RESEARCH PAPER

The Foaming Process of Poly Styrene-Co-Acrylonitrile (SAN) with Co Blowing Agents

H. R. Azimi[1],*

* h.azimi@azaruniv.ac.ir

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Chemical Engineering Department, Faculty of Engineering, Azarbaijan Shahid Madani University, Tabriz, Iran.

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Abstract: *In this work, the poly styrene-co-acrylonitrile (SAN) beads and three blowing agents (CO2, N2, and n-pentane) were used to investigate the foaming process via our batch foaming system. The solubility and diffusivity of three blowing agents were determined by the MSB. The solubility of blowing agents was increased by pressure and decreased by temperature increment. It has resulted in higher solubility and diffusivity data for SAN/n-pentane/CO2 system (Using co-blowing gent) than other samples. According to the scanning electron microscopy (SEM) results, it was concluded that the cell and foam densities were decreased with temperature increment and increased by pressure release rate in all foamed beads. With using co blowing agents, higher pressure release rate, and low temperature without adding any fillers, we could improve the foam characteristics and produce the SAN foams with smaller cell sizes and greater cell and foam densities.*

Keywords: *SAN, MSB, Foaming process, Co Blowing agents, Cellular structure.*

1. INTRODUCTION

The production of cellular materials with different blowing agents has been famous recently because of their various applications [1-4]. The porous structure is achieved through the expansion of a blowing agent like normal pentane (n-pentane), supercritical carbon dioxide (CO_2) and nitrogen (N_2) dissolved in a thermoplastic by a batch or continuous foam process [5-7]. In the initial stage of the foaming process, the blowing agent is solved in the polymer and a homogeneous phase is produced. In the following step via a thermodynamic instability, like pressure release, the cellular structures are established [8-9]. Decreasing the cell size in produced polymer foam will improve the thermal properties of the foam [10-12]. But a few studies have investigated the foam porosity [13]. We can improve the cell sizes by using two blowing agents at the same time in which at the first the polymer sample was pre-impregnated by one blowing agent at low temperature and pressure and then was saturated by another one at the desired temperature and pressure. Also, we can do porosity increment by adding a different nucleating agent to the polymer but the process control in using co blowing agents is so simple, and polymer modifying is not necessary. Using co blowing agents was done by different researchers, for instance, Zhao et al. studied the polyvinyl alcohol/micro fibrillated cellulose composites [14]. The foaming process was done with CO_2–H_2O as blowing agents that H_2O affected the plasticization and in the following decreased the melting point [14]. The same method was studied by R. Gendron which the blending of CO_2 with ethanol was used for foaming the extruded PS [15]. It was found that the addition of ethanol generates more uniform cell morphology [15]. Wang worked on the continuous foaming process of polystyrene by using the mixture of supercritical CO_2 and supercritical N_2 [16]. He concluded that Supercritical CO_2 has higher solubility and plasticization effects. At the same time, super-critical N_2, exhibit better cell nucleating power than supercritical CO_2 [16]. Gendron and Moulinié [17] foamed PMMA with a mixture of supercritical CO_2 dissolved into liquid isopropanol in an autoclave. The main result was that premixing blowing agents blends had a higher plasticization effect than injected gas blends, separately. Supercritical CO_2 and ethyl lactate mixtures were used to foam polyesters in the work of Salerno et al. [18]. In this study, it was shown that the addition of a small amount of ethyl lactate to the $scCO_2$ decreased the glass transition temperature

of the polymer-solvent system below the operating temperature and finally improved cell uniformity of produced foams. Some other polymers and blowing agents were used for producing the polymer foams [18].

The forming process has been conducted by different researchers via a batch or continuous process[19-21]. A few foaming experiments have focused on in-situ visual foaming dynamics, for example, Kentaro Taki et al. used visual observation of batch and continuous foaming using CO_2 to study the bubble nucleation and growth behaviors [22]. Leung et al. used the batch visualization system and obtained the experimental data for foaming dynamics of polymers and in the following modeled experimental results with the theoretical model [23]. Salejova studied the first step of the foaming process of polystyrene in a similar batch system [24]. Azimi et al. worked on the foaming dynamics of St-MMA copolymers and investigated the effects of different operating parameters on the foaming process [25-26].

Final properties of produced foams are affected by the type and the amount of the dissolved blowing agent in the polymer so the solubility and diffusivity of blowing agents were investigated by many researchers. Azimi et al. determined the solubility and diffusivity of carbon dioxide in St-MMA copolymers [27]. A similar work was done by Li in which the solubility and swelling of carbon dioxide and nitrogen in the polylactide at a different temperature range and pressures up to 28 MPa were determined by using a magnetic suspension balance (MSB) [28]. Chen measured the solubility of CO_2 in polypropylene experimentally and corrected it with using of Sanchez–Lacombe (S–L) equation of state [29]. In recent studies, it was concluded that the solubility and diffusivity increased with pressure and decreased with temperature increment [29]. In our previous work, we investigated the bubble nucleation and growth for polystyrene with supercritical carbon dioxide as a blowing agent and the effect of different parameters was studied [30].

In this study, we used the poly styrene-co-acrylonitrile (SAN) particles and different blowing agents (CO_2, N_2, and n-pentane) to investigate the foaming dynamics via our batch foaming system. Using co blowing agents in the foaming process of SAN is done for the first time in this study. Beforethe foaming process, we determined the solubility and diffusivity of blowing agents in the SAN matrix by using the magnetic suspension balance (MSB). The effect of different foaming conditions, like temperature, impregnation pressure, and pressure release rate on the batch foaming process, will be investigated. Also, the results will be obtained using co blowing agents in the high-pressure cell. The morphological study was done for foamed polymer beads by using the scanning electron microscopy (SEM). We will investigate the effects of temperature and pressure release rate on the foam characteristics, such as cell size, cell density, and foam density according to the SEM results.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The poly(styrene-co-acrylonitrile) (SAN) was supplied from the Tabriz petrochemical company. The molecular weight of used SAN was 150,000 with a polydispersity of 2.3. The glass transition temperature was about 105 ˚C obtained by the differential scanning calorimetry (DSC). Supercritical CO_2, N_2 and, high-pressure of normal pentane were used as the blowing agents. The solubility and diffusivity of the mentioned blowing agents in SAN were measured using an MSB (Rubotherm and Bell Japan). The bead-shaped samples were used for further foaming dynamics and morphological experiments.

2.2. Experiments

By weighing a foamed bead of known volume, the foam density (ρ_f) is estimated and foam porosity is observed by scanning electron microscopy (SEM). Image analysis is performed according to the SEM images. Cell density (N_{cell}) relative to unfoamed polymer is estimated according to the following equation:

$$N_{cell} = \left(\frac{nM^2}{A}\right)^{3/2} . \frac{\rho_s}{\rho_f} \quad (1)$$

where n is the number of cells in the SEM picture,

M is the magnification, A is the surface area of the picture (cm^2), and ρ_s and ρ_f are the solid and foamed sample densities, respectively.

The solubility and the diffusivity of supercritical CO_2, N_2, and high pressure of normal pentane in SAN at different conditions were determined by using a magnetic suspension balance (MSB) [25]. The MSB (Rubotherm and Bell Japan) consists of a measuring chamber and a balance (Mettler AT261, Switzerland) in which the balance is located outside the chamber under atmospheric conditions. In the measuring chamber, the sample is hooked up to a so-called suspension magnet, which consists of a permanent magnet, a position sensor, and a device for coupling/decoupling the measurement load (sample). High pressure and temperature condition are realized in this measuring chamber. In this system, an electromagnet is attached to the under-floor weighing hook of the balance and situated outside the chamber so as to have the suspension magnet in a freely suspended state controlled by an electronic control unit. Using this magnetic suspension, the weight of the sample in the chamber can be transmitted to the balance without direct contact. The MSB used in this study can measure the mass of two samples with only one suspension magnet by using the device for coupling/decoupling measuring load [27]. The measurements were done at three temperatures and in different pressures of blowing agents, up to 11.0 MPa. Our system consists of a high-pressure stainless steel vessel, pressure gage, temperature controller, and two sapphire windows on both sides. The schematic view of the system is shown in fig 1. The bead shape samples were placed inside the cell and were saturated with CO_2, N_2 and n-pentane, separately, at a determined temperature and pressure for 20 hours. This time was enough for saturation of beads with all of the blowing agents, separately. After the saturation period, the pressure was released by opening the valve 1 and the foaming process was started at a certain temperature. In this system we use two pressure release rates (1.6 and 3 MPa/s) and the effect of the pressure release rate will be considered.

The analytical solution for the Fick's second

$$c = c_0 - \sum_{n=0}^{\infty} \frac{4(c_0 - c_i)(-1)^n}{2n+1} \cos\left[\frac{(2n+1)\pi x}{2L}\right] \exp\left[\frac{-D_{mut}(c_0)(2n+1)^2 \pi^2 t}{4L^2}\right] \quad (2)$$

where L is the thickness of the sample. c_i and c_o, are the concentration of n-pentane at the initial state and the surface of the sample in equilibrium with n-pentane inside the chamber during the measurement, respectively. The solution of the equation (2) could be written as:

$$\frac{\Delta w_{Pen}(t)}{\Delta w_{Pen}(t=\infty)} = 1 - \sum_{n}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D_{mut}(2n+1)^2 \pi^2 t}{4L^2}\right] \quad (3)$$

where $\Delta w_{Pen}(t)$ is the weight of dissolved n-pentane in samples at time t. More details of these equations have been published in our previous work [27].

3. RESULTS AND DISCUSSION

The solubility of different blowing agents in SAN at different pressures and temperatures obtained by MSB are shown, in fig 2. In this fig the solubility of blowing agents in SAN increases with increasing pressure and decreases with temperature increments. The solubility value for SAN/CO_2 is slightly greater than SAN/ n-pentane and nearly 3.5 times greater than SAN/N_2. In another experiment, we used co-blowing agents in two different steps. At the first step, the beads were pre-impregnated by n-pentane at a pressure of 8 bar and temperature of 50 ˚C.

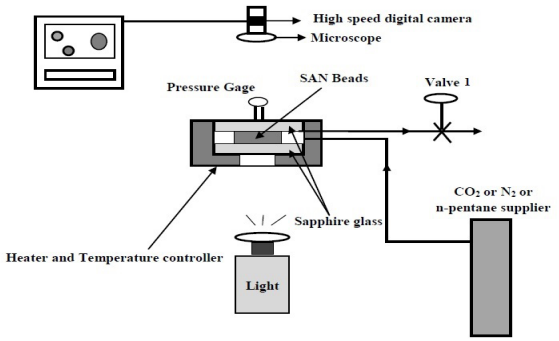

Fig. 1. Schematic diagram of the visual observation batch System.

This step was done inside a small vessel in which the n-pentane was weighted (4g) and poured inside the vessel and after a short period (2 h), the vessel was put into an ice bath suddenly. Finally, the samples were brought out from the vessel, weighted, and got ready for a further experiment under the pressure of CO_2. We named this sample as "SAN/n-pentane/CO_2". As is clear in fig 2, the solubility of CO_2 in this sample was greater than the SAN/CO_2 system at the same temperature in all pressure range.

The diffusion coefficients of CO_2, N_2 and n-pentane in SAN versus pressure at two temperatures (95 ˚C and 120 ˚C), are shown in fig 3. As shown in fig 3, the diffusion coefficient is strongly increased with increasing of the temperature and slightly increased with pressure increments. The rate of diffusivity increment for N_2 is greater than other blowing agents due to its low molecular weight.

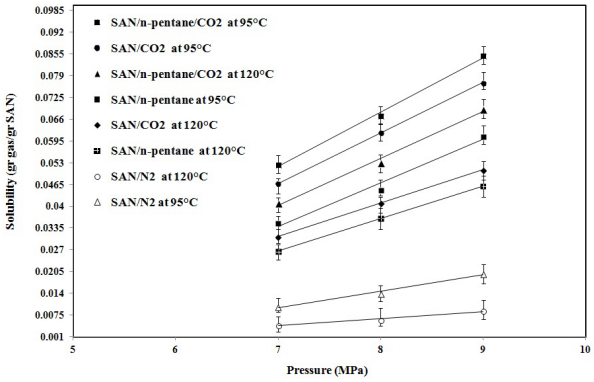

Fig. 2. The solubility of different blowing agents in SAN at different temperatures versus pressure.

The diffusion coefficient values for SAN/n-pentane/CO_2 and SAN/CO_2 systems are almost the same at T= 95 ˚C. But with temperature rise to T=120 ˚C, the diffusion coefficient is distinctly increased for SAN/n-pentane/CO_2 compared to SAN /CO_2. In the SAN/n-pentane/CO_2 system, the n-pentane dissolves in styrene groups in SAN and with increasing of the temperature, the diffusivity of n-pentane, and CO_2 in the polymer increased. This increment of diffusivity is because of the presence of two blowing agents, so the final diffusion coefficients for SAN/n-pentane / CO_2 are greater than SAN /CO_2. The results of the solubility and diffusivity experiment revealed that N_2 has low solubility and high diffusivity values in all temperature and pressure range, compared with CO_2 and n-pentane.

This behavior also is in agreement with the solubility results in which pressure increasing leads to the solubility increment and finally the greater foaming ratio and the opposite trend occurred for temperature rise. With increasing temperature, the diffusion coefficient is increased and at the same time, the blowing agents' solubility in SAN bead decreased. In the case of the SAN/n-pentane/ CO_2 system, the final foaming ratio is increased due to the co-blowing agents' effect.

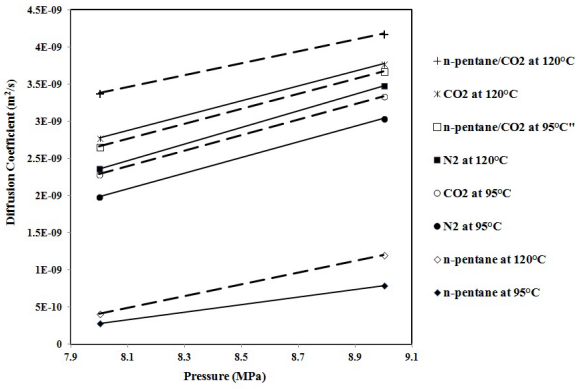

Fig. 3. The diffusion coefficient of blowing agents in SAN at different temperatures versus pressure. (The solid lines are plotted to guide the eyes).

We have studied the effects of temperature and pressure release rate on the foam characteristics, such as cell size, cell density, and foam density. The samples are saturated at 95 ˚C and 8 MPa for 20 h. The SEM images of SAN/CO_2 and SAN/n-pentane/CO_2 systems in two different depressurization rates are presented in fig 4 (a-c). It is clear that in SAN/CO_2 and SAN/n-pentane/CO_2 systems with increasing the pressure release rate, the uniformity in cellular structure is increased. The cell sizes in SAN /CO_2 are larger than the SAN/n-pentane/CO_2 system in the same pressure release rate. With increasing the pressure release rate in fig 4, from 1.6 to 3.6 MPa/s, in SAN/CO_2 the average cell size is decreased from 15 μm (Fig. 4a) to nearly 8 μm (Fig. 4b) and cell size decrement for SAN/n-pentane/CO_2 system is from 6μm (Fig. 4c) to nearly 4μm (Fig. 4d). It seems that at the same temperature and pressure, with using co blowing agents and without any modifying of the polymer,

we can produce the SAN foams with cell sizes less than 5 μm. From SEM pictures for SAN/n-pentane/CO_2 in fig 5 (a and b), it appears clearly that cell size greatly increased with increasing of the foaming temperature at constant pressure release rate. This fact is shown for SAN/n-pentane/CO_2 system at temperatures of 95 and 120 ˚C. With increasing temperature, the solubility of n-pentane and CO_2 in SAN decreased (fig 2) and less amount of the blowing agent contributed to cell nucleation and growth that produced large cells. We investigated the cell and foam density in (figs. 6&7), respectively. As it is expected, the cell density is slightly increased for SAN/CO_2 compared to SAN/n-pentane and strongly increased for SAN/n-pentane/CO_2 system in the same pressure release rate and temperature (T=95 ˚C, P=8 MPa, and dp/dt=1.6 MPa/s). An increase in cell and foam densities in higher pressure rate (3.6MPa/s) compared to foams prepared by low-pressure release rate (1.6 MPa/s) is because more n-pentane and carbon dioxide are used for cell nucleation instead of cell growth in the SAN matrix. Therefore, in a high-pressure release rate, the cells are smaller than at a low depressurization rate. With temperature increment due to a decrease in solubility of n-pentane and CO_2 in SAN beads (fig 2), the cell sizes are increased (fig 5b) and consequently the cell and foam densities decreased (figs. 6&7). The foam density for SAN/n-pentane/CO_2 system in fig 7 is the highest (0.39 g/cm^3) in the same condition. Faster depressurizing conditions result in higher foam densities. According to figs 6 and 7, we can produce the foam with a cell density of 10^{10} cells/cm^3 and foam density of 0.39 g/cm^3 for the SAN/n-pentane/CO_2 system at T=95 ˚C, P=8 MPa, and dp/dt=3.6 MPa/s.

4. CONCLUSION

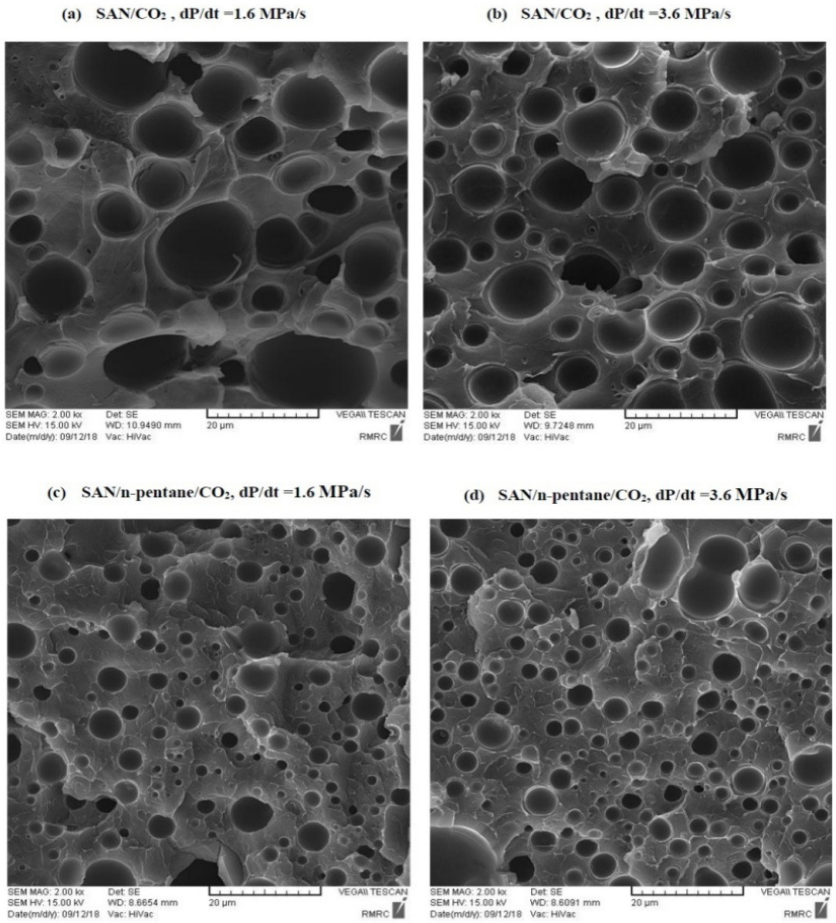

Fig. 4. SEM micrographs and corresponding cell size distribution of SAN foams; a) SAN /CO_2 at 1.6 MPa/s, b) SAN/CO_2 at 3.6MPa/ s, c) SAN/n-pentane/CO_2 at 1.6 MPa/s, d) SAN/n-pentane/CO_2 at 3.6 MPa/s. The temperature and pressure of 20 h foaming are 95 ˚C and 8MPa, respectively.

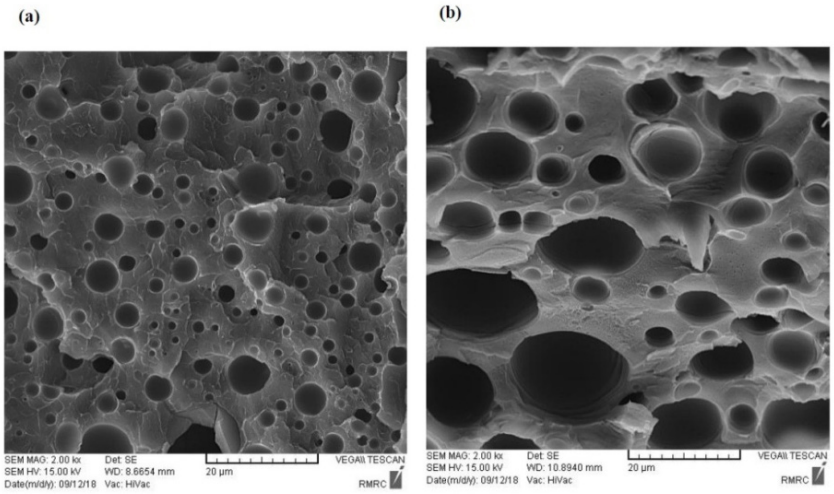

Fig. 5. Effect of temperature (a: 95 ˚C and b: 120 ˚C) on the cellular structure and cell size distribution of SAN/n-pentane/CO_2 at a pressure of 8MPa and pressure release rate of 1.6 MPa/s.

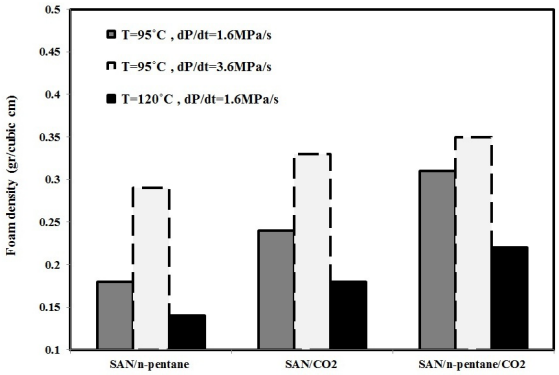

Fig. 6. The variation of cell density for different SAN foams under two pressure release rates and different temperatures.

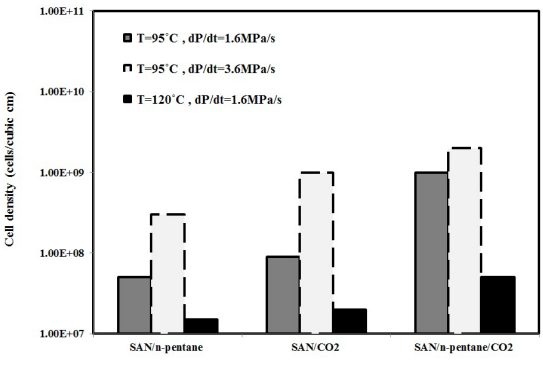

Fig. 7. Effect of temperature and pressure release rate on the foam density of different SAN foams.

The poly styrene-co-acrylonitrile (SAN) particles and three blowing agents (CO_2, N_2, and n-pentane) were used to investigate the foaming process via our batch foaming system. We determined the solubility and diffusivity of CO_2, N_2 and n-pentane in the SAN matrix by using the magnetic suspension balance (MSB). The results show that the solubility and diffusivity of blowing agents were increased with pressure and decreased with temperature increments. The effect of different foaming conditions, like temperature, pressure, and pressure release rate on the batch foaming process, were investigated. The morphological study was done for foamed polymer beads by using the scanning electron microscopy (SEM). It was concluded that in the case of the SAN/n-pentane/CO_2 system, the cell sizes are smaller and the cell and foam densities are greater than other systems, at the same temperature and pressure release rate. The cell and foam densities were decreased with temperature increment and increased by the pressure release rate in all foamed samples. The results show that the pressure release rate, temperature, and using co blowing agents, are the main parameters in controlling the final foaming ratio and cellular structures of SAN. Using coblowing agents, higher pressure release rate, and low temperature without adding any fillers, were the best conditions for foaming the SAN beads in the SAN/n-pentane/CO_2 system in which the produced cell sizes was less than 5 µm.

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