

Foaming of Aliphatic Polyester Using Chemical Blowing Agent

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ABSTRACT: Poly(butylene adipate-co-succinate) (PBAS), a saturated aliphatic polyester cured by dicumyl peroxide (DCP), was prepared and the viscoelastic property was investigated. The viscosity of crosslinked PBAS increased, and it exhibited rubbery behavior as the content of curing agent was increased. The results suggested that the viscosity and elasticity of PBAS could be regulated by adding a small amount of DCP; hence, the processibility could be improved. Prior to foaming, a proper formulation of blowing agent (blowing agent/urea activator = 100:8 phr) was examined to prepare expanded PBAS foam. Low-density PBAS expanded foams were prepared using a chemical blowing agent and DCP. The effect of the foaming temperature, additive content, and curing agent content on the blowing ratio and morphology of expanded PBAS foams was investigated. A closed-cell structure PBAS foam of high blowing ratio (density about 0.05 g/cm³) could be obtained by adding 3 phr DCP. To manufacture expanded PBAS foam under 0.1 g/cm³ using a chemical blowing agent, the storage modulus of the matrix polymer should exceed the loss modulus by enough to stabilize growing bubbles. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2443–2454, 2001

Key words: poly(butylene adipate-co-succinate); viscoelasticity; peroxide curing; foam

INTRODUCTION

Most foamed packing materials are polyolefin foam and have a closed-cell structure, which provides resiliency for packing applications.¹ However, these products have environmental problems. Since the early 1970s the subject of biodegradable plastics has acquired a rapidly growing literature of academic research articles. The utility of biodegradable polymers² has received much attention due to their potential

impact upon the complex issue of plastic waste management. Among them, aliphatic polyesters are getting more attention as a class of biodegradable polymers. About 65 years ago Carothers et al. performed systematic work on the polycondensation reaction of aliphatic polyesters to produce synthetic fibers, but they could not successfully increase their molecular weights over 5000; hence, reaction products made of them were weak and brittle.³ Takiyama et al.^{4–6} started to develop biodegradable aliphatic polyesters in a glass flask in 1989, and in 1990 they succeeded in increasing the molecular weight to in excess of 5000 with the use of new catalysts and coupling reactions. Poly(bu-

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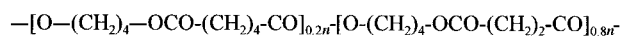
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tylene adipate-*co*-succinate) (PBAS) is one of the promising biodegradable aliphatic polyesters. One of the major potential applications of biodegradable polymers is foamed articles. The expansion process of a thermoplastic polymer relies upon the expansion of a gaseous phase dispersed throughout the polymer melt.¹ The gaseous phase may be generated by the separation of a dissolved gas, the vaporization of a volatile liquid, or the release of a gas from a chemical reaction in a chemical blowing agent (CBA). In processes where foam expansion is accomplished by heating, bubbles need to be stabilized by crosslinking the polymer. This is particularly true for a process employing a CBA that decomposes exothermically. Crosslinking stabilizes the expanding bubbles by sharply increasing the extensional viscosity of the polymer, thereby preventing the cell walls from draining. Crosslinking is also required for a physical blowing agent (PBA) process in which foam expansion is accomplished by heating rather than by decompression. Thus, to prepare low-density aliphatic polyester foam by use of a decomposable CBA, it is necessary to crosslink the polymer. We identified that PBAS can be crosslinked by a peroxide.⁷ In this work we studied the viscoelastic behavior and expansion characteristics of peroxide crosslinked PBAS. To formulate an appropriate CBA, the gas evolution behavior of the blowing agent was investigated. The density, morphology, and hardness of expanded PBAS were measured. The effect of the foaming temperature, additive, and curing agent content when foaming PBAS using a CBA was investigated.

EXPERIMENTAL

Materials

The PBAS used in the experiment was from a sample of SG2109 provided by SK Chemicals Co., Ltd.. To minimize moisture effects and hydrolysis, the PBAS was dried in a vacuum oven at 70°C for 12 h before use. Dicumyl peroxide (DCP) was from Nippon Oil & Fats Co. The CBA (4:1 azodicarbonamide:*N,N*-dinitroso penta-methylene, ACP) and urea activator (Cellex A) were obtained from Kum Yang Co. All chemicals were used without further purification. The chemical structure of PBAS is shown below.



Poly(butylene adipate-*co*-succinate) (PBAS)

Rheometric Dynamic Spectrometer Examination

The PBAS was compounded with DCP in a Brabender Plasticorder (PLE331) equipped with a cam-type rotor (model W50). The PBAS was melted at 115°C for 3 min, then DCP was added and mixed for 3 min. The compound was subsequently compression molded into sheets (2-mm thickness) using a hydrodynamic press (150°C). The viscoelastic properties of PBAS and crosslinked PBAS were ascertained on a Rheometrics RDS using a parallel plate frequency sweep. Frequencies of 0.16–100 rad/s and 2% strain were used.

CBA Decomposition Behavior

The decomposition temperature¹ of the ACP CBA was measured with respect to the urea activator content. The foaming agent (0.15 g) was placed in a test tube, and the tube was connected to a gas buret by a rubber hose and then set in a thermostatic oil bath. The released volume of gas from the decomposition of the CBA was measured.

Foam Preparation

The PBAS was compounded with DCP and foaming agent in a Brabender Plasticorder at 110°C and was subsequently compression molded into sheets (2.5-mm thickness) using a hydrodynamic press (100°C) for 1 min. The sheet was cut into 20 × 20 mm specimens and expanded in a forced convection oven at 150, 160, and 170°C.

Measurements

The foam density was measured with a densimeter (Mirage Co.) and the blowing ratio was calculated using the following equation:

$$\text{Blowing ratio} = \frac{\text{PBAS density (1.22 g/cm}^3\text{)}}{\text{foam density (g/cm}^3\text{)}}$$

The cross-sectional morphology of the expanded foam was observed with optical microscopy (AxioLab Pol 0.5, 12.5× magnification, Zeiss), and the Asker C hardness was tested.

RESULTS AND DISCUSSION

Viscoelastic Properties

The viscoelastic properties of a polymer are an important factor for processing. Figure 1 shows

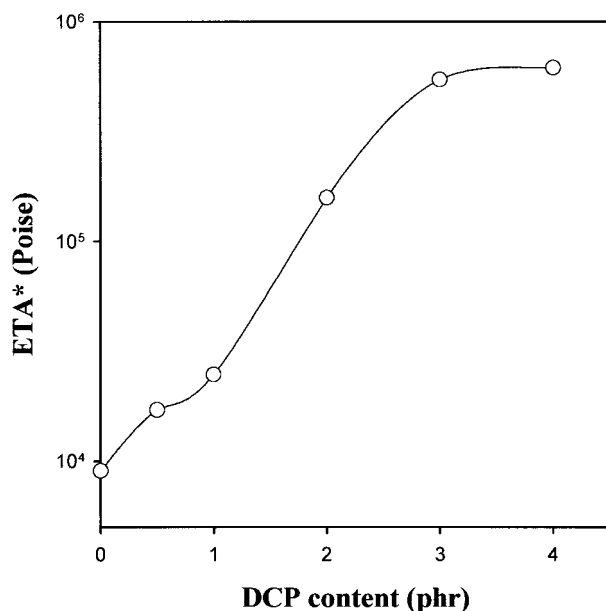


Figure 1 The effect of the DCP content on the viscosity of crosslinked PBAS at 170°C (1 rad/s frequency).

the viscosity of crosslinked PBAS with respect to the DCP content at 170°C.

It is noteworthy that the melt viscosity of crosslinked PBAS increased as the DCP content was increased. A possible justification could be that the viscosities of the polymer melts and polymer solution were considerably larger than those of low molecular weight liquids. Experimental observations showed that the viscosity of polymers is dependent on the molecular weight.⁸ Another justification is that as a polymer flows, polymer chains slip past each other. In addition, crosslinking restricts interchain slippage and the viscosity rises. Thus, this indicates that PBAS, a saturated aliphatic polyester, was effectively crosslinked by the simple addition of the organic peroxide DCP. Figure 2 shows the storage modulus (G') and loss modulus (G'') change of PBAS with the frequency.

In the PBAS the G'' surpassed the G' in most frequency ranges, and the gap between G' and G'' was decreased with increasing frequency; thus, the G'' exceeded the G' over 40 rad/s. This implied typical time dependent viscoelastic behavior of the thermoplastic polymer: as the strain rate became higher, the elasticity became higher as well. Table I summarizes the crossover frequency in the G' and G'' of PBAS cured by DCP. The crossover frequency shifted to low frequency with increasing crosslinking and lower temperature. In the PBAS cured with 2

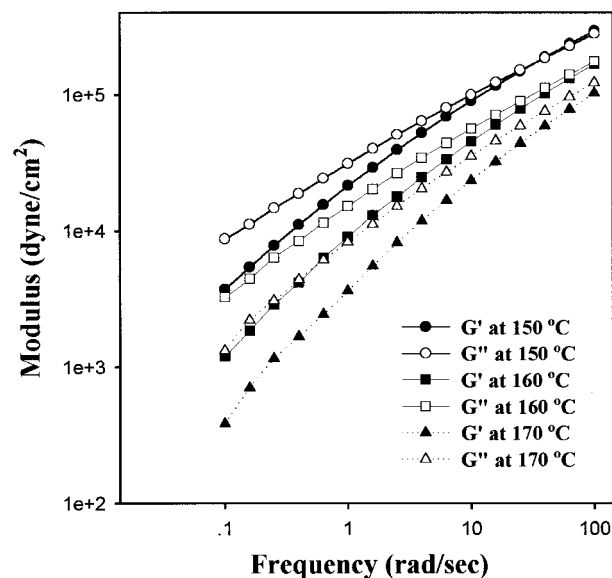


Figure 2 The modulus change of PBAS as a function of the frequency at various temperatures.

phr DCP, the G' was above G'' in the entire frequency range (Fig. 3). It was notable that the G' and G'' of PBAS cured with 4 phr DCP exhibited little time dependency (Fig. 4).

This may be explained by the following: first, generally, the higher the molecular weight of a polymer, the higher the elasticity, because chain entanglement restricts chain slippage, which is an irreversible deformation; second, enhancement of the entropy elasticity⁹ by crosslinking could be considered to be as in the rubber.

On the other hand, the test procedure that is usually used for the melt strength involves in-

Table I Crossover Frequency in G' and G'' of PBAS Cured by DCP with Frequency Range of 0.16–100 rad/s

Code	Temperature		
	150°C	160°C	170°C
PBAS	40 rad/s	Non ^a	Non
PBAS + 0.5 D ^b	10 rad/s	25 rad/sec	Non
PBAS + 1D	2.5 rad/s	4 rad/s	10 rad/s
PBAS + 2D	All ^c	All	All
PBAS + 3D	All	All	All
PBAS + 4D	All	All	All

^a G'' surpassed G' in the entire frequency range.

^b The number means the content of DCP (phr).

^c G' surpassed G'' in the entire frequency range.

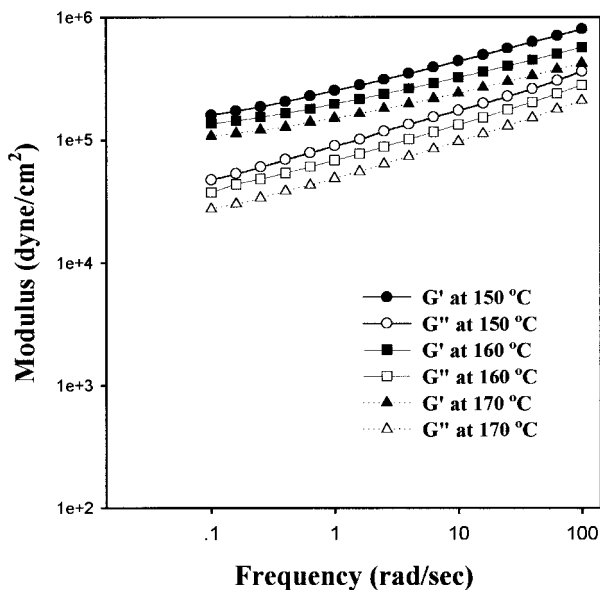


Figure 3 The modulus change of PBAS cured with 2 phr DCP as a function of the frequency at various temperatures.

creasing the wind-up speed and noting the force level when the filament breaks.¹⁰ If the melt strength of a polymer is not sufficient, it is difficult to process the polymer in the course of film and foam manufacturing. The melt strength of a polymer depends on the viscosity, G' , and G'' . Much of work was generated by the inherent dif-

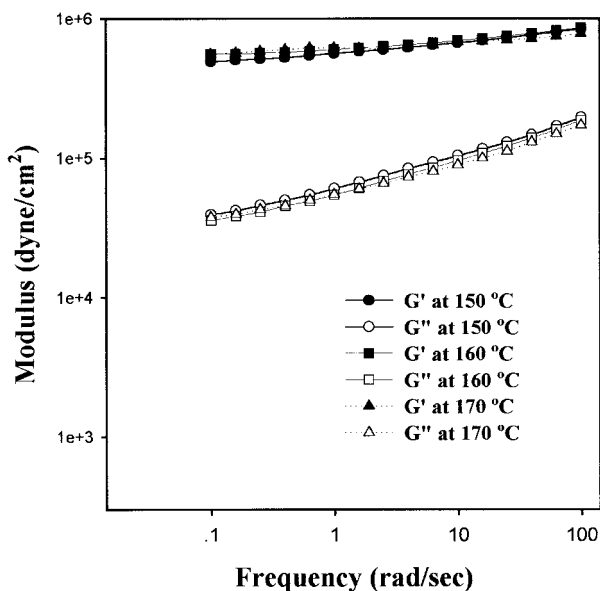


Figure 4 The modulus change of PBAS cured with 4 phr DCP as a function of the frequency at various temperatures.

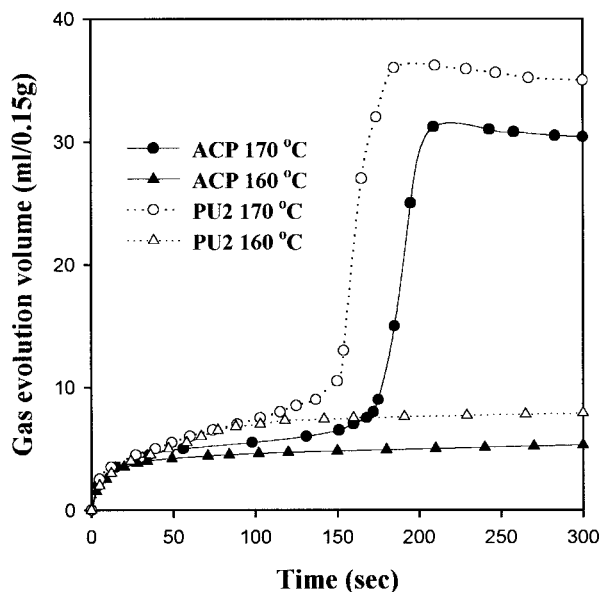


Figure 5 The gas evolution behaviors of foaming agent ACP and ACP with 2 phr urea activator (PU2).

ficulty in synthesizing high molecular weight aliphatic polyesters through the polycondensation of diols and dicarboxylic acids.¹¹ In response to this limitation, the use of chain extending agents, as well as multifunctional alcohols and acids, was reported.^{12,13} One of the major purposes of this work was to improve the melt strength of ali-

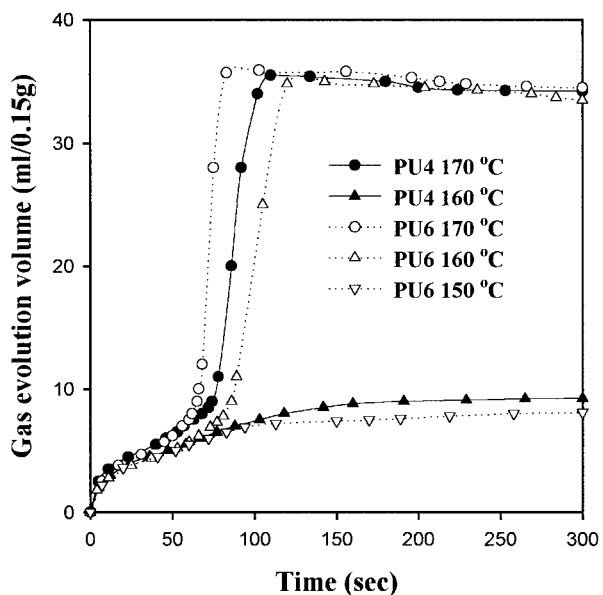


Figure 6 The gas evolution behaviors of foaming agent ACP and 4 phr urea activator (PU4) and ACP and 6 phr urea activator (PU6).

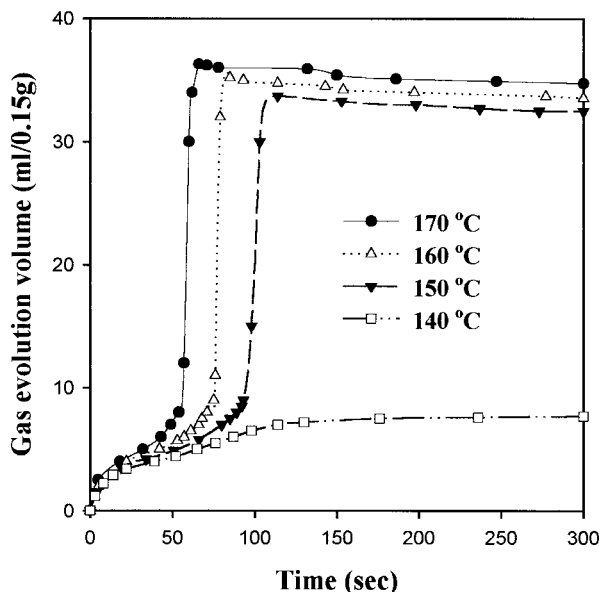


Figure 7 The gas evolution behaviors of foaming agent ACP and 8 phr urea activator (PU8).

phatic polyesters in order to enhance the processibility of PBAS. Taking our results into consideration, we concluded that the simple addition of organic peroxide can increase the viscosity and elasticity of aliphatic polyesters without any functional group.

CBA Decomposition Behavior

The various compounds used for foaming polymers may be classified in several ways.¹ The

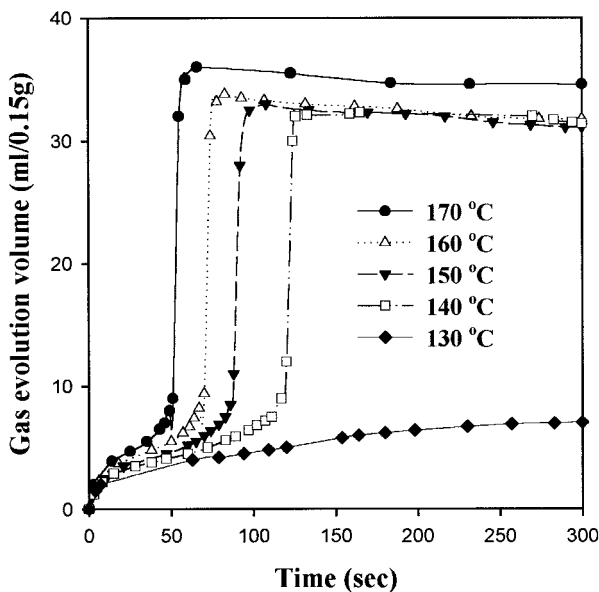


Figure 8 The gas evolution behaviors of foaming agent ACP and 10 phr urea activator (PU10).

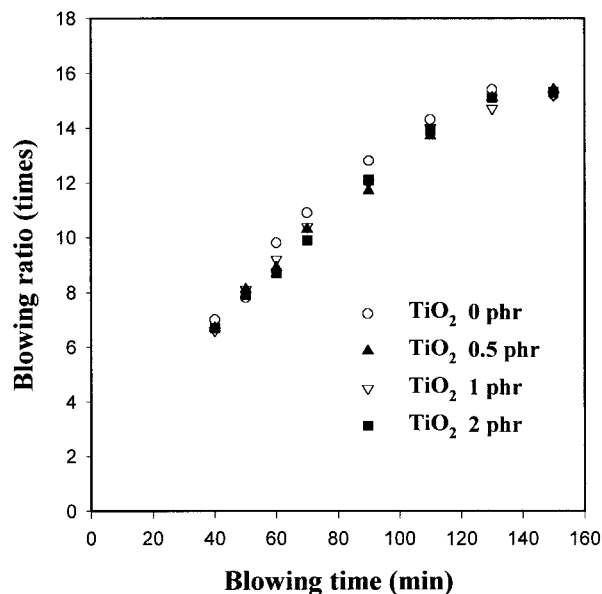


Figure 9 The effect of the TiO₂ content on the blowing ratio of 2 phr DCP cured PBAS foam (150 °C foaming temperature, 10 phr PU8 blowing agent).

most general classification scheme is based on the mechanism by which gas is liberated by these compounds, which are blowing agents in this case. CBAs are individual mixtures of compounds that liberate gas as a result of a chemical reaction, including thermal decomposition, or as a result of a chemical reaction of CBAs or interactions of CBAs with other components of the formulation. Most CBAs are solid. There are two advantages to using CBAs.¹ It is easy to introduce them into the composition to be foamed, and they are easily processed with ordinary equipment. Production costs are thus considerably lower for CBAs than they are for volatile liquids and gases, which must be stored in specialized equipment. ACP is an organic blowing agent of the azodicarbonamide group.¹⁴ Azodicarbonamide conforms to German Federal Health Office (BGA) and FDA recommendations for the manufacture of articles for food contact applications. It has excellent storage stability. Unlike a number of other CBAs, it is self-extinguishing when in contact with an unprotected flame and it does not support combustion. The decomposition reaction of the CBA must take place when the polymer is at the proper melt viscosity or degree of cure. Activators that can lower the blowing agent's decomposition temperature are available, thus affording greater

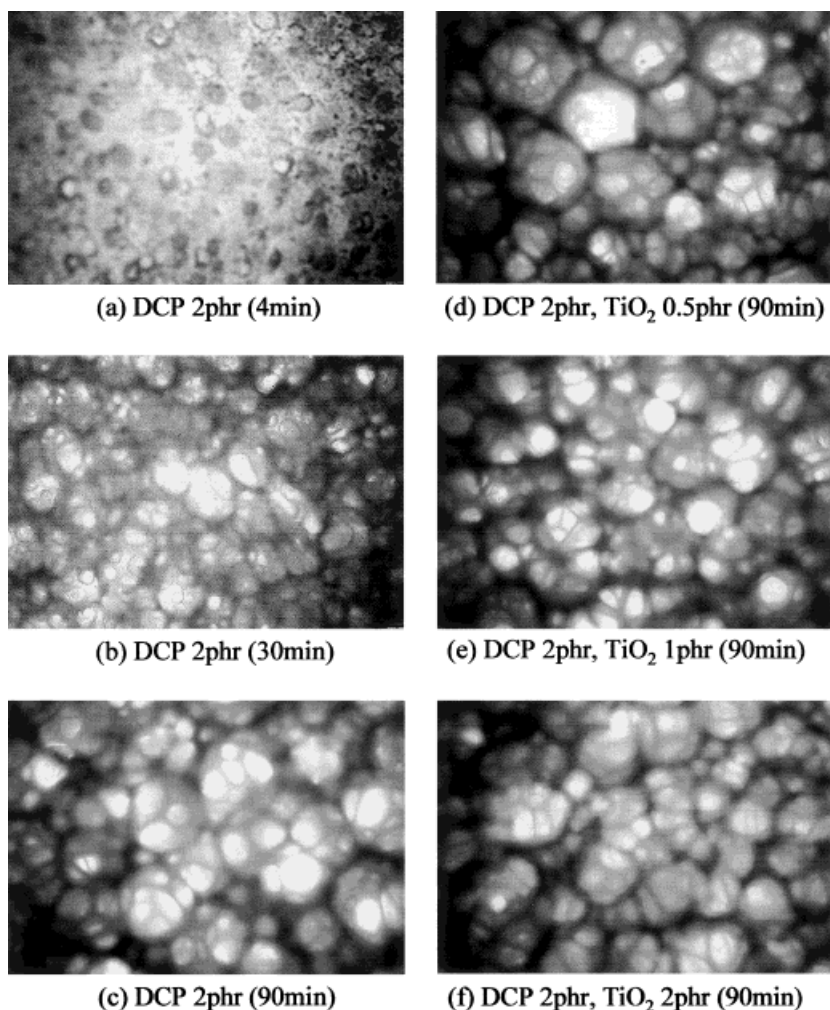


Figure 10 Cross-sectional microphotographs of PBAS foam (150°C foaming temperature, 10 phr PU8 blowing agent).

flexibility to the formulator. The gas evolution behaviors of the foaming agents are shown in Figures 5–8.

The ACP initiated decomposition at 170°C after 3 min. The decomposition time of the foaming agent PU2 (ACP + 2 phr urea activator) was shortened about 20 s, but the decomposition temperature was not shifted to a low temperature. As the urea activator was added to the ACP in small amounts, the decomposition time of the blowing agents was shortened and decomposition was initiated at lower temperatures. The properties that an ideal CBA should possess were described in detail previously.^{14,15} These requirements are still valid today. The primary criterion governing the choice of a blowing agent for expanding a particular plastic

is its decomposition temperature. The blowing gas must be evolved within a defined temperature range that includes the processing temperature of the plastic concerned, and the blowing agent should not decompose at the processing temperature range. In this study we set up the foaming temperature of PBAS within 150–170°C by taking the thermal stability of the PBAS compounding temperature (110°C) into consideration. A compound of ACP and 8 phr urea activator (PU8) initiated decomposition at 150°C. When ACP was combined with 10 phr urea activator (PU10), it decomposed even at 140°C and there was a possibility of premature foaming during compounding. Thus, it was expected that the optimum formulation for the blowing agent for PBAS was PU8.

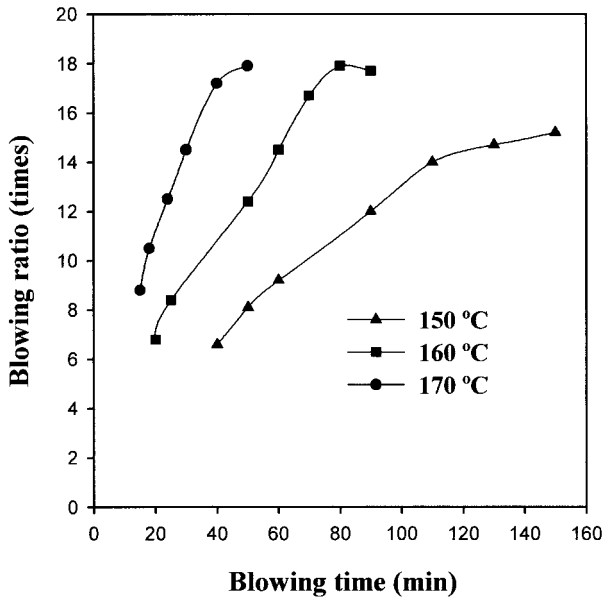


Figure 11 The effect of the temperature on the blowing ratio of PBAS foam for PBAS + 2 phr DCP + 10 phr blowing agent (PU8) + 1 phr TiO₂.

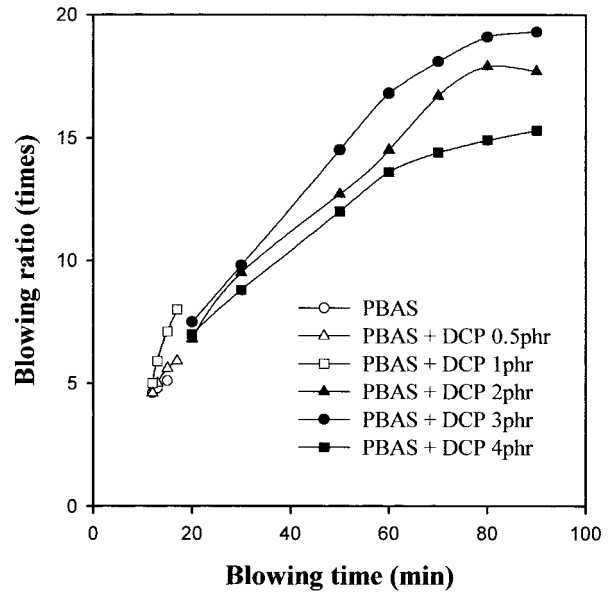


Figure 13 The relationship between the DCP content and the blowing ratio of PBAS foam (160°C foaming temperature) for PBAS + 10 phr PU8 blowing agent + 1 phr TiO₂.

Foam Preparation

Effect of Expanding Condition

The first step in producing a foam is the formation of gas bubbles in a liquid system.¹⁶⁻¹⁹ If the bub-

bles are formed by supersaturation of gas, which is an initially truly homogeneous liquid, the process is called self-nucleation. If a second phase is initially present, especially if it is in the form of

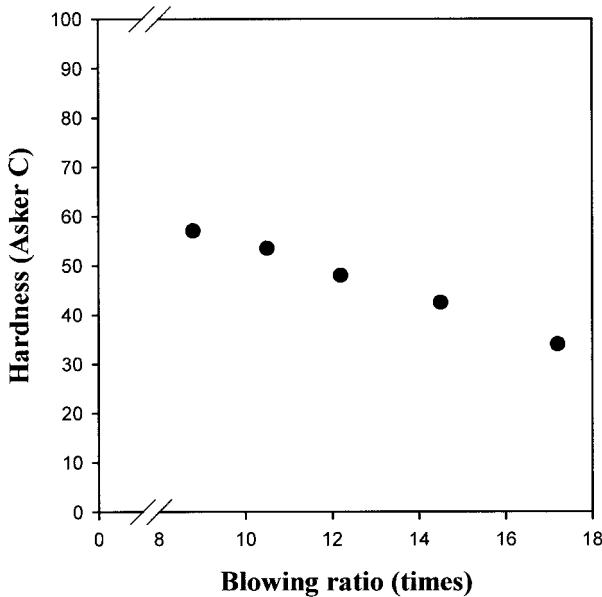


Figure 12 The hardness (Asker C) change of the PBAS foam with respect to the blowing ratio (170°C foaming temperature) for PBAS + 2 phr DCP + 10 phr PU8 blowing agent + 1 phr TiO₂.

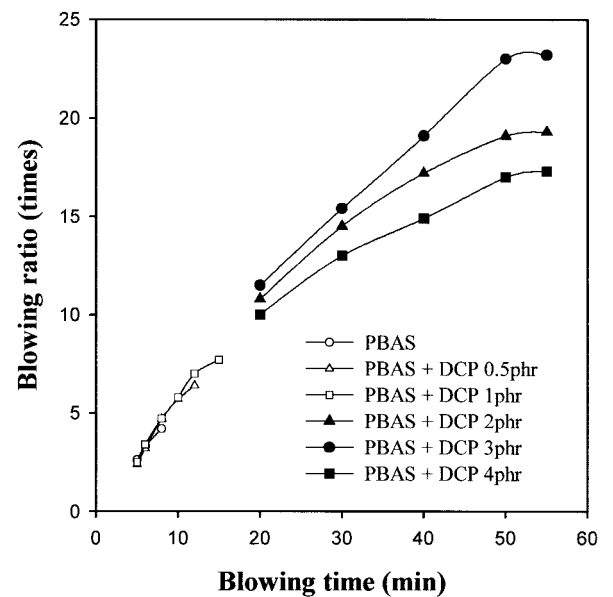


Figure 14 The relationship between the DCP content and the blowing ratio of PBAS foam (170°C foaming temperature) for PBAS + 10 phr PU8 blowing agent + 1 phr TiO₂.

Table II Actual Measured Foam Densities (g/cm^3) of PBAS Cured by DCP at Foaming Temperature of 170°C for PBAS and 10 phr PU8 Blowing Agent + 1 phr TiO_2

Blowing Time (min)	PBAS	PBAS + 0.5D ^a	PBAS + 1D	PBAS + 2D	PBAS + 3D	PBAS + 4D
5	0.462 ^b	0.500	0.480			
6	0.364	0.375	0.353			
8	0.286	0.255	0.254			
10		0.211	0.207			
12		0.188	0.171			
15			0.156			
20				0.111	0.104	0.120
30				0.083	0.078	0.092
40				0.070	0.063	0.081
50				0.063	0.052	0.071
55				0.062	0.052	0.069

^a The number means the content of DCP (phr).

finely divided solids, the bubbles will usually form more easily at the liquid–solid interface; the bubbles are said to form by a nucleation process. The solid particles are called nucleation agents. Titanium dioxide (TiO_2) is widely used as white pigment for plastics and rubber.²⁰ The whiteness of TiO_2 originates from its high refractive index. The foaming agent used in this work exothermically decomposes (28.6 kcal/mol) and can cause yellowing. So, the effect of TiO_2 as a cell nucleating agent and white pigment was examined. Figure 9 shows the blowing ratio of crosslinked PBAS (2 phr DCP) foam with respect to the TiO_2 content. Figure 9 shows that the blowing ratio was not affected by TiO_2 . Figure 10 displays cross-sectional microphotographs of PBAS foam.

After foaming for 4 min [Fig. 10(a)], the morphology appeared to be mixed nucleated cells and growing cells. As time elapsed the growing cells met each other to form a straight line boundary [Fig. 10(b)], and then a stabilized cell structure [Fig. 10(c)] was observed. It could be that the morphology of the PBAS foam was not influenced by TiO_2 [compare Fig. 10(c–f)], and we supposed that the decomposition residuals of CBA acted as a cell nucleating agent. Although the surface of the foam was thinly yellow, 1 phr TiO_2 almost eliminated the yellowness and hereafter the content of TiO_2 was fixed at 1 phr. The temperature dependence of the foaming characteristics of PBAS is shown in Figure 11. The blowing ratio was increased and

the foaming time was decreased with increasing temperature. The hardness (Asker C) of the PBAS foam was measured (Fig. 12) and compared with polystyrene foam. The density and hardness of the polystyrene foam were $0.03 \text{ g}/\text{cm}^3$ and 45, respectively. In spite of the high density, the hardness of the PBAS foams was higher than polystyrene foam. This may be due to the higher glass-transition temperature of polystyrene (about 100°C) than PBAS (about -28°C).

Effect of DCP Content

Regardless of the type of blowing agent, the expansion process involves three fundamental steps: bubble initiation (nucleation), bubble growth, and stabilization.²¹ Nucleation begins at an initiation site within a polymer melt that has been supersaturated with blowing agent. This supersaturated state is achieved by either decompressing an equilibrium system of a polymer and a PBA or heating a polymer containing a decomposable CBA. Once a bubble reaches critical size, it continues to grow as the blowing agent rapidly diffuses into it. This growth continues until the bubble stabilizes or ruptures. The thin, highly stretched cell walls of a thermoplastic melt are unstable and are bound to rupture if not stabilized. Two methods of stabilization are used: viscosity rise–solidification (PBAs) and crosslinking (CBAs). In processes where foam expansion is accomplished by heating, bubbles need to be

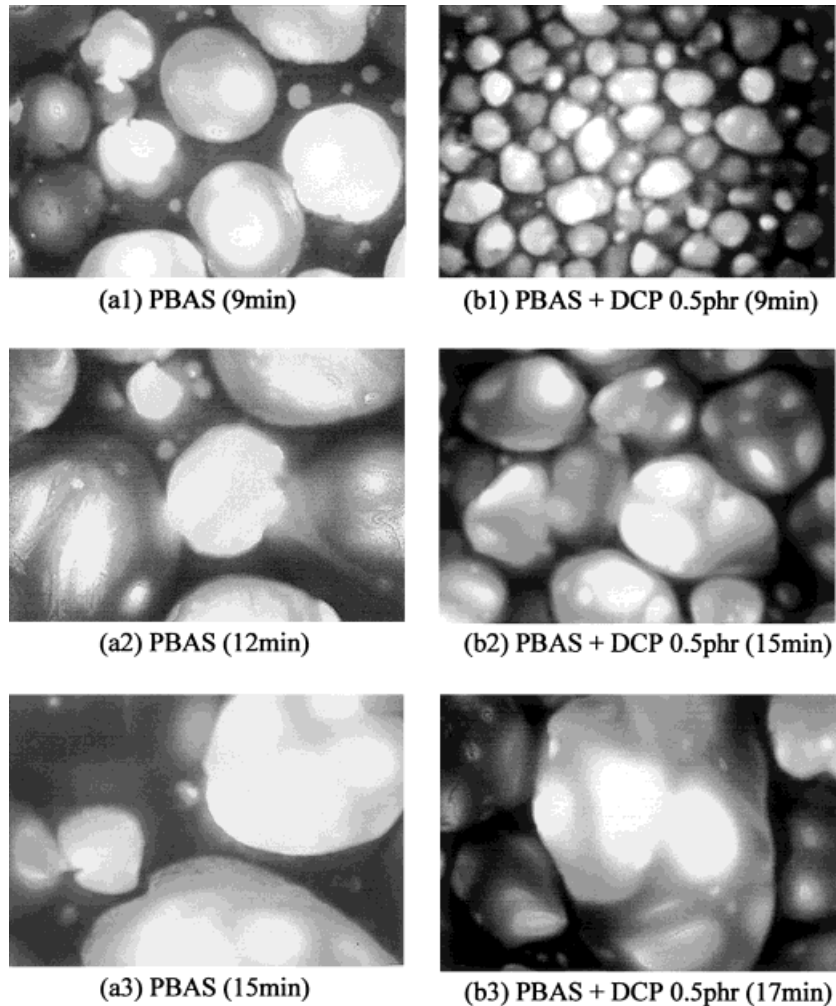


Figure 15 Cross-sectional microphotographs of PBAS foam with respect to the blowing time and DCP content (160°C foaming temperature) for PBAS + 10 phr PU8 blowing agent + 1 phr TiO₂.

stabilized by crosslinking the polymer. This is particularly true for a process employing a CBA that decomposes exothermically. Crosslinking stabilizes the expanding bubbles by sharply increasing the extensional viscosity of the polymer, thereby preventing the cell walls from draining. Benning²¹ reported that excessive crosslinking restricts foam expansion, while insufficient crosslinking results in bubble rupture. Optimum crosslinking is the most critical requirement for optimum foam expansion. The optimum level of crosslinking is normally determined by actual foam expansion trials for a given process and product. Figures 13 and 14 and Table II show the effect of the DCP curing agent content on the blowing ratio of crosslinked PBAS foam.

The blowing ratio of PBAS was raised about 4–5 times and further expansion caused cell rupture. The blowing ratio was increased to 6 and 8 with the addition of 0.5 and 1 phr DCP, respectively, but further expansion caused cell rupture. However, above 2 phr DCP the blowing ratios of crosslinked PBAS foams were sharply increased to over 15-fold. An expanded foam of maximum blowing ratio was obtained by adding 3 phr DCP. When 4 phr DCP is added, it is assumed that the viscosity and elasticity are so high that cell growth is restricted. Considering these results from the viscoelastic behavior of crosslinked PBAS, it is manifest that to manufacture expanded PBAS foam of under 0.1 g/cm² using CBA, the G' of the matrix polymer should ex-

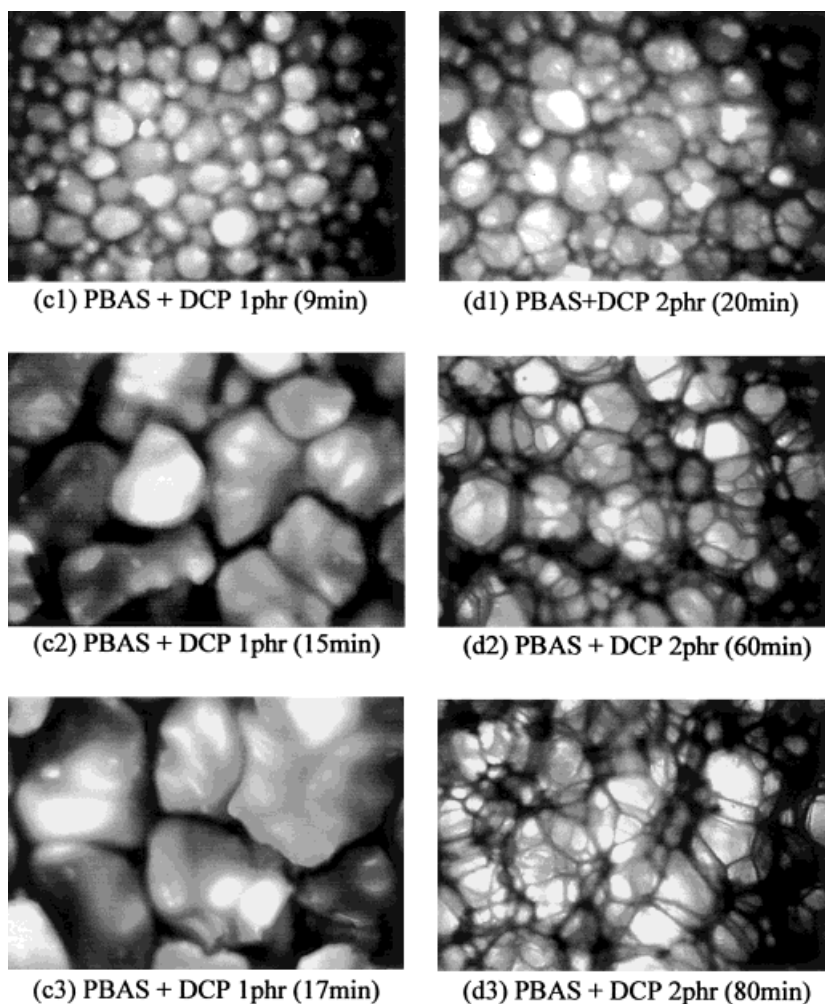


Figure 15 (Continued)

ceed G'' by enough to stabilize growing bubbles. Figure 15 shows the cross-sectional morphology of the expanded foams.

After expanding for 9 min [Fig. 15(a1)] in the case of PBAS, the morphology appeared as oval shaped cells were formed and the walls between cells were thick. As time elapsed the growing cells met and collapsed [Fig. 15(a2)], and finally large continuous structure cells existed (a3). A morphological observation of foams with 0.5 and 1 phr DCP in the early stage of expanding [Fig. 15(b1,b2)] revealed a large number of cells were; as expanding progressed, the morphology was similar to that of PBAS. When adding above 2 phr DCP, honeycomb shaped cell structure PBAS foams [Fig. 15(d–f)] were maintained in the course of expansion even at the high blowing ra-

tio. This indicated that the growing cells were effectively stabilized by crosslinking.

CONCLUSION

The viscosity and elasticity of crosslinked PBAS increased as the content of curing agent was increased. This indicated that the processibility of PBAS could be improved by the simple addition of DCP. A proper formulation of the blowing agent (ACP/urea activator = 100:8 w/w ratio) was obtained to prepare expanded PBAS foam. The morphology of the expanded foam was little influenced by TiO_2 and we supposed that the decomposition residuals of CBA acted as cell nucleating agents. Adding more than 2 phr DCP allowed a closed-cell

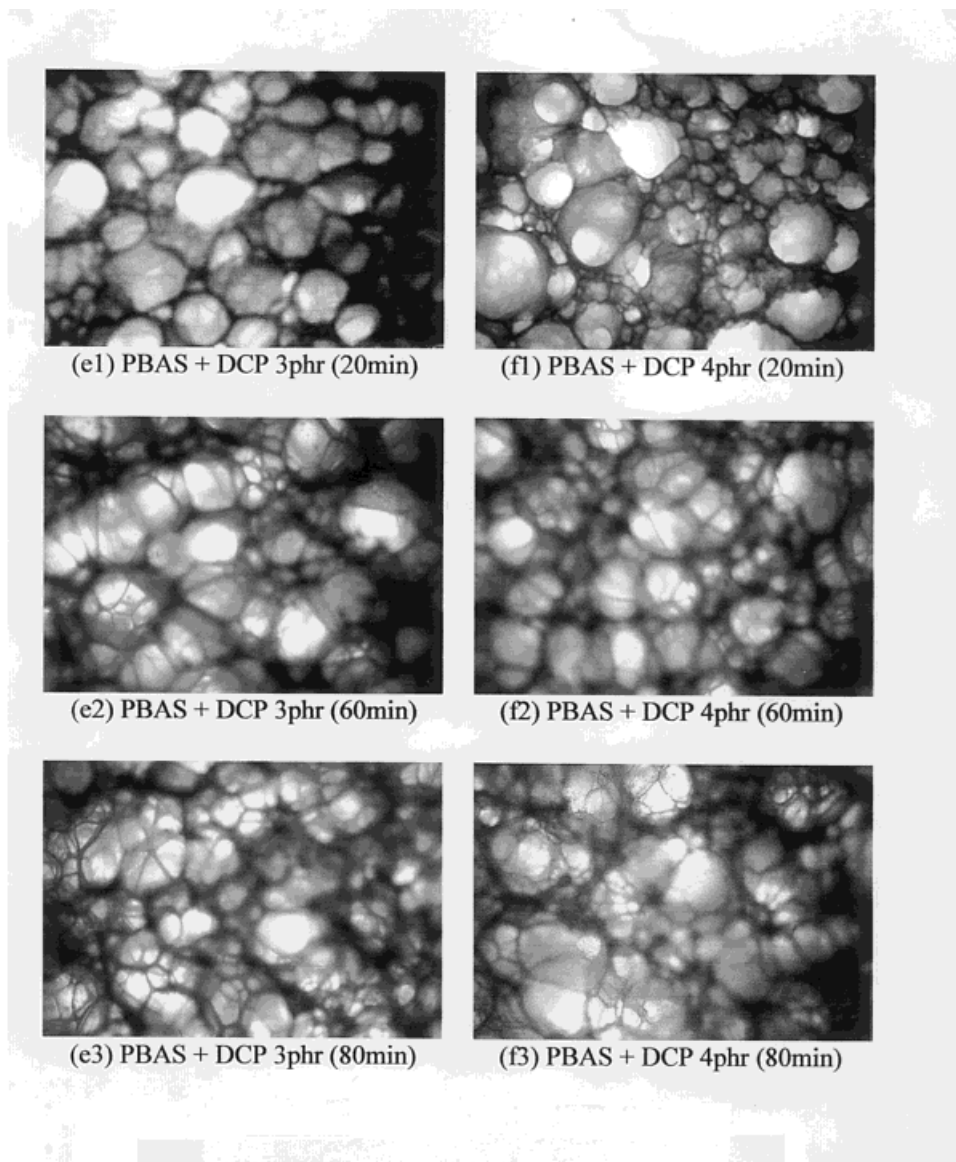


Figure 15 (Continued)

structure PBAS foam of high blowing ratio (about 0.05 g/cm^3 density) to be obtained. To manufacture expanded PBAS foam of under 0.1 g/cm^2 using CBA, the G' of the matrix polymer should exceed the G'' enough to stabilize growing bubbles.

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