

Rheological Properties and Foam Preparation of Biodegradable Poly(butylene succinate)

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ABSTRACT: To produce biodegradable poly(butylene succinate) (PBS) foam by compression molding, high viscosity PBS was prepared with dicumyl peroxide (DCP) as a crosslinking agent and trimethylolpropane trimethacrylate (TMPTMA) as a curing coagent by crosslink method. The influences of various factors on the foaming process and the properties of PBS foams were investigated. The results show that the use of DCP and TMPTMA simultaneously can effectively increase the melt viscosity of PBS. Zinc oxide/zinc stearate was used to reduce the thermal decomposition temperature of the blowing agent azodicarbonamide, which can balance well the vulcanization of PBS and the decomposition of blowing agent. Finally, closed-cell PBS foams with degradable property have been successfully prepared by a traditional chemical compression molding foaming way. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: poly(butylene succinate) (PBS); crosslinking agent; blowing agent; rheological property; foam

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INTRODUCTION

At present, a wide variety of polymers can be formed into foams with many applications, such as thermal insulation, chemical resistance, cushioning performance, and buoyancy.¹ Due to the accumulation of polyolefins foam wastes, the environmental pollution problems are getting more serious in recent years. Thus, biodegradable polymers, a promising solution to these problems, were the focus of many studies in the last couple of decades. Aliphatic polyesters are considered as high performance environment friendly biodegradable plastics.^{2,3} These polymers are leading candidates for substitution of nonbiodegradable plastics because they are readily susceptible to biological attack in nature ecosystems, such as compost, sludge, and lake, and to break down into carbon dioxide, water, and humus.^{4,5} Till now there are few reports for the preparation of aliphatic polyesters foam because of relatively low-melt strength due to its low molecular weight, which limits its wide applications in foam industry. As one of the typical examples, biodegradable polyester-caprolactone foam can be obtained using DCP as a crosslinking agent and CO₂ and/or N₂ as foaming agent under different process conditions.^{6,7} On the other hand, poly(butylene succinate) (PBS) is one of the important synthetic biodegradable aliphatic polyesters, which exhibits not

only good degradability and processability but also excellent mechanical properties similar to polypropylene (PP).^{8–10} However, the low-melt strength of PBS because of its low molecular weight and linear structure limits its wide applications in foam industry. To increase the melt strength of PBS, crosslinking or branching was recognized as an effective method. For example, Song et al.¹¹ increased the gel content of PBS by γ -irradiation and found that the crosslinked PBS had higher heat resistance and higher biodegradability. Suhartini et al.¹² prepared PBS/TMIC crosslinked composites by electron beam irradiation, and the adding of TMIC and irradiation improved the heat stability of PBS while decreased its biodegradability. Kim et al.¹³ improved the mechanical and thermal properties of PBS through the crosslinking reaction between dicumyl peroxide (DCP) and PBS. Lim et al.¹⁴ added two types of polyisocyanate as branching agents into PBS matrix to increase the viscosity and finally prepared PBS foams. Jin et al.¹⁵ reported the preparation of crosslinked PBS by adding benzoyl peroxide (BPO) and multi-functional co-agent. Huang et al.¹⁶ prepared ultraviolet-induced crosslinking of PBS in the presence of a photoinitiator and a crosslinking agent, which retarded the enzymatic degradation rate of PBS. Bahari et al.¹⁷ investigated the radiation crosslinked poly(butylene succinate) foam and its

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Table I. PBS Compound Formulations for Rheological Measurement

Mix number	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
PBS (phr wt)	100	100	100	100	100	100	100	100	100	100
DCP (phr wt)	0	3	4	5	6	4	4	4	4	4
TMPTMA (phr Wt)	0	0	0	0	0	2	4	6	8	10

biodegradation. Based on these previous studies, crosslinking or branching reaction of PBS is one of the efficient methods to enhance the viscosity of polymers and it is a prospective way to produce PBS foams through a traditional chemical compression molding foaming process.

To prepare PBS foams, crosslinked PBS using DCP as a crosslinking agent and trimethylolpropane trimethacrylate (TMPTMA) as a curing co-agent was firstly prepared. The effect of DCP and TMPTMA on the rheological properties and gel content of crosslinked PBS has been discussed, and the optimum formulation for PBS crosslinking reaction has been determined. Then the decomposition of blowing agent (AC) and the curing reaction of DCP and TMPTMA were investigated to make them match to each other well to prepare PBS foams. Finally, PBS compounds with DCP, TMPTMA, AC, and activators were successfully foamed by chemical compression molding. The morphology of the as-prepared PBS foams was observed by scanning electron microscopy (SEM), and the density and degradability of PBS foams were also investigated.

MATERIALS AND METHODS

Materials

PBS with a melt flow index of 15 g/10 min (190°C/2.16 kg), a density of 1.26 g/mL, and melt temperature of 115°C was produced by Anqing Hexing Chemical (Anqing, China). AC (a fine, yellow powder) was provided by Shanghai Xiangyang Chemical (Shanghai, China). DCP was supplied by Shanghai Fuzhe Chemical (Shanghai, China). TMPTMA manufactured by Guangzhou Jindong (Guangzhou, China) was used as curing co-agent. All other additives and activators [zinc oxide (ZnO), zinc stearate (ZnSt₂), and stearic acid (HSt)] were industrial-grade products obtained from Shanghai Yuanji Chemical (Shanghai, China).

Preparation

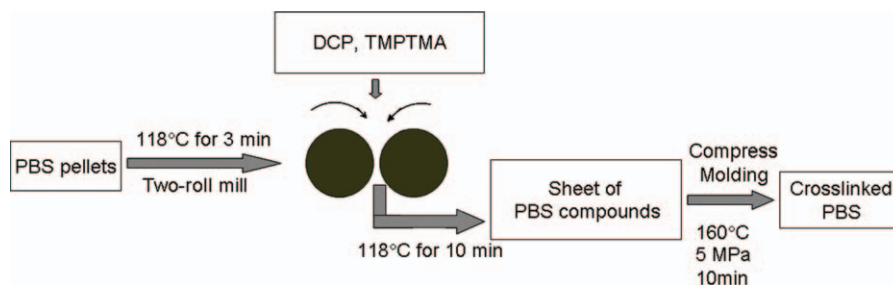
Crosslinking of PBS. PBS pellets were fed firstly on a two-roll mill and melted at 118°C for 3 min, and then mixed with the ingredients according to the formulation in Table I for 10 min at the same temperature. After this compounding process, the precrosslinked PBS was gotten. Then the precrosslinked PBS with DCP and TMPTMA according to Table I were compressed into crosslinked sheet (thickness ~ 1 mm) at 160°C and 5 MPa for 10 min. The crosslinked sheets were used for the following characterization of rheological properties and gel content. The process flow chart is given in Scheme 1.

Preparation of PBS Foams. According to Table II, PBS pellets were fed on a two-roll mill and melted at 118°C for 3 min, and then they were compounded with the ingredients at 118°C for 10 min by a two-roll mill to ensure the homogeneous distribution of these ingredients. The final PBS compounds were taken out from the mill after forming sheets, and then were stored at room temperature for 24 h before foaming. The compounds were pressed in a closed mold at 160°C and 10 MPa for 15 min. After the mold was open and cooled to room temperature, PBS foams were obtained out of the mold. The process of compression molding foaming is given in Scheme 2.

Characterization

Rheological Properties. The rheological properties were detected by a rotational rheometer (Gemini 200HR, Bohlin Instruments, East Brunswick, New Jersey (NJ), USA) through a parallel plate of 25 mm in diameter and a gap of 1 mm. In the dynamic frequency sweep mode, G' , G'' , and η^* were measured as functions of frequency in the range from 1 to 80 Hz at a constant strain 5% at 160°C.

Gel Content Measurement. The precrosslinked PBS samples were kept at 160°C for 10 min first, then weighed (W_1) and extracted by hot chloroform for 96 h using a Soxhlet extractor. Prior to the final weight (W_2), the extracted samples were dried in a vacuum at 60°C for 24 h. Gel content was calculated as the



Scheme 1. The preparation process of crosslinked PBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. PBS Compound Formulations for Foaming Process

Samples		PBS (phr)	AC (phr)	DCP (phr)	ZnO (phr)	ZnSt ₂ (phr)	HSt ₂ (phr)	TMPATM (phr)
The effect of DCP content	B1	100	2	3	2	1	1	6
	B2(C2)	100	2	4	2	1	1	6
	B3	100	2	5	2	1	1	6
	B4	100	2	6	2	1	1	6
The effect of AC content	C1	100	1	4	2	1	1	6
	C2(B2)	100	2	4	2	1	1	6
	C3	100	3	4	2	1	1	6
	C4	100	4	4	2	1	1	6

weight of the dried extracted sample divided by the weight of the original one.

The gel content was calculated as:

$$\text{Gel content} = \frac{W_1}{W_2} \times 100\%$$

TGA. Thermogravimetric analysis (TGA) data of the crosslinking agent DCP, chemical blowing agent AC and PBS foams were obtained with a TAG7 thermogravimetric analyzer (PerkinElmer, Waltham, Massachusetts, USA). About 10 mg of samples was placed on a microbalance and heated from room temperature to 800°C with the rate of 20°C/min. A stream of dry N₂ was used for purging of oxygen.

Vulcanization and Blowing Measurements. The vulcanization and blowing characteristics of PBS were measured on a moving die rheometer (MDR, Model UCAN-2030, U-can Dynatex Nantou, Taipei, Taiwan) according to ASTM D-5289 method. The measurement condition was 160°C for 15 min.

SEM. The cellular morphologies of the foam samples were observed by scanning electron microscopy (SEM, Model S-2150, Hitachi, Chi City, Japan). Samples were razor-cut and the razor-cut surface was sputter-coated with gold before observation.

Density Measurements. Density was calculated from the mass and volume specimens with surfaces skin according to ISO 845-1988.

RESULTS AND DISCUSSION

In general, to prevent the cells from rupturing during the preparation process of PBS foam, PBS must have sufficient melt strength. And the melt strength of a polymer usually depends on its viscosity, dynamic storage modulus, and loss modulus.^{18,19} It is well known that high molecular weight could produce high melt strength for a given polymer. However, it is inherently difficult to synthesize high molecular weight of PBS through the polycondensation reaction of diols and dicarboxylic acid.^{20,21} To overcome this limitation, crosslinking PBS will be an efficient way.

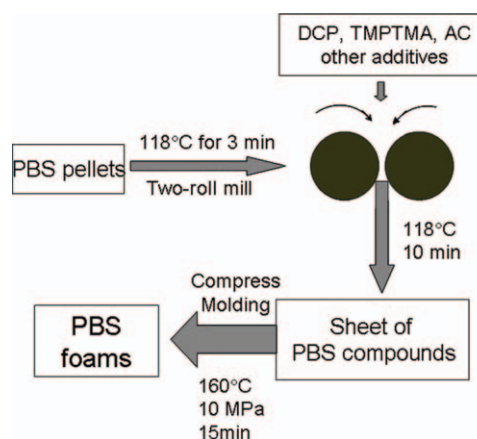
DCP is one of the alkyl peroxides because the extent of DCP decomposition was minimal below 120°C,²² and the crosslinking might hardly occur during compounding of PBS and fillers. So DCP is the most suitable for polymers, such as PBS, melting

at 100–120°C.^{13,23} Moreover, to further improve the viscosity of PBS, TMPTMA, a kind of polyfunctional monomers, will be used as curing co-agent, which could improve the crosslinking reaction between DCP and polymer, and yield high gel content.^{24,25}

In this study, DCP and TMPTMA were used to increase the melt strength of PBS and ultimately to achieve a three-dimensional polymer network to produce foam.

Rheological Properties of Crosslinked PBS

The Effect of DCP. The rheological measurements were made to evaluate the effect of DCP on the rheological properties of PBS. Figure 1 shows the change of dynamic storage modulus (*G'*) and loss modulus (*G''*) at 160°C as a function of frequency. It could be found that both *G'* and *G''* increase with the frequency for all compounds, which is the typical behavior of polymers under the effect of frequency.²⁶ In lower frequency, there is sufficient time to allow chains to reorganize themselves, and polymer displays the soft properties and lower modulus. In higher frequency, the time to response to the outer change is very short, so polymer shows hard properties. Figure 1 clearly reveals that *G'* and *G''* increase with the amount increase of DCP, indicating that the reorganization of polymer chain becomes difficult and its movement is limited. Obviously, such phenomenon was contributed by DCP driven by the forming of crosslinking structure of PBS.



Scheme 2. The preparation process of PBS foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

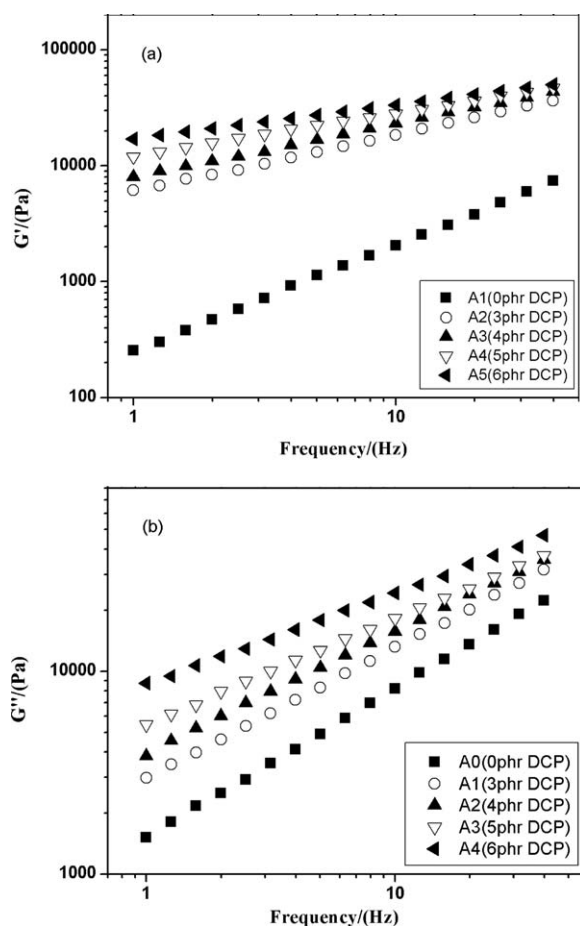


Figure 1. Storage modulus (G') (a) and loss modulus (G'') (b) as a function of frequency of cured PBS with various content of DCP.

Figure 2 shows the change of complex viscosity of PBS with frequency and the gel content of crosslinked PBS with respect to different content of DCP. For all samples, the complex viscosity η^* decreases with the increase of frequency, showing the pseudoplastic behavior of PBS compounds.¹⁸ It is clear in Figure 2 that η^* of PBS compounds increases with the amount increase of DCP, the value of viscosity increases nearly 10 times when 6 phr DCP (A5) is used comparing to that of pure PBS, indicating that chemical crosslinking reduces polymer chain slippage and enhances the viscosity. This could also be confirmed by the phenomenon of the gel content increasing obviously with the increase of DCP content (Figure 2), indicating that the crosslinking structure is formed because of the addition of DCP. While, in order to produce PBS foam, 10 times increase of viscosity is still not enough to get the high melt strength and fail to obtain PBS foam. Since PBS is a slow crosslinking polymer and the reaction between DCP and PBS is not so active, TMPTMA as a curing co-agent is used to improve the efficiency of the reaction between PBS and DCP to get higher viscosity and finally to obtain higher melt strength.^{13,27}

The Effect of TMPTMA. As mentioned above, DCP can enhance the melt strength of PBS, but is still not enough to maintain the released gas. Curing co-agent can improve the effi-

ciency of crosslinking of DCP, such as TMPTMA.^{24,25} It could enhance the degree of crosslinking, and increases the reaction rate of DCP at the meantime. Here the influence of TMPTMA on DCP is studied through the change of modulus and viscosity compared with the same content of DCP without TMPTMA, and the results are given in Figure 3.

As shown in Figure 3(a), when 6 phr TMPTMA (A8) is added, the value of dynamic storage modulus (G') is almost 10 times higher than that of 0 phr TMPATM (A3) added, and almost 200 times than that of pure PBS. Similar phenomenon is observed in Figure 3(b), although the increase of G' is smaller than that G' at the same content of TMPTMA. The storage modulus (G') and loss modulus (G'') apparently increase with the addition of TMPTMA, indicating that advanced crosslinking structure is formed as we would expect. Furthermore, in Figure 3, when TMPTMA is added, the slope of G' and G'' curves decreases with the increase of TMPTMA content, indicating that the change of dynamic storage modulus (G') and loss modulus (G'') with the frequency becomes smaller. This is because the high degree of crosslinking limits the reorganization of polymer chains, which leads melted PBS matrix to high modulus even at low frequency.^{28–30}

Figure 4 shows the complex viscosity of PBS as a function of frequency, the viscosity slope of higher content of TMPTMA is much steeper than that of lower content of TMPTMA, and the viscosity increases more than 50 times when TMPTMA is added, further confirming the influence of TMPTMA on the crosslinking. The high degree crosslinking of PBS compound restricts the movement of chains and ultimately raises its melt's viscosity. The influence of TMPTMA could also be seen by the increase of gel content in Figure 4. The gel content of PBS increases rapidly with the adding of TMPTMA, also indicating that TMPTMA improves the crosslinking of PBS. With the high viscosity or melt strength, preparation of foam materials would become possible.

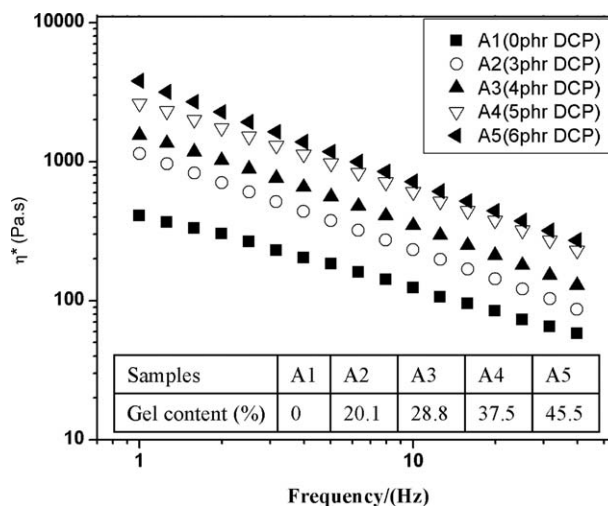


Figure 2. Complex viscosity (η^*) as a function of frequency of cured PBS with various contents of DCP.

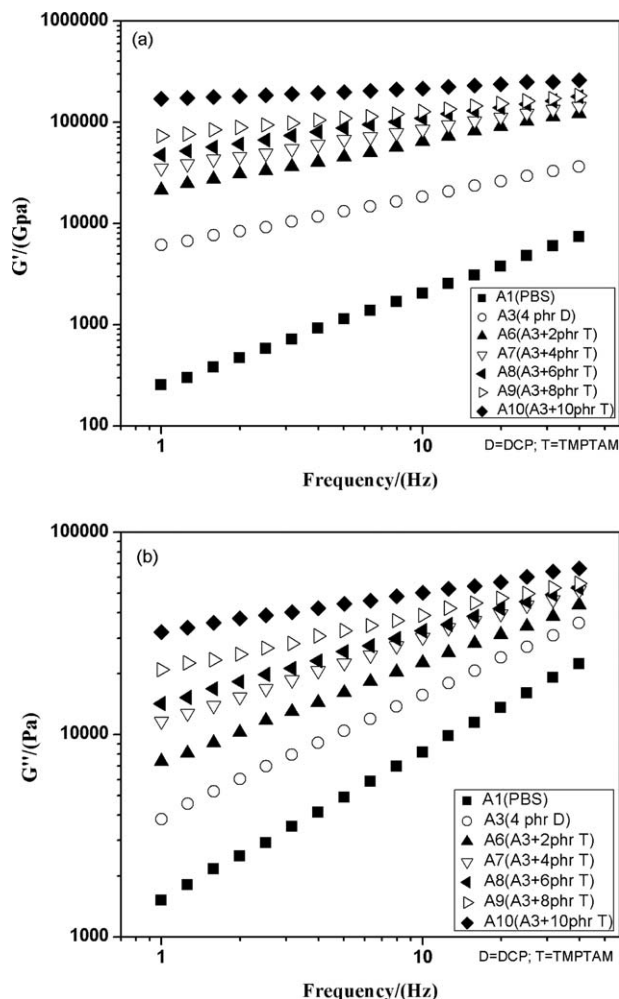


Figure 3. Storage modulus (G') (a) and loss modulus (G'') (b) as a function of frequency of cured PBS with various contents of TMPTAM.

The Balance Between the Reaction Rate of Decomposition and Vulcanization

During the process of preparing foam, there are three major stages of foam processing: nucleation, bubble growth, and stabilization. Once nucleated, a bubble will continue to grow until the bubble is stabilized by the high melt strength or it ruptures if the melt strength is relatively low. When cells cracked, and not only the cell density and foaming structure deteriorate, but also volume expansion ratio decreases greatly due to gas loss through the opened cell wall.

Previous studies^{31,32} indicated that the simultaneously occurring reactions, the crosslinking of polymer and the release of blowing gas, must be finely tuned in order to get ideal foams. The decomposition of blowing agent must take place when polymer is at the proper melt viscosity, because too high viscosity of polymer led by the high degree of crosslinking will limit the growth of bubble; while too low viscosity could not maintain the melt strength of polymer matrix and gas will escape and then ruptured foams will be formed.³¹ It is important to make the reaction of blowing agent AC match to the decomposition of DCP.

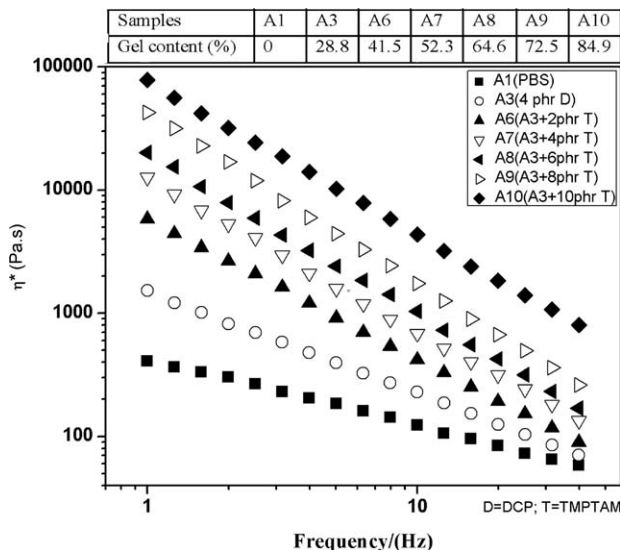


Figure 4. Complex viscosity (η^*) as a function of frequency of cured PBS with various content of TMPTAM.

The Effect of Activator in AC. Temperature is of significance for producing PBS foams because it could influence the decomposition of chemical blowing agent (AC), crosslinking agent (DCP), the melt viscosity of polymer and further affect the properties of foams. Figure 5 shows the decomposition behavior of AC and DCP with heating temperature. From Figure 5, one can see that the onset decomposition temperature of DCP [Figure 5(1)] is about 100°C, and a large amount of decomposition starts for DCP is about 160°C. However, it is found that AC [Figure 5(2)] starts to decompose at around 205°C, meaning the crosslinking process happens because of the decomposition of DCP at 160°C while the reaction of AC does not start yet. This situation also implies that the crosslinking reaction is finished before the decomposition of AC, and lead to high viscosity of PBS matrix and ultimately difficulty to obtain foams. Therefore, it is important to lower the decomposition temperature of AC to make these two reactions happens synchronized.

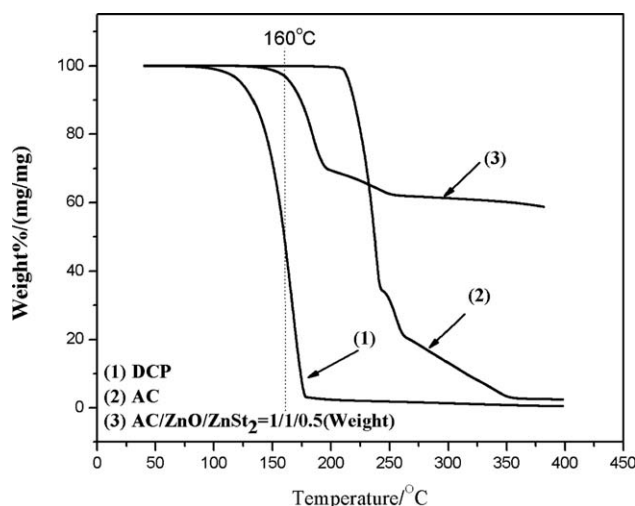


Figure 5. TGA curves of DCP, AC, and AC with activators.

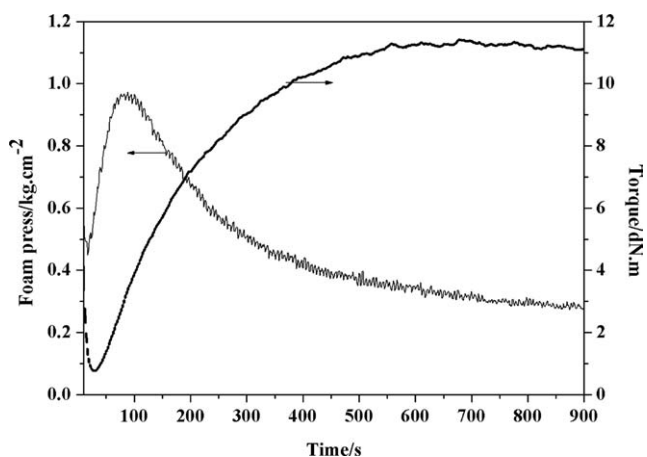


Figure 6. Rheographs and blowing curves of A2 at 160°C.

Activators can lower the decomposition temperatures of AC. For example, the addition of ZnO into the blowing agent AC not only lowers the decomposition temperature but also accelerates its decomposition.³¹

It is found that the addition of ZnO could decrease the decomposition temperature of AC from 205°C to 175°C, but AC could not decompose completely with the addition of ZnO only.³³ Therefore the co-activator ZnSt₂ is added to AC/ZnO to decrease the decomposition temperature of AC to appropriate value. In Figure 5(3), the onset decomposition temperature of AC is lowered to around 150°C after 1 phr ZnO and 0.5 phr ZnSt₂ are added, and much gas releases because of the decomposition of AC at around 160°C, which match well to the decomposition temperature of DCP.

The Relationship Between Vulcanization of DCP and Decomposition of AC. The moving die rheometer (MDR) is equipped with a pressure sensor at the upper die, which can detect the pressure of PBS compound during vulcanization process in mold and thus reflect the degree of the decomposition of blowing agent AC. The torque difference indicates the change of shear dynamic modulus, which indirectly relates to the crosslink density of compounds.³¹ MDR is used to find the relationship between PBS vulcanization and blowing agent decomposition,

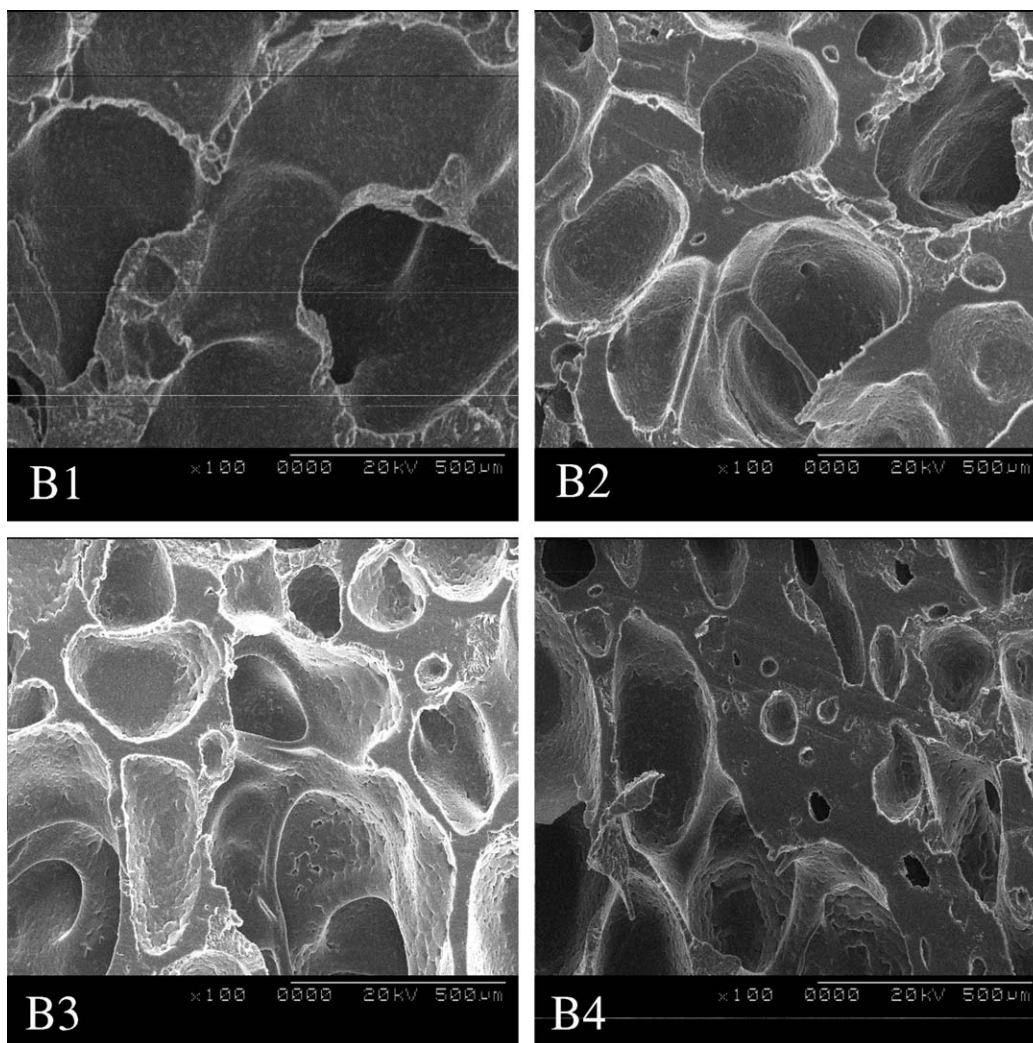


Figure 7. SEM photomicrographs of freeze-fractured cross sections of PBS foams with different content of DCP. B1 (3 phr DCP); B2 (4 phr DCP); B3 (5 phr DCP); B4 (6 phr DCP).

Table III. The Density of PBS Foams with Various Amount of DCP or AC

DCP content	0 phr DCP	B1 (3 phr DCP)	B2 (4 phr DCP)	B3 (5 phr DCP)	B4 (6 phr DCP)
Density (g/cm ³)	Failed	0.28	0.41	0.44	0.61
AC content	0 phr AC	C1 (1 phr DCP)	C2 (2 phr DCP)	C3 (3 phr DCP)	C4 (4 phr DCP)
Density (g/cm ³)	1.25	0.70	0.41	0.31	0.26

and the results are given in Figure 6. It is found that PBS matrix has relatively high melt strength due to the formation of crosslinking structure at the biggest rate of blowing agent decomposition, indicating that they can match well at 160°C. Therefore, PBS foams are produced through the addition of blowing agent activators and the adjustment of the decomposition temperature of AC and DCP.

The Properties of PBS Foams

The preparation of PBS foams was carried out with the addition of blowing agent DCP only or the addition of DCP/TMPTMA at 160°C and 10 MPa for 15 min. The results show that it is difficult to produce PBS foams if only DCP is added, the cells

are almost cracked and the strength of foam articles is relatively low. If TMPTMA is added to the compound, the PBS foams can be successfully produced (Figure 7). This phenomenon could be assigned to the difference of viscosity or melt strength with or without TMPTMA, and has been discussed above.

The Effect of DCP. SEM micrographs of crosslinked PBS foams, which are prepared according to Table II, are shown in Figure 7. One can see that the foam articles for compound B1 have cells with quite big size ($\sim 500 \mu\text{m}$), thin walled and few number cells ($\sim 10 \text{ bubbles}/\text{mm}^2$) because the insufficient DCP in B1 leads to low-melt strength, in which the cell expands quick and then forms big size cells with little limitation of melt strength when

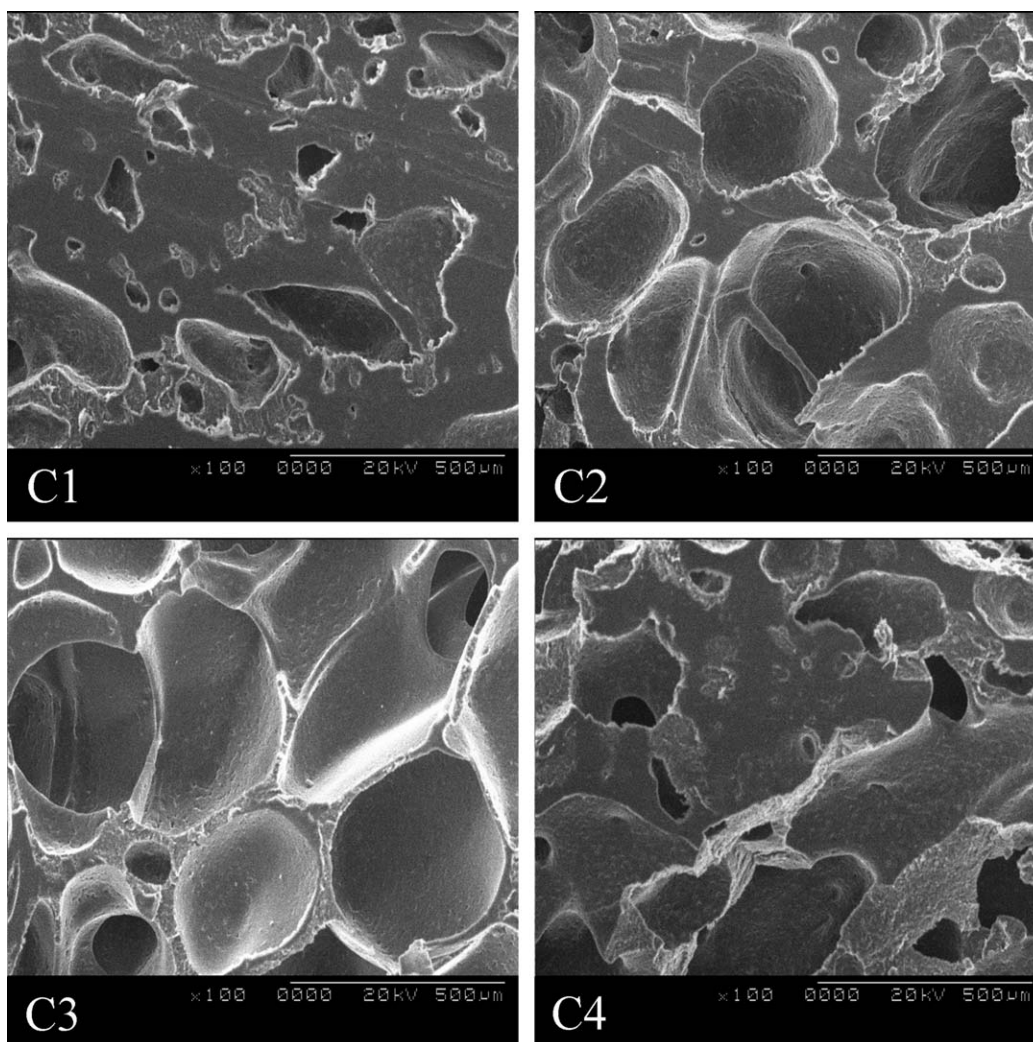


Figure 8. SEM photomicrographs of freeze-fractured cross sections of PBS foams with different content of AC. C1 (1 phr AC); C2 (2 phr AC); C3 (3 phr AC); C4 (4 phr AC).

the blowing agent begins to release gas. If the crosslinking density of PBS compound increases to optimum level, the melt strength is high enough to prevent cell walls from expanding too much, and the bubbles could grow and then be stabilized by increasing the extensional viscosity of PBS at the beginning of foaming process. During the period of foaming, there exists cell to cell diffusion because higher gas pressure of small cells would lead the larger cells ($\sim 200 \mu\text{m}$) to inlay among small cells ($\sim 50 \mu\text{m}$) [Figure 7 (B2 and B3)] and increase the total number of cells (~ 20 bubbles/ mm^2). Figure 7 (B4) shows if the crosslink density of PBS continues to increase, the melt strength increases and limits the cell growth, resulting in foams with higher density and with many small, thick walled cells ($10\text{--}300 \mu\text{m}$). Therefore, the crosslink density of compound is the key factor for foaming. According to our experiment, 4 or 5 phr of DCP is the optimum content to produce PBS foams. Concerning to the content of TMPTMA, 6 phr of TMPTMA is appropriate to have the PBS foams through the similar analysis.

Table III shows the relationship between the content of crosslinking agent DCP and foam density. It can be seen that the foam density of PBS compound increases with the increase of DCP. Although there is gas escaped from PBS matrix in B1 (3 phr DCP), the density of PBS foam is still the lowest. The results indicate that the appropriate content of crosslinking agent can improve the morphology of foams and enhance the efficiency of blowing agent AC.

The Effect of Blowing Agent Content AC. PBS pellets were compounded with ingredients to prepare foam articles according to the formulation listed in Table II. SEM photomicrographs of crosslinked PBS foams with different content of AC are shown in Figure 8. As it is shown in C1, the foam articles have a few small cells ($30\text{--}100 \mu\text{m}$) and few big cells ($\sim 300 \mu\text{m}$) with thick cell wall ($100\text{--}300 \mu\text{m}$) and about 10 bubbles/ mm^2 big cells when the blowing agent content (AC) is 1 phr. It is apparent that the gas released by the blowing agent is not enough to make the matrix supersaturated with gas. When the blowing agent content is up to 2 phr, both the size ($\sim 300 \mu\text{m}$) and cell number (~ 17 bubbles/ mm^2) of cells increase obviously in C2 and C3. Particularly in C3, with the growth of bubble, the cells become more regular and cell walls become thinner. When the blowing agent content is 4 phr in C4, there are quite a few open cells (8 bubbles/ mm^2), which indicates the bubble pressure is higher than the cell walls strength, so the gas escapes out of the matrix and leads to open cells with ruptured cell walls.

In Table III, it also shows the relationship between blowing agent AC and the density of PBS foams. The density of PBS foam obviously decreases with the increase of AC content. The density can reach to 0.31 g/cm^3 when 3 phr AC is added. The density of 0.31 g/cm^3 is relatively low concerning PBS is biodegradable polymer with low melt strength.³⁴ Different from polycaprolactone (PCL) foams⁶ prepared by Di Maio et al. with 0.03 g/cm^3 or PLA foams³⁵ using supercritical CO_2 or N_2 method by Ema Y et al, the densities of PBS foams obtained by a traditional chemical compression molding foaming way are pretty lower. When the AC content is 4 phr, as it was discussed above, cell collapse or cell coalescence happens which would

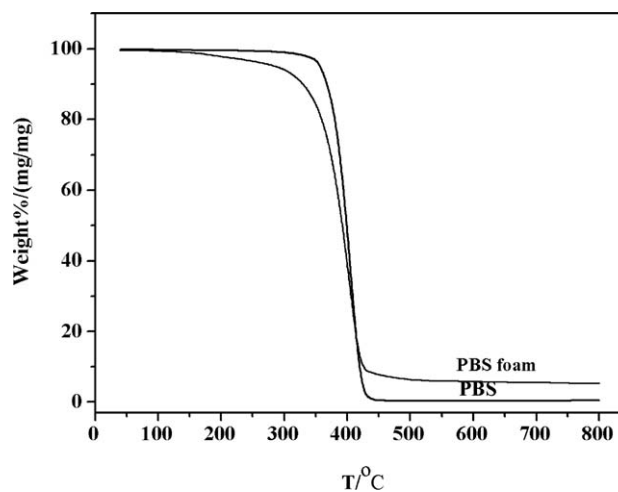


Figure 9. TGA curves of PBS foams and PBS pellets.

deteriorate the density and that is why for C4 there is just a slight decrease in density. In addition, cell collapse would worsen the physical properties of foams.³¹

Thermal Degradation of PBS. Figure 9 shows the thermal decomposition behavior of PBS foams and PBS pellets. It could be seen that the cellular not only reduces the onset degradable temperature of PBS foams, but also makes PBS more vulnerable at the same temperature. Thus, it is easier to degrade PBS foams under the thermal influence.

CONCLUSIONS

PBS was widely used in applications due to its biodegradability, good mechanical properties, and favorable processability. To explore the applications of PBS, the preparation of PBS foam has been investigated. The important results are given as follow:

1. The G' , G'' , η^* and gel content of compounds increased with the increase of DCP content. And the complex viscosity of crosslinked PBS increased 10 times compared with that of pure PBS.
2. The values of G' , G'' , η^* and gel content were increased significantly and the gel content reached to 84.5% (10 phr TMPTMA) after TMPTMA was added, indicating that PBS molecules were effectively crosslinked.
3. The relationship between the rate of the crosslinking of PBS and the decomposition of blowing agent AC was matched well at 160°C for 10 min with the addition of activators.
4. PBS foams have been successfully prepared. SEM showed foams with a well-closed cell structure could be produced with appropriate content of DCP and AC.
5. The density of foams decreased with the increase of blowing agent content, the density of good PBS foams could reach about 0.31 g/cm^3 .

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