

In Situ Cyclization Reactions During the Preparation of High-Performance Methacrylic Acid/Acrylonitrile/Acrylamide Ternary Copolymer Foam

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ABSTRACT: A new high-performance methacrylic acid/acrylonitrile/acrylamide ternary copolymer foam was prepared by radical bulk copolymerization, and the reaction mechanism of *in situ* cyclization taking place during copolymer foaming as well as the heat treatment was examined too. Then, the crucial mechanism was validated via optical microscopy, infrared absorption spectroscopy (Fourier transform infrared), differential thermal analysis (differential scanning calorimetry), and thermogravimetric analysis. The results showed a weak exothermic peak at 149.17°C and a strong endothermic peak at 270.85°C in differential scanning calorimetry curves of the methacrylic acid/acrylonitrile/acrylamide copolymer after the foaming and heat treatment at 160°C for 2 h and at 200°C for 2 h. The peak temperature of the differential thermogravimetry curve was 175.87°C, whereas the weight-loss rate was less at 276.58°C

in the thermogravimetry curves. In the case of the Fourier transform infrared curves, the —OH absorption peak at 930–970 and 1480 cm^{-1} weakened, and the C—N absorption peak of the imide increased. The $>\text{C}=\text{O}$ absorption peak at 1700 cm^{-1} occurred as an excursion phenomenon toward the low-frequency field; at the same time, the second absorption peak increased. Furthermore, the —C≡N absorption peak at 2240 cm^{-1} weakened, and a new —C=N— absorption band appeared. All these data revealed that *in situ* cyclizations had taken place in the copolymer molecule chains, so some rigid ring structures appeared in the copolymer molecule chains, such as six-membered imide rings and ladder polymer structures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1462–1469, 2007

Key words: foams; high performance polymers

INTRODUCTION

Polymethacrylimide (PMI) foam plastic is a high-performance polymer foam whose matrix resin is a methacrylic acid (MAA)/methacrylonitrile (MAN) copolymer. When the densities are identical, PMI polymer foams possess the highest strength and rigidity of all existing polymer foams in the world; at the same time, they have excellent heat resistance and creep resistance too. The successful development of PMI polymer foams by Degussa Co., Ltd. (Germany), in 1972 resulted in many product series with different properties and purposes in America, Japan, and European countries and regions.^{1–3} They are extensively used as high-performance sandwich structure composites in the high-technology realm, such as aviation and space flight.

After analyzing PMI polymer foams from Degussa, we reached some conclusions: (1) as one of the main components of PMI polymer foam synthesis, MAN is

manufactured only in small amounts by Asahikasei Corp. (Japan) every year, so it is very expensive and difficult to obtain, and (2) the primary reason that PMI polymer foams have excellent properties lies in the fact that some cyclization reactions take place between adjacent MAA and MAN monomeric units and then some rigid six-membered imide ring structures form in the matrix resin molecular chains.⁴ Accordingly, a new design has been carefully engineered to replace MAN with acrylonitrile (AN), which has a very low cost and can be easily purchased in the market, and make AN copolymerize with MAA. At the same time, acrylamide (AM) has been introduced as the third copolymerization monomer to obtain more rigid ring structures. Through the design, we have obtained a new style of MAA/AN/AM expandable copolymer and have prepared an MAA/AN/AM copolymer foam, whose merits are low density, high strength, rigidity, and heat resistance.

On the basis of these considerations, the main objective of this article is to introduce and validate the crucial mechanism of the *in situ* cyclization reaction taking place during polymer foam preparation via MAA/AN/AM copolymer structure analysis and characterization.

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EXPERIMENTAL

Instruments and equipment

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 the set-point value. 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 mechanical properties of the copolymer boards or foams.

A Fourier transform infrared (FTIR) spectrograph (NP-1, Shenyang Science Apparatus Plant, Shenyang, China) was used to analyze the molecular chain structure of the foams. A differential scanning calorimeter (DSC2910, TA Instrument, New Castle, DE) and a thermogravimetric analyzer (TGA Q50, TA Instrument) were used to observe the variations of the copolymer heat flow and mass with increases in the temperature, respectively.

Materials

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

Preparation of the MAA/AN/AM expandable copolymer

The MAA/AN/AM expandable copolymer was prepared by radical bulk copolymerization and cast-molding.

After all supplied materials were blended according to the mixture ratio given in Table I, the homogeneous and transparent compound was poured into a vitreous mold; afterward, the mold was sunk in the water bath at 40–60°C for 48–72 h.

Preparation of the MAA/AN/AM copolymer foam

The prepared expandable copolymer board was foamed freely and turned into an isotropic foam at

180°C for 30 min in the bake oven. At last, the foam board was cooled and shaped at room temperature.

Heat treatment of the MAA/AN/AM copolymer foam

The foam was heat-treated at 160°C for 6 h in the bake oven.

Characterization of the copolymer and foam structure

Differential scanning calorimetry (DSC)

Five-milligram specimens were cut from the copolymer or foam and then analyzed with the DSC method. The temperature rising range of DSC was 0–280°C, with 10°C/min as the temperature rising rate.

Thermogravimetric analysis (TGA)

Ten-milligram specimens were cut from the copolymer or foam and then analyzed with the TGA method. The temperature rising range of DSC was room temperature to 280°C, with 10°C/min as the temperature rising rate. The intermediate value was used as the criterion.

Infrared spectroscopy analysis (FTIR)

First, 0.1 mg of the powder from the copolymer or foam was filed for specimens. Second, these powders were blended with 0.4 mg of KBr sufficiently, and the compound was ground uniformly in an agate mortar and then pressed into thin pieces with a sampling machine. At last, they were analyzed with the FTIR method.

MAA/AN/AM copolymer foam property test

Preparation of the mechanical property test specimens

For the preparation of foam tensile specimens, a strip (160 mm × 20 mm) cut from the copolymer board was made into a dumbbell specimen with an all-purpose specimen machine (Shenzhen, China). The size of the specimen gauge length segment was 50 mm × 10 mm (the reinforced slip was stuck on the foam segment clip).

For the preparation of the foam compressive specimens, a block cut from the copolymer foam with a mechanical cutter was made into a specific size (50 mm × 50 mm × 25 mm).

For the preparation of the foam shear specimens, a foam board (120 mm × 50 mm × 10 mm) cut from the copolymer foam with a mechanical cutter was stuck on shear property testing clamps with E-51 epoxy resin and cured at 60°C for 2 h.

TABLE I
Main Materials and Recipe

Material	Role	Recipe (mass share)
MAA	Monomer 1	60
AN	Monomer 2	40
AM	Monomer 3	2
AIBN	Initiator	1–2
1-Amyl alcohol	Foaming agent	2–8

Density test

The density of the copolymer foam was tested according to ASTM D 1622-98. The dimensions of the specimen were measured with a Vernier caliper or steel rule, whose precision was ± 0.1 mm. The specimen mass was weighed with an analytical balance, whose precision was ± 0.001 g. The density of the copolymer foam was calculated according to the following equation, and the precision was 1 kg/m^3 . Three specimens were tested at least, and the mean value was used as the density criterion:

$$\rho = \frac{m}{a \times b \times d} \times 10^6$$

where ρ is the density of the copolymer foam (kg/m^3), m is the specimen mass (g), a is the specimen length (mm), b is the specimen breadth (mm), and d is the specimen thickness (mm).

Mechanical property test means

The tensile properties of the copolymer foam were tested according to ASTM D 638 M. The load speed for testing the tensile strength was set at 5 mm/min , and the load speed for testing the tensile modulus was set at 2 mm/min . The deformation of the specimen gauge length segment was measured with an elongation instrument.

The compressive properties of the copolymer foam were tested according to ASTM D 1621. A load was applied to the specimen in such a manner that it was distributed as uniformly as possible over the entire loading surface of the specimen. The rate of the crosshead movement was 2.5 mm/min . The maximum value of the compressive strength before 10% compressive deformation was recorded.

The shear properties of the copolymer foam were tested according to ASTM C 273. A load was applied to ends of rigid plates in tension through a spherical bearing block to distribute the load uniformly across the width of the specimen. Tensile shear plates could be attached with bolts or pins to the load fixture. The load speed was set at 0.5 mm/min . The desired failure mode was 100% shear failure of the core, so specimens that exhibited adhesion failure between the core and plate were rejected. The thickness of the adhesive bond to the core (adhesive-filled depth in the core cells) could affect the core shear strength and modulus values, depending on the core thickness. The relative displacement between the steel plates was measured via transducers, compressometers, or extensometers. The displacement apparatus could be on the specimen side or in the back, and it was close to the center as possible.

RESULTS AND DISCUSSION

Mechanism

Here we introduce a new *in situ* cyclization mechanism for motion cyclization first.

As a rule, enhancing the molecular chain rigidity is an approach that can enhance the mechanical properties and heat resistance of a copolymer or a corresponding polymer foam, and this approach can be achieved through the introduction of some rigid ring structures into the same molecular chain or among different molecular chains.⁵ However, frequent collisions among functional groups are a necessary precondition to form ring structures,⁶ so the molecular chains must possess enough mobility that numerous distant functional groups in the same molecular chain or among different molecular chains can react and form ring structures with one another, such as a copolymer in a state of plastic flow or liquor. In the aforementioned instance, this kind of cyclization reaction will take place via the approach and collision of functional groups along with molecular chain motion, and it may be called motion cyclization. Accordingly, the collision probability among functional groups in the entire reaction system and the number of ring structures (all fairly numerous) can be imagined.

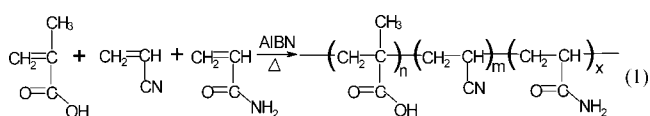
On the other hand, to obtain compact, well-proportioned, and high closed-cell ratio bubble structures during the copolymer foam preparation, rigid ring structures are not fit to appear before the foaming because rigid bubble walls will prevent air bubbles from growing. However, the copolymer matrix strength is not enough to close the air to form big, asymmetric bubble structures if ring structures form after the copolymer foaming, so bubble walls are destroyed or collapse. Therefore, the cyclization reactions ought to go on in parallel with the copolymer foaming. However, the copolymer is an elastomer or soft glass here, so there are not large numbers of motion cyclization reactions because the molecular chain motion has been frozen, whereas there exist only finite *in situ* cyclization reactions among adjacent functional groups.

Accordingly, *in situ* cyclization may be defined as follows: First, functional groups that are able to form ring structures are joined to the copolymer molecular chain through the copolymerization reaction in advance, and cyclization reactions do not occur here. Second, adjacent functional groups that are able to form ring structures collide with one another and form ring structures on the spot via structural rearrangement or an elimination reaction in parallel with the copolymer foaming or heat treatment. The mechanism ought to be valuable for the preparation of high-performance polymer foams.

In this study, we applied *in situ* cyclization reactions among adjacent MAA, AN, and AM monomeric units to form rigid ring structures, such as six-membered imide rings and ladder polymer structures, to obtain a new high-performance MAA/AN/AM polymer foam.

MAA/AN/AM copolymer foam structure analysis

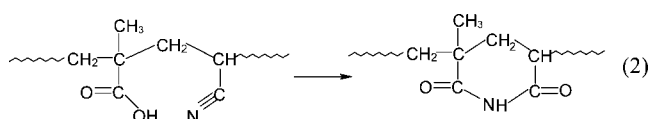
The chemical reactions taking place during expandable copolymer synthesis are ternary copolymerization reactions among MAA, AN, and AM. According to the Q-E theory, the reactivity ratios of MAA and AN are 5.37 and 0.13, respectively. The activity and homopolymerization ability of MAA are stronger, whereas the alternate copolymerization ability of AN is stronger; thus, the copolymerization of MAA and AN is block copolymerization.⁷ After the introduction of the third copolymerization monomer (AM), the total reaction equation of the copolymerization process is as follows:



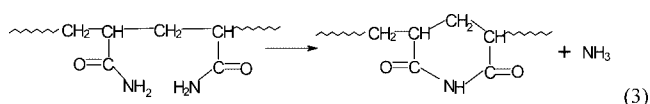
Accordingly, we can more conclude that *in situ* cyclization reactions taking place during the foaming and heat treatment ought to include the following sorts.

Forming six-membered imide ring structures

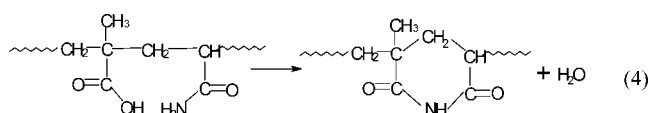
The structural rearrangement and cyclization reaction take place between adjacent MAA and AN monomeric units, and the reaction equation is given in eq. (2):



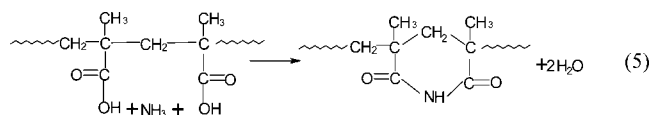
Adjacent AM monomeric units form six-membered imide ring structures via the release of ammonia, and the reaction equation is given in eq. (3):



Adjacent MAA and AM monomeric units form six-membered imide ring structures via a dehydration reaction, and the reaction equation is given in eq. (4):

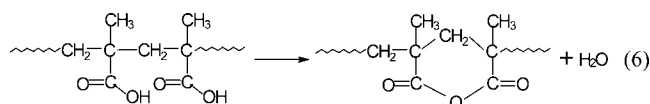


The ammonia released by eq. (3) can further react with MAA monomeric units, at last forming six-membered imide ring structures via a dehydration reaction, and the reaction equation is given in eq. (5):



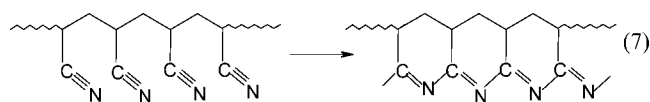
Forming six-membered acid anhydride ring structures

In the MAA/AN/AM copolymer foam molecular chain structure, the probability of an MAA monomeric unit being adjacent to AN and AM monomeric units is not enough to make all MAA monomeric units form six-membered imide ring structures, so some of the adjacent MAA monomeric units perhaps form six-membered acid anhydride ring structures via a dehydration reaction when the foam is heated,⁸ and the reaction equation is given in eq. (6):



Forming ladder polymer structures

The homopolymer of AN is able to start the cyclization reactions and form ladder polymer structures above 180°C.⁹ A large number of studies have shown that 75% of the AN monomeric units are able to form ladder polymer structures below 200°C, and cyclization reactions will be most intensive at 250°C.¹⁰ When the copolymerization reactions between MAA and AN are taking place, the carbonyl catalysis can lower the temperature necessary for AN monomeric unit cyclization.¹¹ Most AN monomeric units can form ladder polymer structures when the temperature of the foaming and heat treatment reaches 200°C especially. The reaction equation is given in eq. (7):



MAA/AN/AM copolymer molecular chain structure characterization

To have a better understanding of the *in situ* cyclization reactions taking place during MAA/AN/AM copolymer foaming and heat treatment, we first characterized the structures of the MAA homopoly-

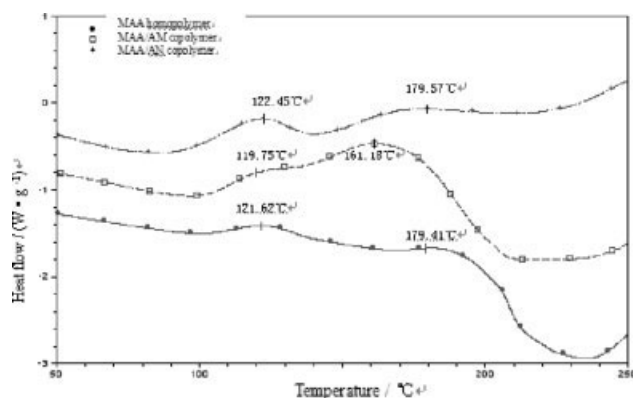


Figure 1 DSC curves of the MAA homopolymer and binary copolymer.

mer and binary and ternary copolymers and then ascertained the exact *in situ* cyclization reactions that had taken place in the polymer molecular chains by a contrast analysis of structural differences.

MAA homopolymer and binary copolymer structure characterization

We analyzed the MAA homopolymer and binary copolymer with DSC and FTIR curves, and the results are given in Figures 1–4.

DSC curves in Figure 1 show the following. First, the MAA homopolymer and binary copolymer had an exothermic reaction peak at about 120°C, and the peak temperature was close to the rapid decomposition temperature of AIBN for the polymer. We think that these peaks were caused by the rapid decomposition of the remaining AIBN. Second, the MAA homopolymer had a weak exothermic reaction peak at about 180°C. Because the glass-transition temperature of the MAA homopolymer was 185°C, the homopolymers reacted to form six-membered acid anhydride ring structures at about 200°C. In our opinion, the exothermic reaction peak corresponded to the reaction forming acid anhydride, but it was

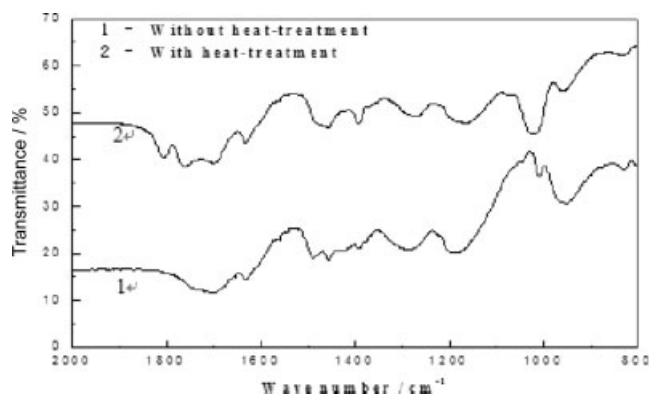


Figure 2 FTIR curves of the MAA homopolymer before and after the heat treatment.

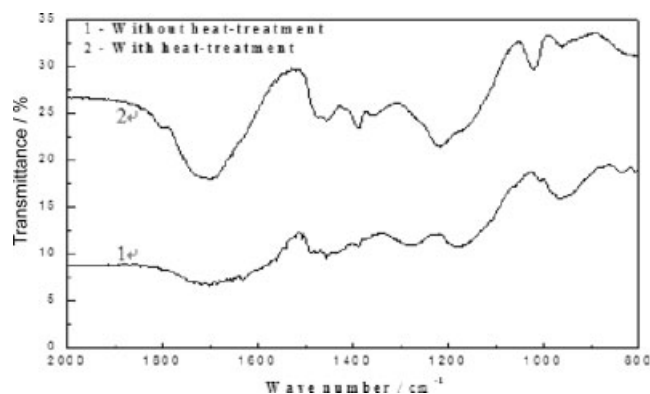


Figure 3 FTIR curves of the MAA/AM binary copolymer.

not very apparent for the counteraction of the glass-transition endothermic reaction. Third, the MAA/AM copolymer had a clear exothermic reaction peak at about 160°C, and the peak temperature was 161.18°C. Compared with that of the MAA homopolymer, the peak temperature descended clearly, and the peak width became larger. Because AM consumption was not enough to make MAA monomeric units react fully, we think that the exothermic peak was formed via the exothermic superpositioning of ring structure reactions. Fourth, the MAA/AN copolymer had an exothermic reaction peak at 179.57°C, and the peak was close to the peak of MAA forming acid anhydride ring structures, but the initial temperature of the reaction was apparently lower.

According to DSC analysis, the MAA homopolymer was heat-treated at 180°C for 2 h. FTIR curves of the MAA homopolymer before and after the heat treatment are given in Figure 2.

For the FTIR curves of the MAA homopolymer, after the heat treatment, some changes occurred in contrast to the situation before the heat treatment, and these changes were as follows: the —OH bend-



Figure 4 FTIR curves of the MAA/AN binary copolymer before and after the heat treatment.

ing vibration peak of —COOH at 930 cm^{-1} weakened, the C—O—C stretching vibration peak of the acid anhydride at 1020 cm^{-1} strengthened, and the >C=O stretching vibration peaks of the acid anhydride appeared at 1820 and 1760 cm^{-1} . All these data reveal that the MAA homopolymer led to an acid anhydride ring reaction during the heat treatment at 180°C . At the same time, the —OH bending vibration peak of —COOH at 930 cm^{-1} did not disappear completely, and the >C=O absorption peak of the carboxylic acid at 1700 cm^{-1} was stronger and thus made the >C=O stretching vibration peak of the acid anhydride at 1760 cm^{-1} stronger than that at 1820 cm^{-1} . These data reveal that the acid anhydride ring reactions during the heat treatment were not complete.

The MAA/AM binary copolymer was heat-treated at 160°C for 2 h. The FTIR curves of the copolymer before and after the heat treatment are given in Figure 3.

Figure 3 shows that after the heat treatment, the —OH bending vibration peak of —COOH at 930 cm^{-1} weakened, the C—O—C stretching vibration peak of the acid anhydride at 1020 cm^{-1} strengthened, the C—N absorption peak of the amide (or imide) at 1220 cm^{-1} was stronger, the >C=O absorption peak at 1700 cm^{-1} was stronger too, and the >C=O stretching vibration peak of the acid anhydride appeared. These data reveal that MAA reacted with AM to form the imide, so the number of C—N bonds increase, and the C—N bending vibration peak at 1220 cm^{-1} strengthened. At the same time, the imide rings that formed via the cyclization reaction had a stronger corresponding stretching vibration peak of >C=O at $1700\text{—}1720\text{ cm}^{-1}$ and a stronger C—N—C stretching vibration peak at $1640\text{—}1680\text{ cm}^{-1}$, so the absorption peak at 1700 cm^{-1} was stronger.

These changes reveal that the MAA/AM binary copolymers reacted to form six-membered imide ring structures during the heat treatment, and some of the MAA monomeric units reacted to form acid anhydride ring structures because the quantity of the AM monomeric units was not enough to make MAA monomeric units form six-membered imide ring structures completely.

The MAA/AN binary copolymer was heat-treated at 180°C for 2 h. The FTIR curves of the copolymer before and after the heat treatment are given in Figure 4.

Figure 4 shows that after the heat treatment, the —OH bending vibration peak of —COOH at $930\text{—}970$ and 1480 cm^{-1} almost disappeared. A stronger C—N absorption peak of the amide (or imide) at 1220 cm^{-1} appeared clearly. The >C=O stretching vibration peak at 1700 cm^{-1} deviated toward the low-frequency area and appreciably strengthened. A

weak >C=O absorption peak of the acid anhydride appeared at 1820 cm^{-1} . A weak C—O—C absorption peak of the acid anhydride appeared at $1000\text{—}1100\text{ cm}^{-1}$. The $\text{—C}\equiv\text{N}$ stretching vibration peak at 2240 cm^{-1} appreciably weakened. All these data reveal that the MAA/AN binary copolymers reacted to form six-membered imide ring structures in the course of the heat treatment. At the same time, the MAA monomeric units were not adjacent to the AN monomeric units fully, and few MAA monomeric units formed the acid anhydride after the heat treatment, so the characteristic absorption peak of the acid anhydride appeared in the FTIR curve.

MAA/AN/AM ternary copolymer structure characterization

The expandable MAA/AN/AM ternary copolymer is made up of a series of copolymers with different polymerization degrees and contains the foaming agent. We analyzed DSC and FTIR curves of the ternary copolymer without the foaming agent, and the results are given in Figure 5.

Figure 5 shows that the DSC curve of the MAA/AN/AM copolymer has three obvious exothermic reaction peaks. The first exothermic peak temperature is 124.2°C , and the reaction peak change is not obvious in contrast to that of the MAA homopolymer or binary copolymer, so it corresponds to the decomposition of the remaining AIBN. The second exothermic peak temperature is 167.9°C , between those of the MAA/AN and MAA/AM copolymers; furthermore, its initiative temperature is basically consistent with those of the MAA/AN and MAA/AM copolymers, so the peak is the exothermic superposition of the MAA binary copolymers forming imide rings. The third exothermic peak temperature is 276.5°C , and the stronger peak corresponds to the reaction of AN monomeric units forming ladder polymer structures.

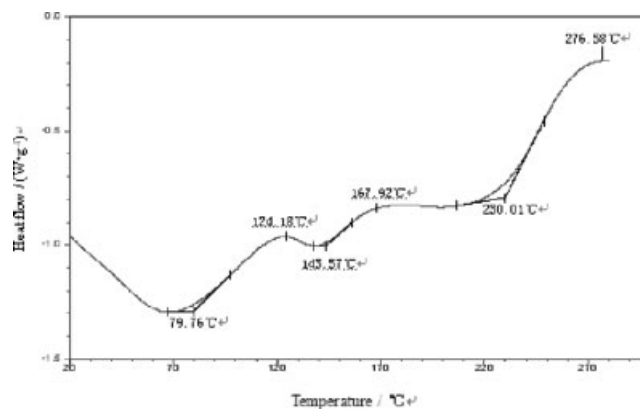


Figure 5 DSC curves of the MAA-AN-AM ternary copolymer.

We analyzed thermogravimetry (TG)/differential thermogravimetry (DTG) curves for the MAA/AN/AM ternary copolymer, and the results are given in Figure 6.

Figure 6 shows that the ternary copolymer had a weight-loss phenomenon below 100°C; however, the weight-loss velocity diminished gradually. This was due to the moisture absorption by the copolymer. The TG curve had a weight-loss speed-up phenomenon at about 170°C, and the peak temperature of the DTG curve was 175.87°C. These two phenomena corresponded to changes in the DSC curve at about 170°C for the MAA monomeric units that reacted with AM monomeric units to form imide ring structures and made the weight-loss velocity accelerate at about 170°C. Furthermore, the TG curve had a lower weight-loss velocity, which corresponded to changes in the AN monomeric units forming ladder polymer structures in the DSC curve around 276.58°C. The reason is that there were some small-molecule release reactions, such as HCN. The copolymer lost gravity quickly and started to decompose above 300°C. At last, 26.63% remained.

According to its DSC curve, the MAA/AN/AM ternary copolymer was heat-treated at 160°C for 2 h and at 200°C for 2 h. From an analysis of the DSC and FTIR curves of the copolymer before and after the heat treatment, the results are given in Figures 7 and 8.

Figures 7 and 8 show that after the heat treatment at 160°C for 2 h, the —OH absorption peaks at 930–970 and 1480 cm^{-1} weakened in the FTIR curve. The C—N absorption peak of the amide (or imide) strengthened at 1220 cm^{-1} . The >C=O absorption peak at 1700 cm^{-1} deviated toward the low-frequency area, and the sub-peak in the low-frequency area strengthened. There was a weak exothermic peak whose peak temperature was 149.17°C, and there was a strong exothermic peak whose peak temperature was 270.85°C in the DSC curve. After more heat treatment at 200°C for 2 h, —OH absorption peaks at 930–970 cm^{-1} basically disappeared. The >C=O absorption peak at 1500–1800 cm^{-1} presented new small side steps at 1540 and 1600 cm^{-1} ,

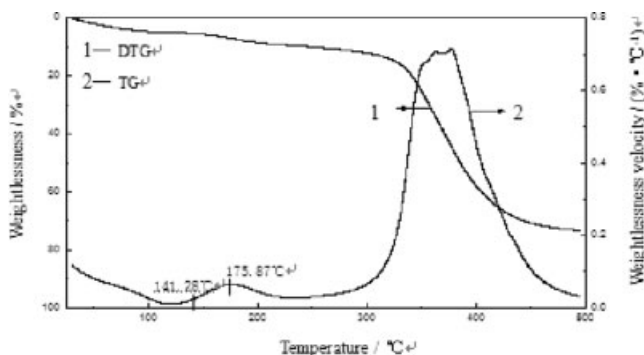


Figure 6 TG/DTG curves of the MAA–AN–AM ternary copolymer.

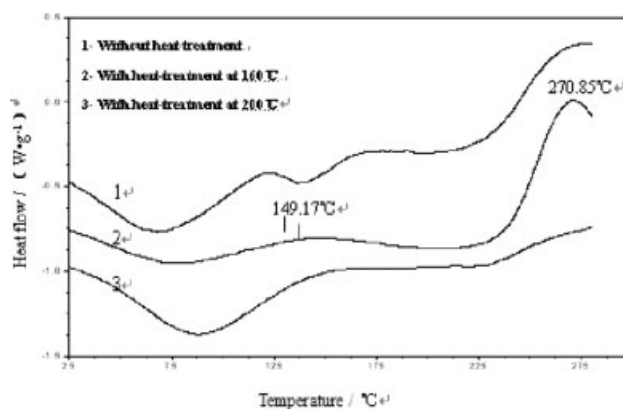


Figure 7 DSC curves of the MAA–AN–AM ternary copolymer before and after the heat treatment.

and then $\text{—C}\equiv\text{N}$ at 2240 cm^{-1} weakened appreciably. Here the DSC curve did not possess any obvious exothermic peak at 100–200°C, except at 270°C.

After analyzing the MAA binary and ternary copolymer structures via DSC, TG, and FTIR, we obtained the following results. The reactions forming the imide by the MAA/AN/AM ternary copolymer mainly took place via dehydration between MAA and AM monomeric units [eq. (4)] and via a structural rearrangement between MAA and AN monomeric units [eq. (2)] after the heat treatment at 160°C. Thus, a lot of imide ring structures were formed, and still there were some MAA and AN monomeric units remaining. In the course of the heat treatment at 200°C, MAA and AN monomeric units reacted to form the imide ring structures via a structural rearrangement [eq. (2)], and AN monomeric units formed ladder polymer structures via a structural rearrangement [eq. (7)] too, but there were no obvious reactions forming acid anhydride ring structures. The reason is that the third monomer to be introduced, AM, and the product NH_3 [eq. (3)] made MAA monomeric units form six-membered imide ring structures completely. In other words, there were six-membered imide ring and ladder

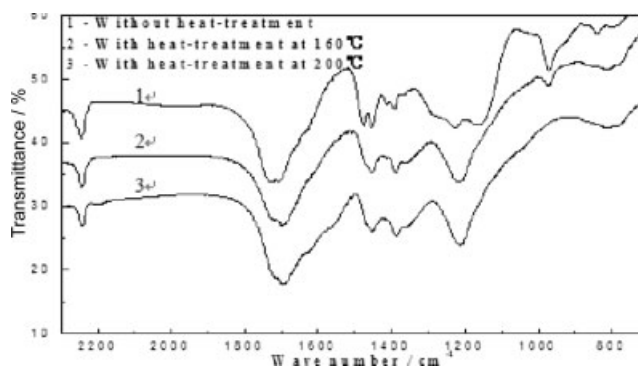


Figure 8 FTIR curves of the MAA–AN–AM ternary copolymer before and after the heat treatment.

TABLE II
Mechanical and Heat-Resistance Properties of the MAA/AN/AM Ternary Copolymer Foams

Density (kg/m ³)	32	43	52	65	75	Testing method
Tensile strength (MPa)	0.7	1.0	1.3	1.8	2.2	ASTM D 638
Modulus of elasticity (MPa)	24	36	46	63	77	ASTM D 638
Compressive strength (MPa)	0.3	0.56	0.8	1.3	1.7	ASTM D 1621
Shear strength (MPa)	0.4	0.6	0.8	1.1	1.3	ASTM C 273
Heat deflection temperature (°C)	210	210	215	240	240	DIN 53424

polymer structures in the final MAA/AN/AM ternary copolymer foam molecular chain; moreover, there were a few remaining AN monomeric units, which did not take part in the cyclization reactions.

Mechanical and heat-resistance properties of the MAA/AN/AM copolymer foam

The mechanical and heat-resistance properties of the MAA/AN/AM copolymer foam are given in Table II. Table II shows that the MAA/AN/AM copolymer foam possesses excellent mechanical and heat-resistance properties.

CONCLUSIONS

A weak exothermic peak at 149.17°C and a strong endothermic peak at 270.85°C were in the DSC curves of the MAA/AN/AM copolymer after the foaming and heat treatment at 160°C for 2 h and at 200°C for 2 h. The peak temperature of the DTG curves was 175.87°C, whereas the weight-loss rate was less at 276.58°C in the TG curves. In the case of the FTIR curves, the —OH absorption peak at 930–970 and 1480 cm⁻¹ weakened, and the C—N absorption peak of the imide increased. The >C=O absorption peak at 1700 cm⁻¹ deviated toward a low-frequency field; at the same time, the second absorption peak increased. Furthermore, the —C≡N absorption peak at 2240 cm⁻¹ weakened, and a new —C=N— absorption band appeared.

A series of *in situ* cyclization reactions took place during the foaming and heat treatment, such as reac-

tions forming six-membered imide ring structures through the release of NH₃ among AM monomeric units, the dehydration reaction between MAA and AM monomeric units, the structural rearrangement reaction between MAA and AN monomeric units, and the reaction forming ladder polymer structures among AN monomeric units.

Rigid six-membered imide ring and ladder polymer structures enhanced the molecular chain rigidity and gave the MAA/AN/AM ternary copolymer foam excellent mechanical and heat-resistance properties.

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