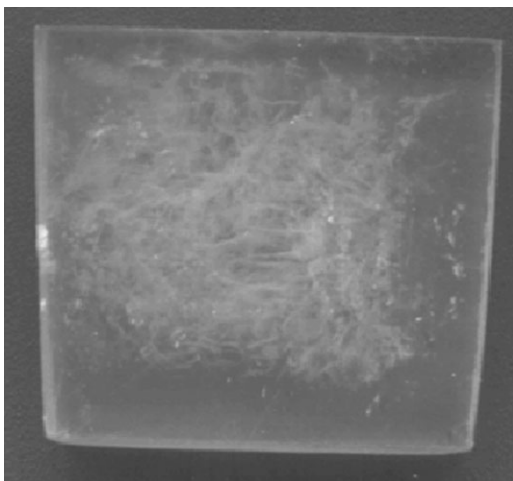


Figure 1 Copolymer board without prepolymerization.

difficult to control the prepolymerization extent? The reasons are that first, thermal initiation prepolymerization is a heat accumulation process for a long time, for example the process would last for 6 h at 50°C when AIBN was used as the heat-sensitive initiator, and in such a long time, the heat conducts from the outside into the system inner continuously; at the same time, the polymerization also generates the reaction heat continuously, and so the accumulation heat energy is so high that it is very difficult to be released even if the prepolymerization has finished. The accumulation heat energy could motivate AIBN to decompose and release more new initial radicals continuously, and then promote the polymerization to carry on unceasingly. Therefore, it is imaginable that the control on the prepolymerization extent is very difficult. Second, photo initiation possesses many advantages, for example the radicals are able to appear or disappear quickly in a short time (less than 1 s); and the total activation energy of the prepolymerization reaction is so low that the prepolymerization can carry on at a rather low temperature. Accordingly, it is very easy to control the radical appearance or disappearance by applying the ultraviolet light or not, and the operability of the controlling photo initiation prepolymerization extent is excellent.

Through the above analysis, it can be concluded that the prepolymerization is the necessary craft procedure during PMI copolymer foam preparation; furthermore, photo initiation possesses more advantages than thermal initiation.

Photo initiation prepolymerization effects on the uniformity of the expandable copolymer and corresponding foam

Because of the flaws such as the reaction extent and volume shrinkage nonuniformity, radical bulk poly-

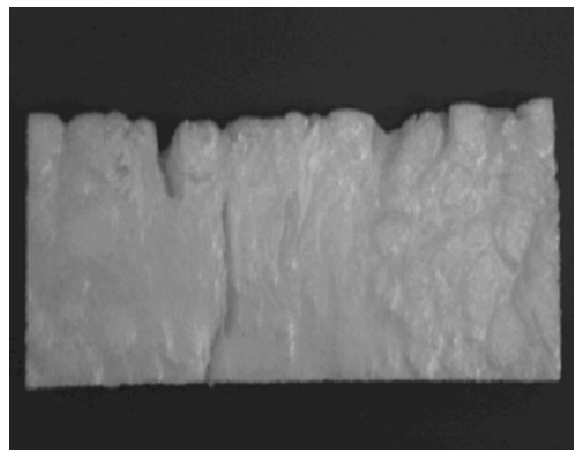


Figure 2 Copolymer foam without prepolymerization.

merization made it easy that a lot of stress concentration parts, whose concrete manifestations were the crazing, microcrack, and nepheloid zone, appeared in the expandable copolymer. And then the expandable copolymer nonuniformity made the corresponding foam presented nonuniform and instable; consequentially, even the stress cracking phenomenon would occur. These undesired phenomena can be observed in Figures 1 and 2.

On the contrary, the expandable copolymer and corresponding foam all presented the uniform and stable characteristic after the photo initiation was used as the prepolymerization craft. The corresponding phenomena are given in Figures 3 and 4.

Photo initiation prepolymerization effect on the foam cell aperture

The experiment results show that the copolymerization of MAA, AN, and AM belongs to the heteropolymerization reaction. The formed polymer

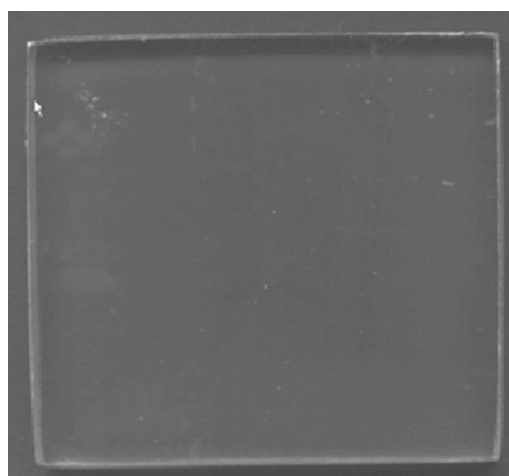


Figure 3 Copolymer board with photo initiation prepolymerization.

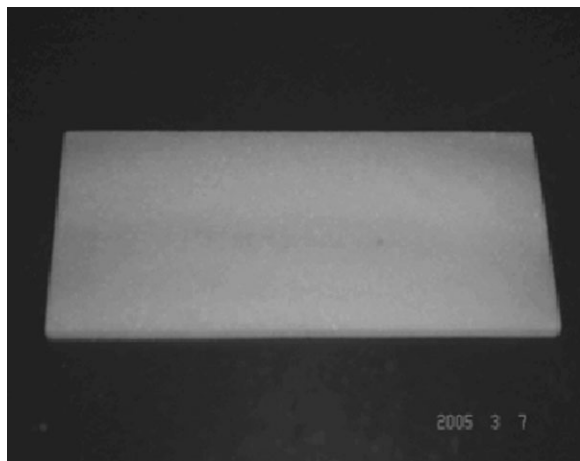


Figure 4 Copolymer foam with photo initiation prepolymerization.

separated from the monomer mixture in the course of copolymerization continuously. Because the system viscosity was rather low for a long time, the copolymer formed in advance would show the sedimentation phenomenon under the gravity function.

In the rather long course of polymerization, this sedimentation phenomenon caused the extent differences of the molecule chain accumulation, arrangement, tangle, and so the polymer density is nonuniform in all polymerization system from the top to the bottom (the top density was less than that of the bottom). As the basal body of the cell wall, the different densities of the copolymer made the intermolecular forces and the expansion resistance forces, which must be overcome by the gas in the cell during foaming, so equivalent that there was an obvious graded distribution phenomenon of the cell aperture in the final foam board height direction.²⁹⁻³⁰ The corresponding phenomenon is given in Figure 5. This undesirable phenomenon cannot meet the high-performance structural foam materials demand for the structure isotropy, obviously.

Figure 5 shows that the cell aperture of the foam without photo initiation prepolymerization presented the obvious graded distribution phenomenon (the density of the top was less than that of the bottom). Whereas photo initiation prepolymerization made the polymerization system reach the desirable viscosity in such a short time that it could make the separated polymer overcome the gravity effect, and not show the sedimentation phenomenon. Conversely, the all polymerization system nearly reached the same polymerization extent after a rather short time because of the ultraviolet light uniformity, and the copolymer and corresponding foam uniform as well as stable would be guaranteed. The corresponding phenomena are given in Figures 6 and 7.

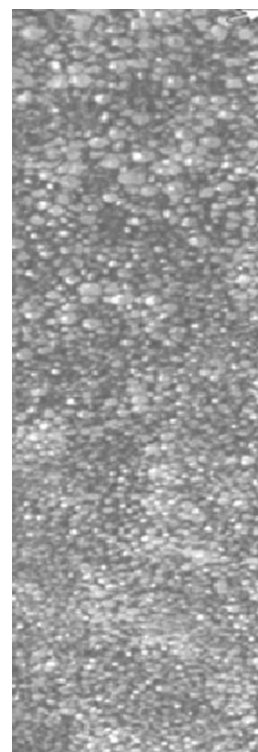


Figure 5 Cell aperture distribution of copolymer foam prepared without photo initiation prepolymerization.

Figure 7 shows that the foam with photo initiation pre-polymerization presented rather the uniform cell aperture than the graded distribution phenomenon.

Photo initiation prepolymerization effect on the foam tensile strength

The tensile strength of the different density PMI copolymer foams were researched, and the tensile strength of the foam with photo initiation prepolymerization was contrasted with that of the foam

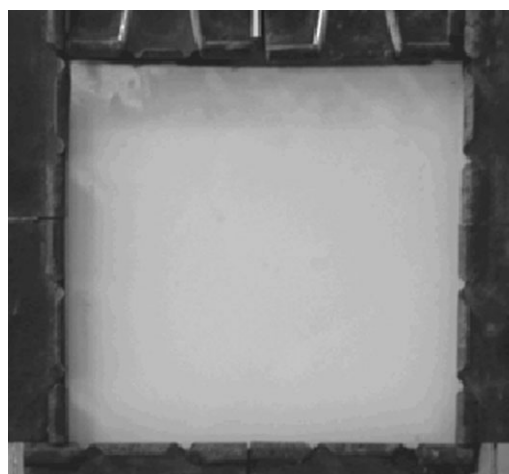


Figure 6 Polymerization system state after photo initiation prepolymerization.

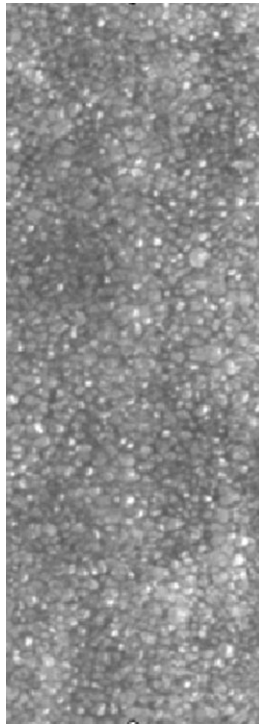


Figure 7 Cell aperture distribution of copolymer foam prepared with photo initiation prepolymerization.

without photo initiation prepolymerization. The results are given in Table III. At the same time, the tensile strength experiment data standard deviation and dispersion coefficient of the foams with and without photo initiation prepolymerization were analyzed too. It is demonstrated that the results were consistent when the foam densities were not identical (32 kg/m^3 , 52 kg/m^3 , 64 kg/m^3 , and 75 kg/m^3) via a large amount of experiments. The foams of 52 kg/m^3 are selected as an example, and their experiment data are given in Table IV.

Tables III and IV show that (1) the tensile strength increased with the density rise of the PMI copolymer foam whether with photo initiation prepolymerization or not. The reason is that as the main load-supporting body, the copolymer content increased with the density rise of the foam, hence the tensile strength is ought to increase gradually with the rise of the foam density. (2) After photo initiation prepolymeri-

TABLE III
Tensile Strength Contrast Between PMI Polymer Foams with and without Photo Initiation Prepolymerization

Density/ kg m^{-3}	Tensile strength/MPa	
	With photo initiation	Without photo initiation
32	1.00	0.99
43	1.55	1.38
52	1.85	1.80
75	2.30	2.19

TABLE IV
Tensile Strength Experimental Data Contrast Between PMI Polymer Foams with and without Photo Initiation Prepolymerization

Specimen serial number	Tensile strength/MPa	
	With photo initiation	Without initiation
1	1.89	1.72
2	1.85	1.82
3	1.83	1.92
4	1.82	1.76
5	1.86	1.73
Tensile strength mean value/MPa	1.85	1.79
Data standard deviation (S)	0.0274	0.0825
Data dispersion coefficient (CV)/%	1.48	4.61

zation, the tensile strength of PMI copolymer foam increased slightly. The main reason is that prepolymerization resolved such questions as the system heat release and volume shrinkage partly, and made the polymer more uniform and stable. As a rule, the tensile strength is sensitive to the internal defects, so the tensile strength of the corresponding foam will increase with the decrease of the internal flaws. (3) The data dispersion coefficient of the foam tensile specimens with photo initiation prepolymerization was less than that of the specimens without photo initiation prepolymerization, and it was further proved that photo initiation prepolymerization made the expandable copolymer more uniform and stable.

Photo initiation prepolymerization extent effect on the copolymer apparent quality

Since photo initiation polymerization possesses many advantages, for example the reaction speed is very fast, and can carry out at a rather low temperature, can we apply it to the entire copolymerization process? This doubt was researched and the result is given in Figure 8.

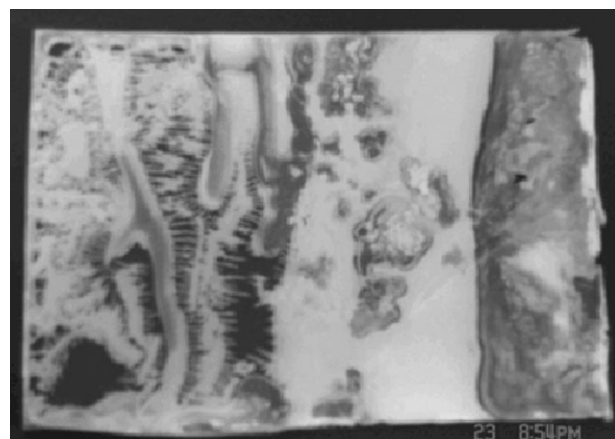


Figure 8 Copolymer board prepared via entire photo initiation polymerization.

Figure 8 shows an expandable copolymer board prepared via an entire photo initiation copolymerization, and reveals that either internal or apparent quality of the copolymer board was bad, and the different size flaws, for example the pore space, micro-crack, and even opaque part, filled the inner of the copolymer board. The main reason is that the ultraviolet ray irradiated into the polymerization system in the course of photo initiation polymerization, then the monomer mixture was initiated and started the polymerization reaction from the outside, and so the polymerization volume shrinkage started from the outside too, and so many of the inner monomer mixture were pulled toward the outside continuously and hence the pore space appeared inside the copolymer board. As the flaws, these pore spaces played the role of the stress concentration points during foaming, so as to some obvious stress crack phenomena appeared in the foam prepared. On the other hand, the copolymerization of MAA, AN, and AM belonged to the heteropolymerization reaction, and so the ultraviolet ray cannot irradiate into the system inner and initiate the new polymerization reaction when the all system turned into the opaque state by and large, and then a lot of incomplete reaction zones would appeared.

On the basis of above analysis, photo initiation polymerization is only fit to be used as the prepolymerization craft.

CONCLUSION

- (1) Photo initiation polymerization is only fit to be used as the prepolymerization craft during the PMI copolymer foam preparation.
- (2) In contrast with the thermal initiation prepolymerization, photo initiation prepolymerization possesses a lot of advantages, for instance the polymerization reaction speed is rapid, and the polymerization extent is easy to be controlled, and the polymerization can carry out at a rather low temperature.
- (3) Photo initiation prepolymerization can eliminate the inner flaws of the copolymer board so effectively that it can make the expandable copolymer more uniform and stable.
- (4) Photo initiation prepolymerization made the PMI copolymer foam tensile strength increased slightly.
- (5) Photo initiation prepolymerization can eliminate the graded distribution phenomenon of the PMI copolymer foam cell aperture so effectively that it can guarantee the foam uniform, stable, and isotropy.

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