

BI-MODAL MICROCELLULAR MORPHOLOGY EVALUATION IN POLYCARBONATE FOAMS DEVELOPED USING TWO-STEP DEPRESSURIZATION FOAMING PROCESS

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Abstract

This report focuses on the manufacturing of microcellular polycarbonate (PC) foams with bi-modal cell size distributions using carbon dioxide (CO₂) as a blowing agent through solid state batch foaming technology. The sorption and desorption behaviours of CO₂ in polycarbonate for various pressures were investigated. The effects of processing parameters such as foaming temperature, foaming time and saturation pressure on relative foam density, cell sizes and cell densities of the bi-modal foams were discussed in detail. The glass transition temperature (T_g) of the polymer/gas blend was found to have a decent linear association with the absorbed carbon dioxide, and foaming takes place above T_g of the polymer/gas blend. For manufacture of bi-modal polycarbonate foams, a two-step batch depressurization process is used which produces both small and large cells, which exhibit good improved properties compared to unimodal foams.

Keywords

Polymer, Bimodal cellular structure, Polycarbonate, solid-state batch foaming, two step depressurization process

1. Introduction

Foam is a substance made by trapping air or gas inside a solid or liquid. In most of the foams, the volume of gas is much larger than solid or liquid, with thin films separating the regions of gas. Foams may be closed-cell or open-cell, the closed cell foams have enclosed cells surrounded by solid material, while in open cell gas pockets connected to each other. The cells are arranged in disorder manner with different sizes.

Polymer foams or cellular plastics are referred as sponge or expanded plastics, generally consists of a minimum two phases, a solid polymer matrix and a gaseous phase derived from a blowing agent[1]. In 1930's the first polymeric foam development was started and first patented foam(1931) was macrocellular poly-styrene with cell size of above 100µm. Suh et al was pioneer professor, who developed the solid state batch foaming. The principal behind this invention was to reduce the material density and reduce the cost[2]. The Polymer foams divided into thermoplastics and thermosets. The thermoplastics can be recycled but thermoset's cannot be recycled because they are heavily cross-linked.

The gas used to produce foam is known as blowing agent, it may either chemical or physical. Chemical blowing agents are chemicals that react chemically in the process. Physical blowing agents are gases that don't react chemically in the foaming process[3].

Microcellular foams are foamed plastics having cell sizes around 10µm with a cell density more than 10⁹ cells/cm³[4]. Martini et al was one who first developed the microcellular foams in high impact polystyrene using nitrogen gas as blowing agent (1982,1984)[5]. Comparison with solid polymers, microcellular foams exhibit enhanced energy absorption rate and fatigue life, high impact strength, low thermal conductivity and high thermal stability, high toughness with great reduced material weight and cost. Therefore microcellular foams have greater applications in packing, insulation, aircraft and automotive industries[6]. Microcellular foaming process is comprised with saturation and subsequent by foaming process. In saturation process, gas molecules penetrate into polymer chains which have free volume and changes its mobility and free volume characteristics[7]. The attraction between polymer molecules become weaker because of dissolved gases and make molecular movement active. If diffused gases are more, the glass transition temperature of polymer will drop[8]. In saturation process microcells or micro pores are formed within the plastic due to induction of thermodynamic instability. Subsequently, immediate foaming process is followed by quenching process to stabilize the cell formation.

In a conventional foaming process, chlorofluorocarbons and flammable hydrocarbons are used as a blowing agent which deflects the ozone layer. Microcellular foaming process uses carbon dioxide and nitrogen as blowing agents which are environmental friendly[9].

Some of the studies are evident that ultra-low dense foams in cyclic batch foaming will produce by cyclic foaming (repeated foaming)[10]; the minimum densities obtained in the cyclic foaming is reported in the Table 1.

Since polycarbonate is a widely used thermoplastic, it has gained considerable attention by introduction of microcellular structure in it. However, bimodal cell size distributions in which larger cells surrounded by small cells are produced using two step depressurization process. The bimodal cell structure exhibits good properties such as low thermal conductivity, reduced mass density and good mechanical properties. By introducing bimodal cell structure into polycarbonate foams, they improve performances and their applications.

The aim of this article is to study the foaming behaviour of polycarbonate sheets using two step depressurization batch foaming process for different parameters.

Table 1: Studies on microcellular foaming

SL. No	Author	Year	Study parameters	Remarks	References
1	Abhishek Gandhi.	2013	Foaming ratio and cell morphology	Ultra low density porous microcellular foams produced using ultrasound excitations	[10]
2	Seo et al.	2011	Weight gain and Foaming ratio, cell morphology	Repeated batch process enhance the formation of MCPs which leads to improve cell morphology and foaming ratio which cannot achieve by single batch process	[11]
3	Cho et al.	2013	Foaming ratio, diffused reflectivity and cell morphology	Repetitive foaming process not only influences foaming ratio but also influences cell morphology. Diffused reflectivity is proportional to foaming ratio of material.	[12]

Table 2: Studies on microcellular foaming on Polycarbonate

SL. No	Author	Year	Study parameters	Remarks	References
1	Jung-Hwan Seo.	2008	Cell Morphology and Light Transmission	The cell density of MCPs increases by decrease in the light transmission ratio, which shows wide change in bandwidth when saturation pressure is low	[13]
2	Ming Yi Wang.	2010	Effect of Vibration Frequency and vibration Amplitude on Cell Morphology.	Foamed samples with better cell morphology were obtained as vibration frequency increased. With the increase of the vibration amplitude, cell morphology initially improved then became worse, which means there exists an optimum vibration amplitude for microcellular foaming of PC plastics	[14]
3	Yong Yang.	2010	Equilibrium Sorption of CO ₂ , Morphology of Foamed blebs and Morphology of Un-foamed Blends of PC and PS, Cell Nucleation and Growth.	Showed that it take at least 18 hours fir PS and 36 hours for PC reach equilibrium sorption and the equilibrium mass uptakes of CO ₂ in them were 6.95wt%, 7.83wt% and 8.17wt%. Blend morphology influences the cell morphology of a foamed blend.	[15]
4	Jung-	2009	Saturation	Diffused reflection occurs via micro	[16]

	Hwan Seo.		Pressure, Desorption time & Cell Morphology, Reflectivity.	cell and reflectivity shows a growing tendency with foaming rate increase.	
5	Young Ho Kim.	2011	Solubility, Foaming Ratio, Dielectric Constant and cell morphology	In accordance with the foaming temperatures, the foaming ratio of specimens tended to be increased while the dielectric constant decreased	[17]
6	Jung-Hwan Seo.	2011	Foaming ratio and Cell Morphology	At same amount of dissolved gas, cell formation was more active in specimens when exposed to lower saturation pressure	[18]
7	B. S. Shi.	2011	Saturation Pressure, Pressure drop rate, Shear rate and cell Morphology	Study investigated the effects of processing parameters on the cell morphology of the foamed PC plastics using a self-designed dynamic simulation foaming setup. A higher pressure drop rate will cause a higher thermodynamic instability of the gas-polymer melt system, which will provide a higher impetus for cell nucleation.	[19]
8	Guan et al.	2012	Effect of Processing Parameters on Tensile properties and tensile Behaviours of Un-foamed and Foamed	the stress-strain curves of unformed and plasticized microcellular foamed PC have different characteristics and that all of the tensile modulus, tensile strength and elongation at break were decreased as the relative density decreases.	[20]
9	Han et al.	2012	Gas Desorption, Foaming ratio, Cell Morphology	The hues (H) of the coloured polymer samples tended to move clockwise in Munsell's hue circle as their cell size became smaller and cell density increased. The value of lightness (V) of a colour increased with a smaller cell size and a greater cell density.	[21]
10	Ma et al.	2014	Gas saturation & desorption, Effect of saturation pressure, Foaming temperature & Foaming time on unimodal & bimodal	Effect of absorbed gas on the glass transition temperature of the polymer/gas mixture was discussed. Bimodal-cell structure foams have been prepared by releasing the pressure in a two-step batch process. The degree of depressurization in the first step and the foaming temperature both influence the cell morphology significantly	[22]

2.Experimental

Materials

Polycarbonate (PC) sheets are used and CO₂ gas is used as the physical blowing agent and supplied gas at 50 bar pressure.

Foaming methodology:

The foaming experiment is conducted with commercially available polycarbonate sheet; specimens were prepared with dimensions of 30 mm x 20 mm x 1 mm. Figure 1 shows the experimental setup of the foaming process. A two-step depressurization process was used to develop the bimodal PC foams. In the first step, the polycarbonate samples were weighed then placed in autoclave and saturated with carbon dioxide (CO₂) at a given pressure and room temperature for 20 hours. Subsequently, the autoclave was depressurized to an given pressure within 10s and maintain the pressure for 4h. Once the second step completely depressurization was conducted, then the samples were taken out from autoclave and weighed the samples to

know the gas absorption, then immersed in the hot glycerine bath at 160° for 40s to get foamed and subsequently followed by water quenching up to 10s.

The percentage of gas absorbed by the specimen was measured by the gravimetric method as described by the Nalawade et al.

$$\text{Percentage of gas absorbed [wt\%]} = \frac{W_f - W_0}{W_0} \quad (1)$$

Here, W_f refers to weight of the specimen after saturation and W_0 refers to weight of the specimen before saturation

Similarly the foaming ratio of the specimen was measured indirectly through the density.

$$\text{Foaming ratio [\%]} = \frac{D_0 - D_f}{D_0} \quad (2)$$

Here, D_0 refers to density of the specimen before foaming and D_f refers to density of the specimen after foaming

Experimental setup:

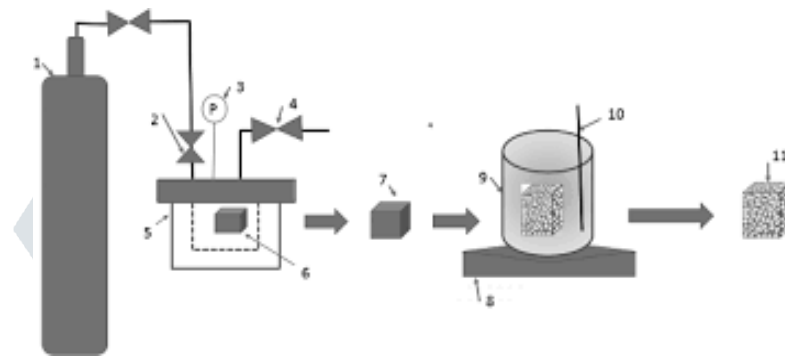


Figure 1: Schematic of microcellular foaming process

1- High-pressure CO2 cylinder, 2- Gas inlet valve, 3- Pressure gauge, 4- Gas outlet valve, 5- High pressure autoclave (Batch foaming vessel), 6- Polymer sample, 7 – gas saturated polymer sample, 8 - Hotplate, 9 - Glycerine containing beaker, 10 – Temperature sensor, 11 – Microcellular foamed polymer sample

Conditions

Table 3: Effect of 1st Saturations pressure on the foam microstructure

Material	Polycarbonate
Blowing agent	CO ₂
Saturation Pressure P1 (bar)	50,40,30,20
Saturation Pressure P2 (bar)	10
Saturation Temperature T1	Room temperature
Time t1 (hour)	24
Time t2 (hour)	4

Table 4: Influence of holding pressure on foam morphology

Material	Polycarbonate
Blowing agent	CO ₂
Saturation Pressure P1 (bar)	50
Saturation Pressure P2 (bar)	40,30,20,10
Saturation Temperature T1	Room temperature
Time t1 (hour)	24
Time t2 (hour)	4

Table 5: Foaming conditions

Heating Medium	Glycerine
Foaming Temperature (°C)	160
Foaming time	40 sec
Quenching Medium	water
Quenching Temperature (°C)	Room Temperature
Quenching Time	10 sec

3.Results & Discussion

Absorption of CO₂ gas

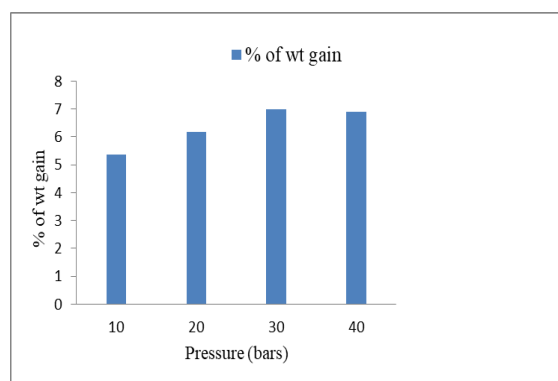
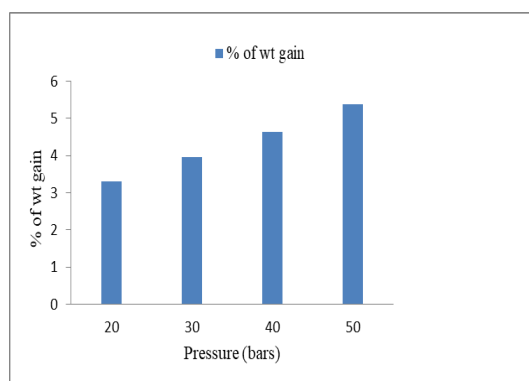
Gas sorption and desorption are important behaviors observe in the solid state batch foaming process. The behaviour of specimens has been obtained in this work under different processing parameters. For each parameter we took polycarbonate samples and then samples were weighed, the weighed samples were placed in the autoclave for 24h in order to get completely saturated. Samples were taken out from the autoclave after 24h and the amount of gas absorbed by the polycarbonate samples have been calculated by weighing the foamed polycarbonate samples. Table 6 and 7 shows the percentage of weight before saturation and after gas absorption by polycarbonate samples for different process parameters. The absorbed gas escapes from the polycarbonate surface by increasing the desorption time. Thus the concentration of gas in the polycarbonate decreases. The desorption of foamed samples was done through glycerine bath at 160°C. Figure 2 (a) and (b) shows % of wt gain for different pressures.

Table 6: Percentage of weight gain by the samples at 50,40,30,20 bar saturation pressures

P ₁ (Bars)	H ₁ (Hrs)	P ₂ (Bars)	H ₂ (Hrs)	Wt of samples before saturation	Wt of samples after saturation	% of wt gain
50	20	10	04	0.8411	0.8863	5.37
40	20	10	04	0.8160	0.8539	4.64
30	20	10	04	0.8344	0.8674	3.95
20	20	10	04	0.8233	0.8505	3.30

Table 7: Percentage of weight gain by the samples at 40,30,20,10 bar holding pressures

P ₁ (Bars)	H ₁ (Hrs)	P ₂ (Bars)	H ₂ (Hrs)	Wt of samples before saturation	Wt of samples after saturation	% of wt gain
50	20	40	04	0.8642	0.9046	6.90
50	20	30	04	0.8464	0.9056	6.99
50	20	20	04	0.8374	0.8892	6.18
50	20	10	04	0.8411	0.8863	5.37



(b)

Figure 2: (a) % of weight gain at saturation pressures of 50,40,30,20 bar (holding pressure at 10 bar) and (b) % of weight gain at holding pressure of 40,30,20,10 bar (saturation pressure at 50bar)

Expansion ratio

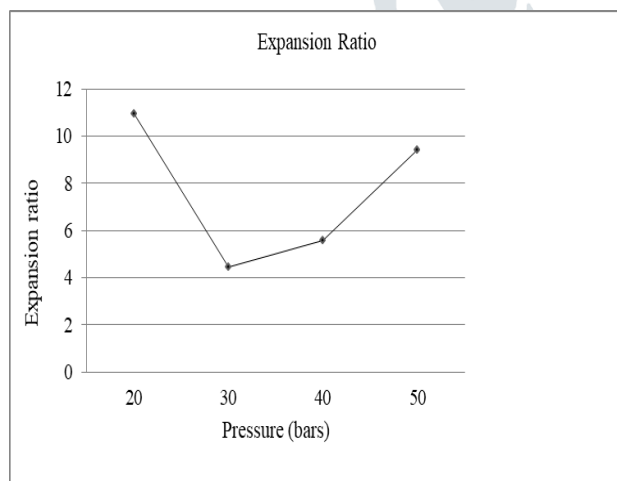
Expansion ratio is defined as the ratio of density of polymer to the density of foamed sample. The saturated sample expands its size by dipping in hot glycerine bath. Expansion ratio was mainly affected by saturation pressure, foaming temperature and foaming time. By changing these parameters, the expansion ratio also changes. The expansion ratio of polycarbonate foams increases by increasing the saturation pressure and foaming temperature. By increasing in the expansion ratio, the formation of bubbles in foams was also high due to this foams exhibit good properties. Table 8 and 9 shows the expansion ratio of the foamed samples. Figure 3(a) and (b) shows pressure versus expansion ratio plot.

Table 8: Expansion ratio of samples (2nd saturation pressure is 10 bar for all the conditions)

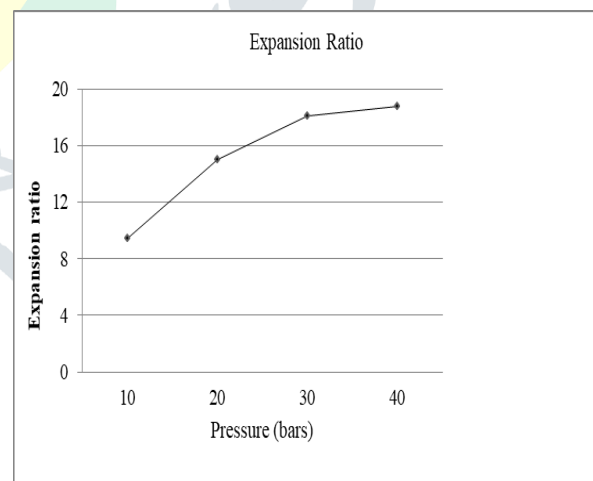
P ₁ (Bars)	H ₁ (Hrs)	P ₂ (Bars)	H ₂ (Hrs)	Expansion ratio
50	20	10	04	9.41
40	20	10	04	5.57
30	20	10	04	4.44
20	20	10	04	10.96

Table 9: Expansion ratio of samples (1st saturation pressure is 50 bar for all the conditions)

P ₁ (Bars)	H ₁ (Hrs)	P ₂ (Bars)	H ₂ (Hrs)	Expansion ratio
50	20	40	04	18.75
50	20	30	04	18.1
50	20	20	04	15.01
50	20	10	04	9.41



(a)



(b)

Figure 3: (a) expansion ratio of 50,40,30,20 bar (holding pressure at 10 bar) and (b) expansion ratio at holding pressure of 40,30,20,10 bar (saturation pressure at 50bar)

Conclusion

The solid state batch foaming of polycarbonate material using CO₂ as a blowing agent has been studied under various parameter like saturation pressure, holding pressure and gas sorption and desorption of polycarbonate sheets were studied. Obtained different sizes of foamed polycarbonate samples and observed their properties under different saturation and holding pressure.

Bi-modal cell distribution foams have been manufactured by two step depressurization batch process. The degree of depressurization influence the foam morphology as well as saturation pressure and holding pressure also influence the cell morphology significantly. The light weight microcellular foams are obtained from this work.

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