Optimization of Process Parameters for Generation of Nanocellular Polymer Foams

Subhendu Bhattacharya[*], Rahul Gupta and Sati N. Bhattacharya

Rheology and Materials Processing Centre (RMPC), School of Civil, Chemical & Environmental Engineering, RMIT University, Melbourne, Australia

Abstract: High melt strength polypropylene nanocomposites, PPNC/Cloisite 20A (clay) with exfoliated and intercalated morphologies were prepared and subsequently foamed in a batch setup under different foaming conditions. The foaming parameters were varied to relate the foam cell structure to these parameters and determine the efficiency of clay in producing fine cell foams. A Box Benkhen design approach was used initially to determine the effect of processing parameters on foam cell morphology and also to perform optimization studies. The optimization process helped in identifying the range of operating conditions needed to minimize foam cell sizes. Saturation pressure and temperature and foaming time and temperature are the four processing variables used in these studies. Nanocellular foam cells were effectively generated for the first time in Polypropylene nanocomposites.

Keywords: Nanocellular, DOE, optimization, batch foaming.

INTRODUCTION

Considerable amount of work has been devoted to the generation of foams characterized by smaller cell sizes and narrower distribution specifically in production of sub microcellular and nanocellular foams [1-2]. The foams with reduced cell sizes have been found to provide improved mechanical and insulating properties as compared to the larger microcellular foams. The addition of a filler to improve nucleation rate propelled by the low energy of activation required in heterogeneous nucleation does provide a way to generate sub micron and nanocellular foams [3]. The internal structure of the material and its rheological characteristics play an important role in determining the potential of a polymer to be used in making fine cell foams. Hence the production of fine cell foams is dependent on the polymer structure, its rheological behaviour, the effect of filler and careful control of processing conditions. The available window for generation of fine cell foams is very small and hence proper control of process parameters is essential for generation of fine cell foams. As such experimental design is difficult to use in the case of generation of fine cell foams. The available processing window for generation of nanocellular foams is unknown hence without knowing proper limits of the parameters affecting cell size it would be impossible to perform an optimization study for controlling cell sizes. Also selection of proper independent parameters are important to ensure that there are no cross interactions and the results are accurate and scalable.

EFFECTS OF PROCESSING PARAMETERS ON FOAM CELL STRUCTURE

The HMS –PP and PPNCs were saturated in the autoclave under different saturation temperature and pressure respectively. Gas solubility studies using supercritical CO_2 have revealed that the highest amount of solubility is attained at lower temperatures and higher pressures respectively [5]. The increase in the saturation temperature imparts increasing amount of kinetic energy to the gas molecules inside the polymer samples, which results in an increased tendency of the gas to escape from the polymer samples resulting in lower solubility and vice versa. Similarly the pressure of the gas used to saturate the polymer sample solubility increases due to increased potential energy of the gas molecules accompanied by the higher penetration power of the gas molecules. Interestingly the pressure differential generated during the subsequent depressurization of the sample is also higher at higher saturation pressure causing an improvement in the degree of supersaturation [7]. Higher solubility of blowing agent within the polymer samples causes supersaturation at lower foaming temperature and improves the nucleation rate within the polymer sample since the nucleation rate is directly proportional to the amount of gas dissolved in the polymer due to the presence of a competing mechanism between cell nucleation and growth. The quicker super saturation of the sample at lower temperature also additionally increases the tendency of the gas to escape from the sample with an increase in the degree of superheat. All these factors when combined cause a reduction in foam cell size by reducing the amount of gas available for foam cell growth and nucleation.

*Address correspondence to this author at the Rheology and Materials Processing Centre (RMPC), School of Civil, Chemical & Environmental Engineering, RMIT University, Melbourne, Australia; Tel: +917925307798; E-mail: subhendu.bhattacharya@gmail.com

The foaming temperature governs the rate of nucleation of foam cells in a foaming process [8]. This can be explained by the fact that the free energy for nucleation is directly proportional to temperature and hence raising the temperature raises the free energy of the gas towards the amount needed for conversion of sub critical micro bubbles into the supercritical state at a faster rate. The molecular diffusion rate is also increased with increase in foaming temperature favouring foam growth as well but interestingly the rate of nucleation is propelled by a higher degree since the net free energy needed to nucleate on a particle surface is lesser than the free energy needed to diffuse through a polymer film into the cells [5, 8]. As a result the overall rate of foam growth is partially retarded resulting in the formation of fine cell foams. At the same time the selected foaming temperature should not be too high as well since with increase in temperature the polymer chain mobility also increases and the melt viscosity reduces. The increased chain mobility reduces the rate of survival of individual micro voids within the polymer producing larger cells [3].

The rate of quenching of the polymer foam sample also affects the final cell size. The aim of the quenching process is to go below the glass transition temperature of the polymer. Since below the glass transition temperature the polymer would behave like a solid and so the foam cell walls would be strong enough to resist further cell growth. The rate of quenching controls the time available to the foam cells to keep growing and then stabilize subsequently. Thus a very low quenching temperature would increase the temperature differential between the foam sample and the quench fluid restricting the foam cell size [10]. Application of a force balance helps in understanding the quenching process. The cell walls experience two different opposing forces during the quenching process. The growing bubbles tend to stretch the cell walls at the same time the cooling of the foam cells tend to contract them. In case of a high quenching rate the cell walls are not able to quickly respond to the abrupt change in temperature and relax which may cause foam collapse. Therefore the best quenching temperature is one where the contracting force on the cell walls is exactly balanced by the stretching force acting on them. Alternatively another way would be to reduce the foaming time resulting in thicker cell walls right from the outset and then quench the sample very quickly to stop any further cell growth

EXPERIMENTAL

The physical foaming process using a batch setup consists of four stages [2]

1)   Saturation of the sample in a batch setup using supercritical CO_2 at the desired temperature.

2)   Depressurization of the sample in the autoclave at the desired rate.

3)   Foam cell growth and nucleation using temperature superheat.

4)   Finally foam cell stabilization *via* cooling process of the foamed system.

The foaming process in a batch setup normally involves using a pressure vessel for saturation as well as foaming. The drawback of using a combined system
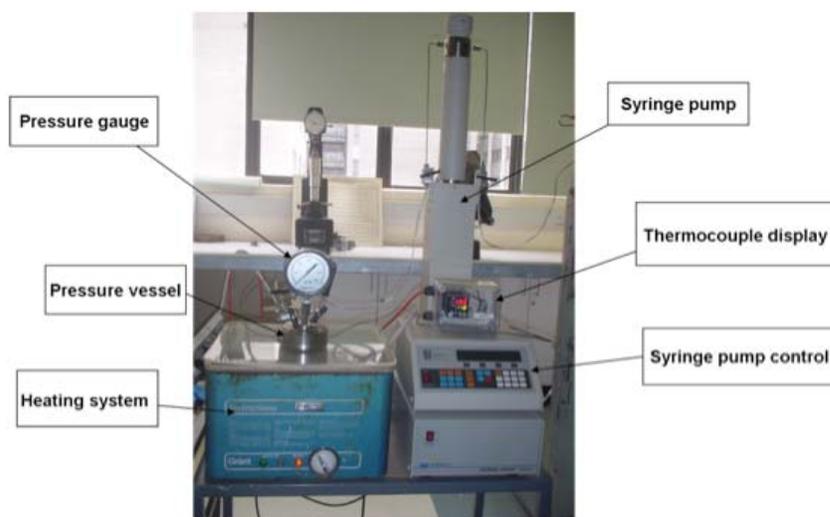
Figure 1: Batch setup for dissolving CO_2 in the polymer samples.

is that, at higher temperatures the solubility of the physical blowing agent in the sample is low and at the same time using a pressure gradient to generate foams doesn't provide proper control of the cell nucleation and foam cell growth since there is a competing mechanism between cell growth and nucleation. Hence a two stage process was used in this study. The saturation of the sample at lower temperatures improves the solubility of the gas within the sample; also using a subsequent super heat to generate the desired foam structure provides better control on cell nucleation and growth.

The Figures **1.1**, **1.2** show the batch foaming setup used in this work.

Pressure Vessel

The pressure vessel (Figure **1**) used was a Parr - 4791 series vessel. It has a volume of 100ml and is a split ring type vessel. This vessel is provided with an externally connected detachable head. A split ring type pressure vessel can be easily dismantled since external bolts are used to hold the head and the vessel together. The pressure vessel is made up of stainless steel and can bear a maximum pressure of up to 3000 psig and a temperature of 250oC. The vessel is externally provided with five connections. A gas inlet valve, a gas release valve, a safety valve, a connection for the thermocouple and a pressure gauge. A fluroelastomeric O-ring (Viton) is required to connect the vessel head to the pressure vessel. The pressure gauge connected to the vessel can measure a pressure of up to 3000 psig (20.68MPa) with a sensitivity of 10 psig. The thermocouple has a sensitivity of 0.10C and can measure a temperature up

to 3500C. The idea of having a smaller vessel was to minimize the time required for depressurization and hence improve the nucleation rate [3].

The Heating and Cooling Systems

The pressure vessel was heated using a temperature controlled water bath (10 -1000C) having a temperature sensitivity of 10C. Foaming was carried out using a temperature superheat in a deep fryer (Figure **2**) with a temperature controlled heater (70 – 2500C) range and a sensitivity of 10C. The generated foams were subsequently quenched using water at room temperature.

Volumetric Method for Measurement of Gas Solubility

Figure **3** below shows a schematic representation of the experimental technique used for determination of equilibrium solubility in the polymer nanocomposites used in this project. The technique is equally accurate as compared to other techniques for measurement of the equilibrium solubility [4]. A mass balance approach is used for determination of equilibrium solubility. The approach physically states that the mass of the gas polymer system before absorption should be equal to the mass of the system after absorption. Hence in simple terms the mass of the gas delivered by the syringe pump should be equal to the amount of gas present in the vessel plus the mass of gas dissolved in the polymer sample. The density of the gas/polymer composite system and the gas is calculated using the Sanchez Lacombe equation of state. The benefit of this approach is that unlike the pressure decay method,
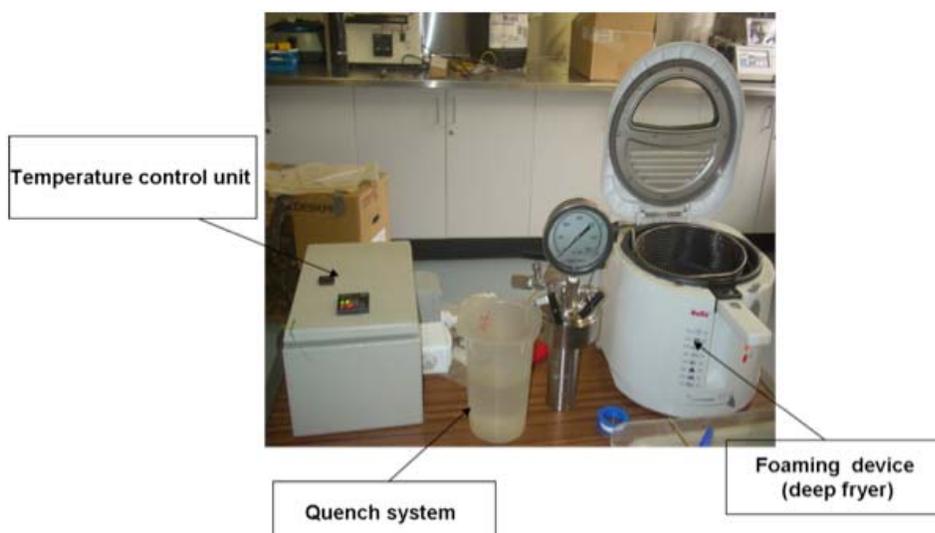
Figure 2: Batch setup for foam generation.

volumetric decay method and the gravimetric method, the use of an expensive instrumentation like magnetic suspension balance is not required to measure equilibrium solubility. The sample chosen for gas solubility study should be of a volume which is significant enough to cause a detectable change in the volume of the gas used to determine equilibrium solubility. The accuracy of the measurement is affected if the sample is very small since then the amount of gas dissolved in the polymer matrix is very small. Also the use of Sanchez Lacombe equation of state for calculating the density of the gas provides approximate results introducing errors in measurement.
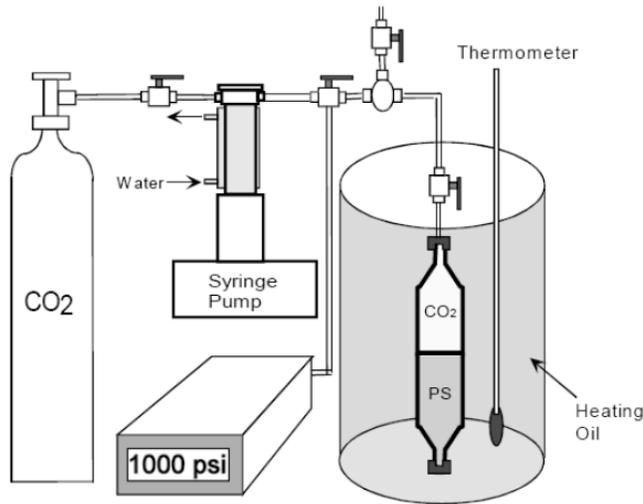
Figure 3: Gas solubility measurement setup.

Equation 1 used for determination of equilibrium solubility

$$m(before sorption) = \rho(40^0 C, P)V_{pump}^{before} + \rho(25^0 C, P)V_{tubing} =$$
$$\rho(40^0 C, P)V_{pump}^{after} + \rho(25^0 C, P)V_{tubing} + \rho(T, P)(V_{vessel} - V_{polymer}) \quad .1$$

$$+ m_{polymer} w = m(after sorption)$$

$m(before sorption)$ is the mass of gas in the system before absorption of gas

$\rho(40^0 C, P)$ is the density of CO_2 at $40^o C$

V_{pump}^{before} is the volume of gas in the syringe pump before pumping

V_{pump}^{after} is the volume of gas in the syringe pump after pumping

V_{tubing} is the volume of the tube

V_{vessel} is the volume of the vessel

$m_{polymer}$ is the mass of the polymer

w is the weight of the gas dissolved in the polymer

m (after sorption) is the mass of the gas in the system after absorption of gas

All the parameters in the equation 1 are known except for w which can be then effectively calculated.

SELECTION OF PROCESS PARAMETERS AND EXPERIMENTAL DESIGN

Saturation pressure, temperature, foaming temperature, foaming time and quenching temperature all affect the foam cell morphology. Consequently the design of experiments becomes intricate in studying the role of all the above mentioned parameters on foam processing. Now the addition of clay particles to the polymer samples further complicates the situation. For this reason a clearly defined experimental approach is needed to reduce the number of experiments required but at the same time it is important to study the effect of all the above mentioned parameters. Interestingly all the above mentioned parameters either affect cell nucleation or cell growth. Hence the two process variables are cell nucleation and cell growth. Cell nucleation and growth is mostly affected by foaming temperature. Saturation pressure and temperature affect the solubility level and degree of super saturation and are like supporting systems to improve cell nucleation. On the other hand foaming time and quench temperature are supporting parameters for foam growth. So, the major process variables that define the foam cell structure are foaming temperature and foaming time. Ideally the solubility of supercritical CO_2 is the highest when the saturation temperature is low and the saturation pressure is high [11, 12], both above the supercritical limits for CO_2. But the effect of temperature on solubility is not very profound till the point where the samples tend to change phase. This simplifies the experimental design. The idea is to first determine the foaming temperature range or processing window for generation of closed cell foam for a polymer sample with a certain amount of filler loading. Once this is determined the next step is to vary the saturation pressure and foaming time for each sample and then determine the optimum values for these two parameters till the point where the cell size stops reducing further down [13-15]. The quench temperature chosen for this system is room temperature for all samples since in actual foaming condition in a continuous process the quench temperature is the atmospheric temperature.

Sat pressure (MPa)	Sat temp (°C)	Foam temp (°C)	Foam time (sec)
17	46	170	20
14	57	152.5	30
17	46	152.5	30
17	35	170	30
14	35	152.5	30
17	46	135	40
17	46	152.5	30
17	57	135	30
17	46	152.5	30
17	46	152.5	30
20	46	135	30
17	57	152.5	20
20	46	152.5	40
17	57	170	30
17	46	170	40
14	46	152.5	40
20	46	152.5	20
14	46	152.5	20
20	35	152.5	30
17	35	135	30
14	46	135	30
14	46	170	30
17	35	152.5	40
17	46	152.5	30
20	46	170	30
17	46	152.5	30
17	57	152.5	40
17	46	135	20
20	57	152.5	30
17	35	152.5	20

Figure 4: Experimental runs using the Box Benkhen method.

A box Benkhen design approach was used initially to determine the effect of processing parameters on foam cell morphology and also to perform optimization studies. The optimization process helped in identifying the range of operating conditions needed to minimize foam cell sizes. Saturation pressure and temperature and foaming time and temperature are the four processing variables used in these studies. The Box Benkhen approach resulted in overall 30 experimental runs.

It is evident from the surface plots (Figures **2-6**) that the foam cell sizes (for closed cells) reduce with increase in saturation pressure and reduction in saturation temperature. Similarly the foam cell sizes also reduce as the foaming temperature is raised and the foaming time is reduced. The U shaped nature of all the surface plots reveals that there is an optimum condition at which smallest cell sizes would be generated. Since the foam cell size is a function of the foaming time, foaming temperature, saturation pressure and temperature, direct linear methods of optimization cannot be used to determine the optimum processing conditions for generation of fine cell foams. Hence a Lang ranges optimization algorithm is used to
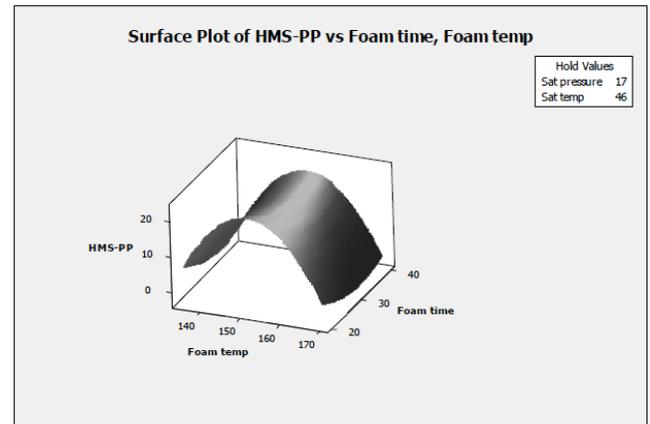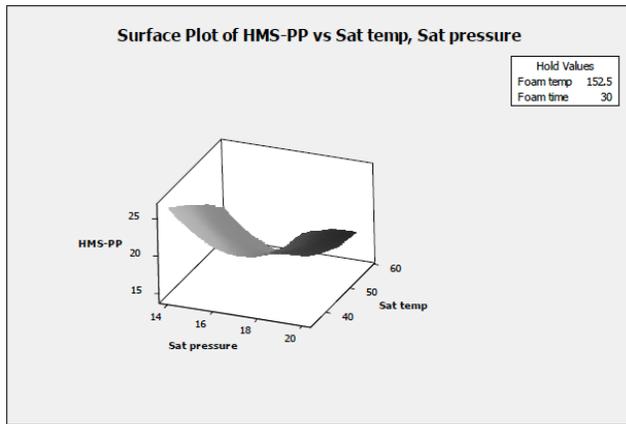
Figure 5: Effect of processing parameters on HMS-PP pure foams (closed cells).
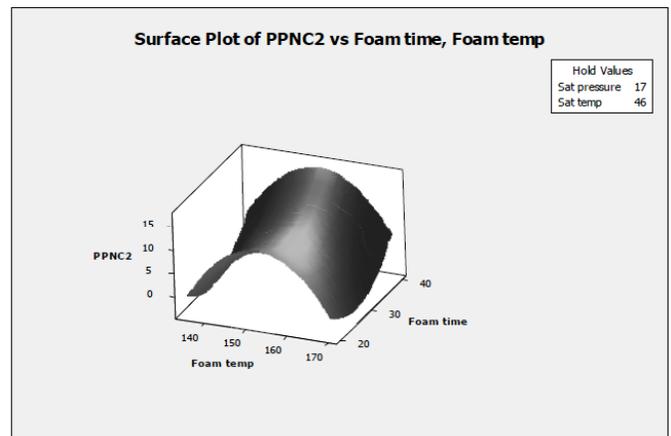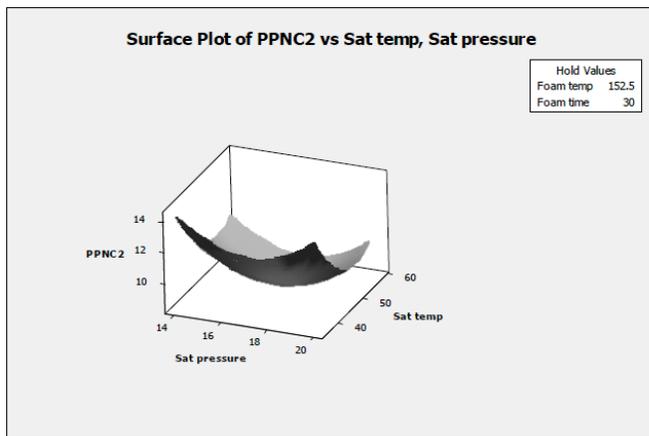
Figure 6: Effect of processing parameters on PPNC 2 foams (closed cells).
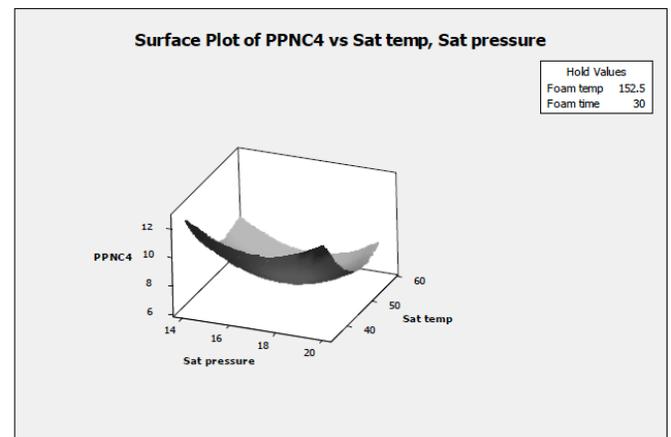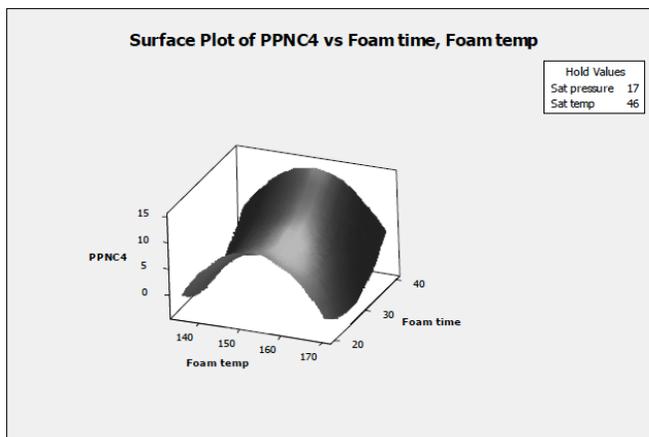
Figure 7: Effect of processing parameters on PPNC 4 foams (closed cells).

determine the optimum processing conditions. The optimization is performed with respect to foam cell sizes. In other words the optimum points (singularities) in the surface plots are determined on the basis of the first derivative of all the mentioned process parameters with respect to foam cell sizes for determination of

Eigen values. Eigen values are like scale factors which can shift a curve with a specific boundary curve proportionally without changing the optimization conditions. The foam cell sizes are inversely proportional to the foaming temperature and directly proportional to the saturation pressure, saturation
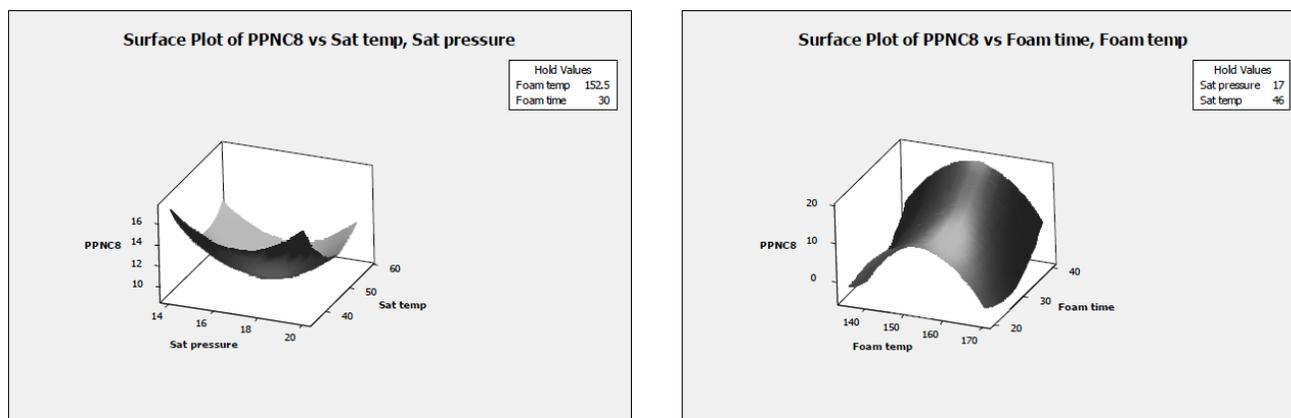
Figure 8: Effect of processing parameters on PPNC 8 foams (closed cells).
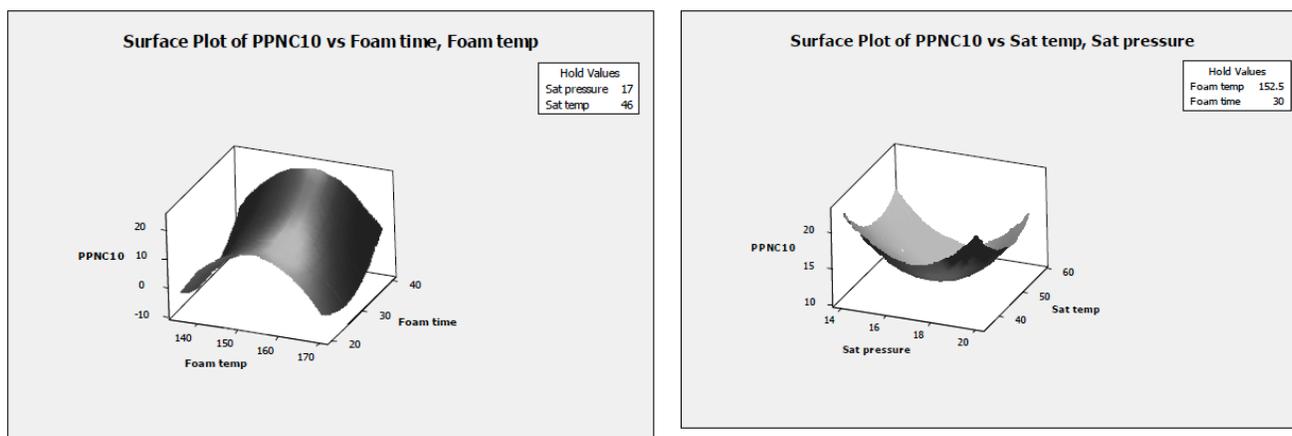
Figure 9: Effect of processing parameters on PPNC 10 foams (closed cells).

temperature and foaming time as seen in the optimization plots (Figure **7**). The dependency of the foam cell sizes on saturation temperature changes trend on addition of clay particles as evident from the plots. Thus the saturation temperature is highly sensitive to the degree of clay concentration, when the aim is to reduce foam cell sizes. All other processing parameters have the same trends in presence or absence of clay except for changes in the overall gradient or slope. From the optimization plot (Figure **7**) (values in red) in the top of the table provide the optimum parameters for reduction in foam cell sizes. The first point of intersection between the blue lines (lines depicting boundaries for reducing foam cell sizes) and the parameter curves provide the optimum processing conditions for generation of fine cell foams with respect to each processing condition. The values of all the processing parameters were correct except for foaming temperature which was later found to be 147°C instead of 151°C.

Based on the above mentioned methodology (Box Benkhen approach), a wide range of foaming temperature for processing foams from 139 -170°C were investigated with a one degree temperature gap. The saturation pressure used was also varied from 1800 -2700 psi. The processing window for generation of closed cell foam was found to be around 143 - 148°C. Now different saturation pressure and foaming time combination was tried for the samples within the processing window with a minimum foaming time and saturation pressure used as per literature. Further the polymer samples were foamed beyond the processing window as well to understand the sensitivity of the foam cell structure to foaming time. It was found that beyond the processing window the variation in foam time always results in generation of open cell foams and high degree of cell coalescence. Figure **1** shows the various processing conditions employed for production of polymer nanocomposites foams. HMS – PP and PPNCs were foamed at six different foaming conditions as shown in Table **1**. When the foaming temperature is very close to the onset melting point, there is no foaming taking place although some amount of gas does dissolve into the sample which

Table 1:   Effect of Processing Parameters on Foam Cell Morphology

Case	Foam Temp (^{o}C)	Foam Time(sec)	Saturation Pressure (MPa)	Saturation Temp (^{o}C)	Visual observations
(1)	139	34	14.3	35	No foaming
(2)	159	30	16.3	42	Predominantly closed but larger cells foams
(3)	170	28	17.7	50	Foam collapse
(4)	149	25	18.6	57	Closed cell sizes crossover to micrometer region
(5)	146	30	16.3	42	Closed cell foam non uniform distribution
(6)	147	30	16.3	42	Closed nanocellular foams
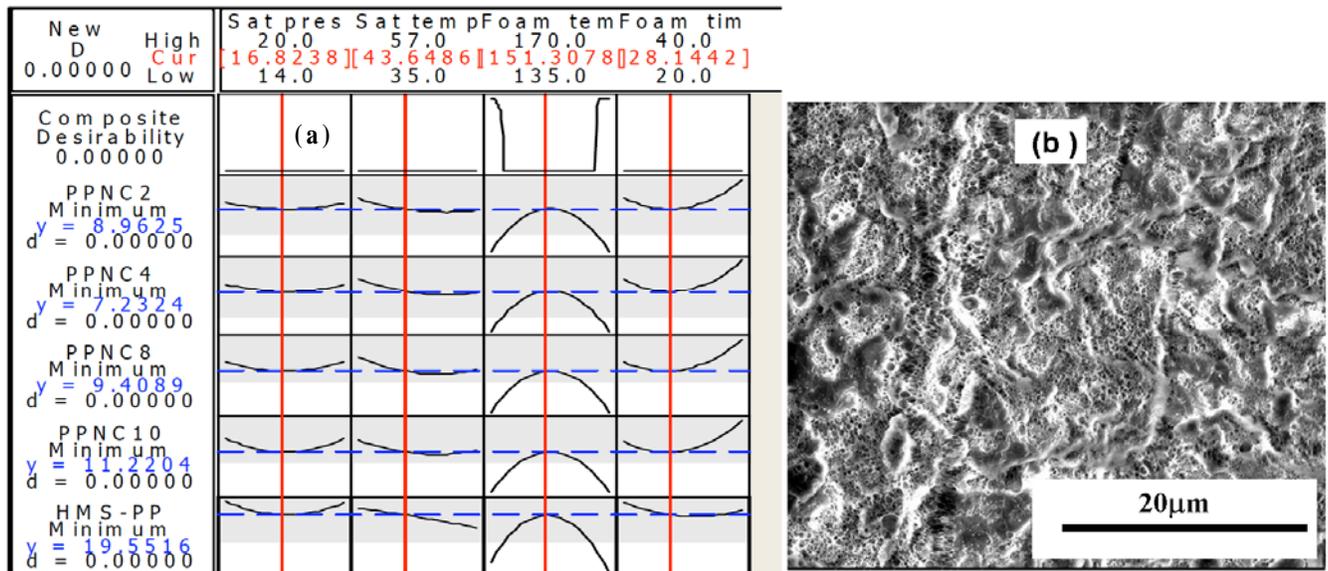
Figure 10: (**a**). Optimization of processing parameters using the Box Benkhen design approach for production of fine cell foams (closed cells).
(**b**). Nanocellular foams generation in PPNC4 case (6).

subsequently escapes from the sample with increase in temperature without the formation of foams. The sample viscosity is very high near to the onset of melting which results in no foam generation. Alternatively, in cases where the foaming temperature is very high (i.e. higher than the melting point) leads to high degree of cell coalescence and a partial collapse of the foam cells formed. The best foam structure is obtained when the foaming temperature is within the melting range but close to the higher end of the melting range used. The foaming temperature employed in case of a batch process needs to be such that the melt viscosity is high enough to restrict foam cell sizes and resist foam collapse but at the same time low enough for the initially nucleated cells to survive and grow. The rate of gas escape from the sample is also a function of temperature and increases with increase in foaming temperature. At higher gas escape rates foam cells get lesser time to grow and nucleation rate improves resulting in smaller cell sizes. Therefore the foaming temperature employed is a balancing act with respect to cell nucleation rate and cell growth rate.

CONCLUSIONS

A factorial DOE approach was used for optimization of process parameter for generation of nanocellular foams. The boundaries of each individual process parameter was carefully selected as per scientific logic. THE DOE approach helps in accurately controlling the parameters for generation of nanocellular foams. As such DOE can be used in cases where the exact limits of parameters are not known for optimization. The results also indicated that the processing window for generation of fine cells in HMS-PP is very small. The

optimization plots help in understanding the sensitivity of nanocell generation to each individual parameter which further helps in reasoning the cell size outcomes theoretically as well.

REFERENCES

[1] Fujimoto Y, Ray S, Okamoto M, Ogami A, Yamada K, Ueda K. Well-Controlled Biodegradable Nanocomposite Foams: From Microcellular to Nanocellular. Macromol Rapid Commun 2003; 24: 457.
http://dx.doi.org/10.1002/marc.200390068

[2] Wagner M, Bastian H, Hachmann P, Meissner J, Kurzbeck S, Münstedtand H, Langouche F. The strain hardening behaviour of linear and long-chain-branched polyolefin melts in extensional flows. Rheologica Acta 2000; 39: 97.
http://dx.doi.org/10.1007/s003970050010

[3] Jahani Y, Barikani M. Influence of nanoclay on rheological properties of polyamide 6/acrylonitrile Foam Application. Iran Polym J 2005; 14: 361.

[4] Chul DFB, Park B, Suh NP. Effect of the pressure drop rate on cell nucleation in continuous processing of microcellular polymers. Polym Eng Sci 1995; 35: 432.
http://dx.doi.org/10.1002/pen.760350509

[5] Ramesh DHRNS, Campbell GA, Numerical and experimental studies of bubble growth during the microcellular foaming process. Polym Eng Sci 2004; 31: 1657.
http://dx.doi.org/10.1002/pen.760312305

[6] Kim WN, Burns CM. Compatibility studies of polystyrene–polybutadiene blends by thermal analysis. J Appl Polym Sci 1986; 32: 2989.
http://dx.doi.org/10.1002/app.1986.070320112

[7] Ramesh DHRNS, Campbell GA. The heterogeneous nucleation of microcellular foams assisted by the survival of microvoids in polymers containing low glass transition particles. Part I: Mathematical modeling. Polym Eng Sci 2004; 34: 1698.
http://dx.doi.org/10.1002/pen.760342207

[8] Ray S. Polymer/layered silicate nanocomposites: a review from preparation to processing. Progr Polym Sci 2003; 28: 1539.
http://dx.doi.org/10.1016/j.progpolymsci.2003.08.002

[9] Hoppner D, Wendorff J. Investigations of the influence on the phase morphology of pp-epdm-blends on their mechanical properties. Colloid Polym Sci 1990; 268: 500.
http://dx.doi.org/10.1007/BF01410292

[10] Ray S, Bousmina M. Compatibilization efficiency of organoclay in an immiscible polycarbonate/poly (methyl methacrylate) blend. Macromol Rapid Commun 2005; 26. 450.
http://dx.doi.org/10.1002/marc.200400586

[11] Tjong S, Liu S, Li R. Mechanical properties of injection moulded blends polypropylene with thermotropic liquid crystalline polymer. J Mater Sci 1996; 31: 479.
http://dx.doi.org/10.1007/BF01139167

[12] Yee A, Maxwell M. Mechanical properties of polymer mixtures: effect of Compatibility. J Macromol Sci Part B 1980; 17: 543.
http://dx.doi.org/10.1080/00222348008212826

[13] Yee A. Mechanical properties of mixtures of two compatible polymers. Polym Eng Sci 1977; 17: 213.
http://dx.doi.org/10.1002/pen.760170310

[14] Barlow J, Paul D. Polymer blends and alloys—a review of selected Considerations. Polym Eng Sci 1981; 21: 985.
http://dx.doi.org/10.1002/pen.760211502

[15] Malik T. Thermal and mechanical characterization of partially miscible blends of poly (ether ether ketone) and polyethersulfone. J Appl Polym Sci 2003; 46: 303.
http://dx.doi.org/10.1002/app.1992.070460211