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Observations of Polymer Foam Development during Rotational Moulding

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Abstract. Large scale buoyant structures typical of offshore wave energy generation devices may be produced using the rotational foam moulding process. Due to the challenging environmental conditions these parts experience during their lifetime at sea, it is important that the structures are optimised to ensure acceptable mechanical performance. Foams containing large cells suffer a reduction in mechanical properties; therefore, an optimal foam contains small, evenly sized, and well distributed bubbles in large numbers. Due to the lower pressures used in the process, this can be challenging to achieve. Careful selection of material and processing conditions is required to achieve an optimal structure. A unique bench-based rig was used to observe developing foam structures. A camera was used to record the foam height change at intervals. Foam height change was obtained using digital image analysis. Several parameters were studied such as the polymer particle size or the mould pressure for example. In addition to the foam height change, foam density were analysed. It is found that mould pressure, polymer particle size, chemical blowing agent concentration, and polymer rheology may be used to control the foamed structures.

Introduction

Large scale buoyant structures typical of offshore wave energy generation devices may be produced using the rotational foam moulding process. Due to the challenging environmental conditions these parts experience during their lifetime at sea, it is important that the structures are optimised to ensure acceptable mechanical performance. Foams containing large cells suffer a reduction in mechanical properties; therefore, an optimal foam contains small, evenly sized, and well distributed bubbles in large numbers [1]. Due to the lower pressures used in the process, this can be challenging to achieve [2].

Chemical blowing agents (CBAs) are the most suitable method of creating foams within the rotational moulding process, due to the thin mould walls used, which do not allow the application of the high pressures required for physical foaming [2]. There are four fundamental steps to foam manufacturing: the formation of a homogenous melt during pre-nucleation, the creation of small discontinuities or cells during nucleation; the growth of these cells to the desired volume; and the stabilisation and retention of the expanded form [3].

Careful selection of material and processing conditions is required to achieve an optimal foamed structure. Resin powder quality plays an important role in the pre-nucleation stage, as the gas from CBA decomposition initially targets the bubbles remaining from incomplete densification [3]. However, the effects of particle size on foam structures have not been conducted in the past, and details regarding powder quality in previous studies are poorly discussed [3-5]. Mould pressurisation techniques to improve densification, as discussed for non-foamed mouldings by Spence and Crawford, have also not been explored [4]. Similarly, studies have reflected on the use of mould pressurisation in the optimisation of the nucleation for the RFM process, but this has never been applied in experimental work [2]. Resin viscosity also has a strong affect the nucleation of rotationally moulded foams. Cell coalescence is reported to occur because of the weak melt strength of the molten

polymer during foaming [3,9]. A balance exists though, as the sintering ability of polymers require a high zero shear viscosity, however, at the growth stage it is reported that 'to maintain high melt flow strength, the melt flow ratio should not be too high. Otherwise, cell coalescence and cell coarsening will occur' [6]. High concentrations of CBA are not good for effective foaming, as mouldings are more expensive to produce, and tends to lead to excessive foam coalescence [3]. Equally, too little blowing agent is also not good, as the desired foam density will not be achieved. In order to make a foamed product with a certain thickness, an optimum amount of CBA is required. The amount of gas generated during decomposition must be known in order to calculate this amount. Eqs. 1 allows for the correction of the gas yield data, which is presented at room temperature conditions typically, to the decomposition temperature instead [7].

$$\emptyset = \emptyset\mathrm{STP} \times \frac{\mathrm{Vc}}{\mathrm{Vroom}} = \emptyset STP \times \frac{\mathrm{Tc}}{\mathrm{Troom}} \quad (1)$$

Where V_{room}, V_c, T_{room}, and Tc refer to gas volume at room, crystallisation, absolute room, and absolute crystallisation temperatures.

The volume expansion ratio (VER) may be then calculated if the concentration of CBA is known using Eqs. 2 [3]. Finally, the density of the foam may be predicted if the desired VER is known using Eqs. 3 [8].

$$VER = 1 + \frac{\mathrm{mCBA}}{\mathrm{mresin}} \times \rho resin \times \emptyset \quad (2)$$

Where m_{CBA} is the mass of CBA, m_{resin} is the mass of resin, ρ_{resin} is the resin density, and $\emptyset$ is the CBA gas yield.

$$\rho foam = \frac{\rho resin}{VER} \quad (3)$$

Where ρfoam is the foam density, and ρresin is the resin density.

The work aimed to develop procedures to provide for the optimisation of foam structures for large-scale lightweight rotationally moulded multi-layer products. The objective of the work was to establish the parameters that control foam, and quantify how much they effect the foam. Trial-and-error type optimisation of material and processing parameters for rotationally moulded foams is common in research and industry alike, which is both monetarily expensive, and time-consuming. This is typically conducted using laboratory-scale rotomoulding equipment, full-scale machinery, or through hot-stage microscope methods. The work presented used a flexible offline platform for observing polymer foaming behaviour during sample growth, developed by the authors to overcome these challenges [10].

Experimental Method

Foam Observation Method. Fig. 1 illustrates the equipment arrangement, as described in [10]. At the start of each run, the prepared test tube containing the mixture was lowered into the oil bath at the predetermined temperature. K-type thermocouples and a Picolog TC-08 were used to constantly monitor the temperature of the polymer melt and oil during the process. The test tube was removed from the heating oil, allowing for a temperature overshoot to reach the peak melt temperature, and placed into the cooling oil bath. A Leybold SCROLLVAC Plus pump, with a pumping speed of 20 m3/h and an ultimate pressure of 0.03 mbar, was used to pull a vacuum in a series of runs, using a bung to cap the test tube.

A Nikon D3200 digital camera was used to capture images of the foam in the test tube during experimentation. A Nikon DX VR AF-S Nikkor 18-55mm 1:35- 5.6 G II lens was attached to the

camera. A steel rule suspended from a retort stand was used to calibrate the scale of each image when conducting digital image analysis at a later stage. A rate of one frame per 20 seconds was found to be sufficient to capture the sample height behaviour changes in the experiment. A Schott ColdVision light source connected to fibre optic light panels were used to evenly illuminate the experiment. A green plastic screen was used to cover the background of the sample in the images captured.

Experimental Programme. From a preliminary study it was identified that mould pressure, polymer particle size, CBA concentration, and polymer rheology were important parameters for controlling polymer foam structures. A detailed experiment was conducted to quantify the effect of these key parameters using the test tube method. Genitron OB from LANXESS AG (Cologne, Germany) was used as the CBA for all samples produced in the experiment. Genitron OB has a decomposition temperature between 140 and 160°C, producing 125 mL/g of gas. The material was used as received. The peak melt temperature was set at 10°C above the upper decomposition temperature, to ensure full decomposition without increasing polymer temperature unnecessarily. The levels of CBA were set at 1wt% unless otherwise stated, in line with recommendations from the manufacturer. Table 1 establishes the conditions used to prepare the foam samples in the experiment.

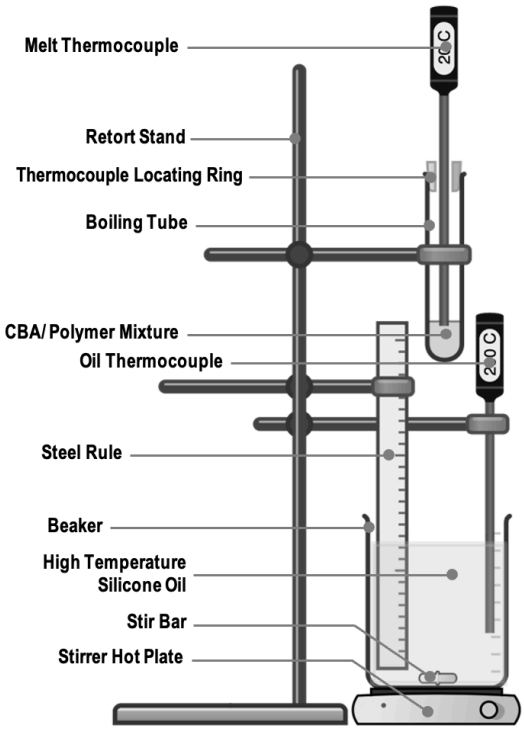

Fig. 1. Experimental Equipment Arrangement.

Table 1. Fixed Conditions used to Prepare the Foam Samples.

Fixed Variable	
Heating Oil Bath Temperature	180°C
Cooling Oil Bath Temperature	50°C
Peak Melt Temperature	170°C
Mould Pressure	Atmospheric*

*Unless otherwise stated.

To represent a typical rotational moulding grade of material that would be widely available in an industrial manufacturing setting, PE-1 was used for the majority of the trials. In order to explore the effects of polymer rheology, PE-2 - PE-6 were used. These materials from the same LDPE product range, and were available in a wide range of the melt flow index (MFI) options to explore the effect

of polymer flow characteristics. The flow regimes covered the processing windows common for most polymer manufacturing processes. PE-2 - PE-5 were supplied in pellet form, and were cryogenically ground using a Wedco Grinder prior to moulding. Table 2 presents the characteristics of the resins used.

The mould pressure, polymer particle size, and CBA concentration were also explored. Table 3 establishes the levels used to study the effect of each of these parameters using PE-1. For the pressure effect study, the vacuum pressure was applied from the start of the heating cycle and remained at a constant pressure until the sample had solidified at the end of manufacture. All samples were repeated three times and the results averaged, expect for the samples made under vacuum pressure due to health and safety concerns.

Table 2. Summary of Resin Characteristics.

Resin	Trade Name	Supplier	Polymer Type	Melt Flow Index (g/ 10 min)	Melting Point (°C)	Density (g/cm3)
PE-1	mM3583 UV	Total Petrochemicals	MDPE	6.0	123	0.935
PE-2	1700MN18C	Total Petrochemicals	LDPE	70	105	0.918
PE-3	1200MN18C	Total Petrochemicals	LDPE	22	106	0.918
PE-4	1070MN18C	Total Petrochemicals	LDPE	7.5	108	0.918
PE-5	FD0274	Lotrene (Produced by Total Petrochemicals)	LDPE	2.4	111	0.923

Table 3. Variables and Corresponding Levels Studied.

Study Name	Level 1	Level 2	Level 3	Level 4
Polymer Particle Size	425 µm -500 µm	300 µm -425 µm	212 µm -300 µm	90 µm -106 µm
CBA Concentration	1 wt%	2 wt%	3 wt%	4 wt%
Mould Pressure	Atmospheric	-25kPa	-50kPa	-75kPa

Image Analysis. MIPAR image analysis software was used for the extraction of transient height change data. The crop tool was used to reduce the image to only the ROI. Due to the complexity of the images, colour segmentation tools were found to be the most useful for extracting the data from the image, establishing the white shades in the foam to separate them from the other background colours of the image. The two segmentations were then be used to select the white foam region when performing the thresholding of the foam sample. The measure tool was then used to place a bounding box around the ROI and extract the length of the long axis of the box, providing a single measurement of foam height change. Once setup, the recipe could be applied to a set of frames from an experiment to obtain results for each time interval in a set of results.

Density Analysis. The density of foam samples was determined using the immersion method, as adapted from BS EN ISO 1183-1:2019. 5 mm thick foam sections were prepared from the same location in every foam sample, followed by manual trimming to form a cuboid. Samples were visibly checked for large entrapment of air bubbles during testing. Specimens were weighed to the nearest 0.1 mg. The density of the foam, ρs, in grams per cubic centimetre, was calculated using Eqs. 4. Note that apparent mass is defined as the 'mass of a body obtained by measuring its weight using an appropriately calibrated balance'.

$$\rho s = (ms, A \times \rho IL) / (ms, A - ms, IL) \quad (4)$$

Where:

ms,A is the apparent mass of specimen in air, in g;
ms,IL is the apparent mass of the specimen in the immersion liquid, in g;
ρIL is the density of the immersion liquid at the recorded temperature, in g/ cm^3.

Results & Discussion

Fig. 2 shows images captured from a typical video recorded during experimentation. The frames from each experiment were imported into MIPAR to extract the transient sample height data. Prior to the development of the method, making real-time observations of foam growth using the pre-existing experimental methods was challenging. The transparent glassware in conjunction with silicone oil to heat the system, provided a unique view of the foam behaviour during experimentation.

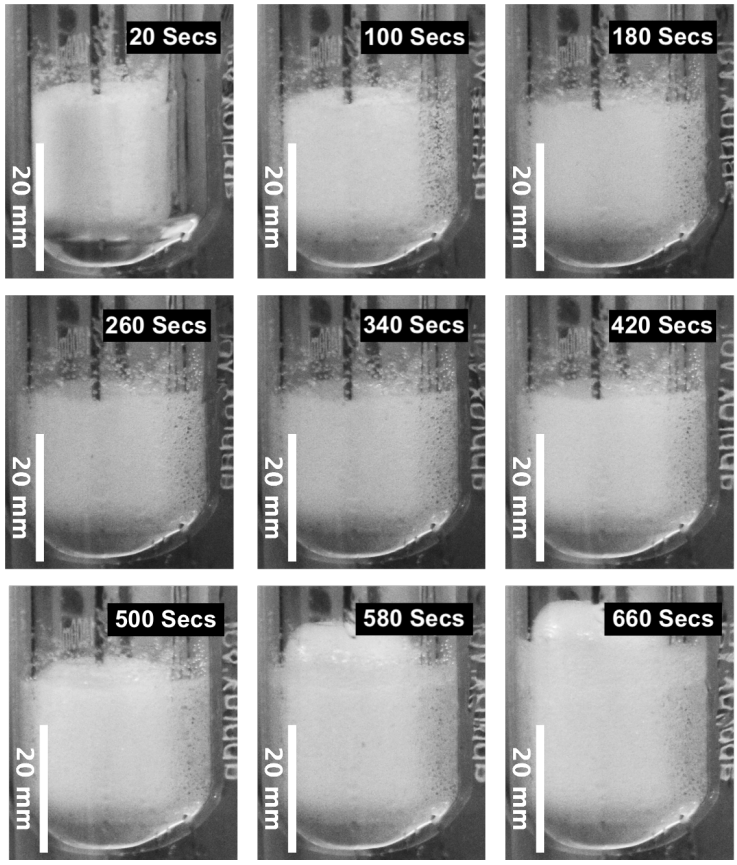

Fig. 2. Typical Sample Development Behaviour.

Polymer Particle Size. Fig. 3 shows the effect of polymer particle size on the height of the foam produced. It is found that decreasing the particle size increases the height of the foam produced. Fig. 4 shows the foam density behaviour, demonstrating that decreasing the particle size of the resin reduces the density of the foam produced. This finding appears to agree with [3, 5], however a detailed study of particle size using the hot stage microscope would be beneficial to confirm that the faster densification provided by the finer resin particle size is the reason for this improvement in foaming behaviour, and not a result of some other factor, such as better mixing quality for example. Consideration should also be given to the economical impact of using a finer particle sizes in future work for this purpose, as a higher grinding quality will increase the cost of the resin.

Polymer Rheology. Fig. 5 demonstrates the behaviour of a range of polymers with varying melt flow properties. The height of the samples is found to decrease with increasing MFI. It can be seen that PE-2 produces the tallest foam, having an MFI of 70 g/10 mins. In contrast, PE-5 produces the smallest foam with an MFI of 2.4 g/10 mins. Fig. 6 shows the foam density behaviour of the various resins. It can be seen that the foam density decreases with increasing MFI. PE-2 with an MFI of 22 g/10 min produced the lowest density foam. Materials with an MFI in the region of 2.4 - 7.5 g/10 mins are found to be most suitable, in agreement with [9].

CBA Concentration. Fig. 7 shows the effect of CBA concentration on the foam sample height. It can be seen that increasing the CBA amount incrementally increases the height of foam produced. It appears there is an upper limit to this effect though, with concentrations above 3wt% presenting a smaller height increases. Fig. 8 shows the variation of density with increasing concentration of CBA in comparison to the predicted foam density calculated using Eqs. 1, 2, and 3. It can be seen that each incremental increase in CBA concentration reduces the density of the foam produced. An optimal value exists though, as concentrations above 3wt% only produce a small reduction in foam density. Comparing the calculated density with the measure density, an under prediction is found for the lower CBA concentrations, and similarly and over prediction at higher concentrations. There is, however, a good approximation between the calculated and measure densities at the optimal value of 3wt%.

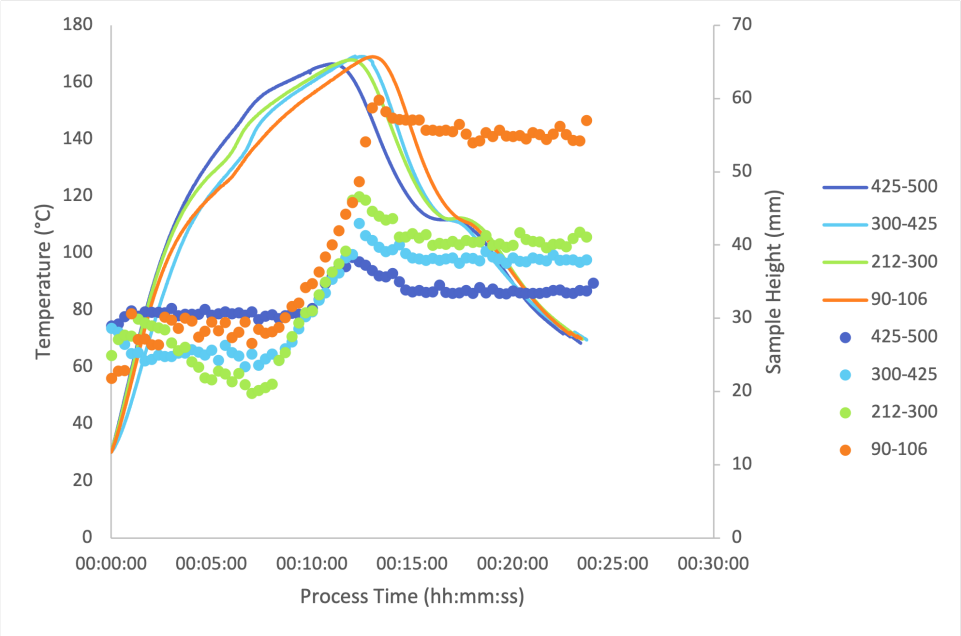

Fig. 3. Effect of Polymer Particle Size on the Sample Height and Melt Temperature.

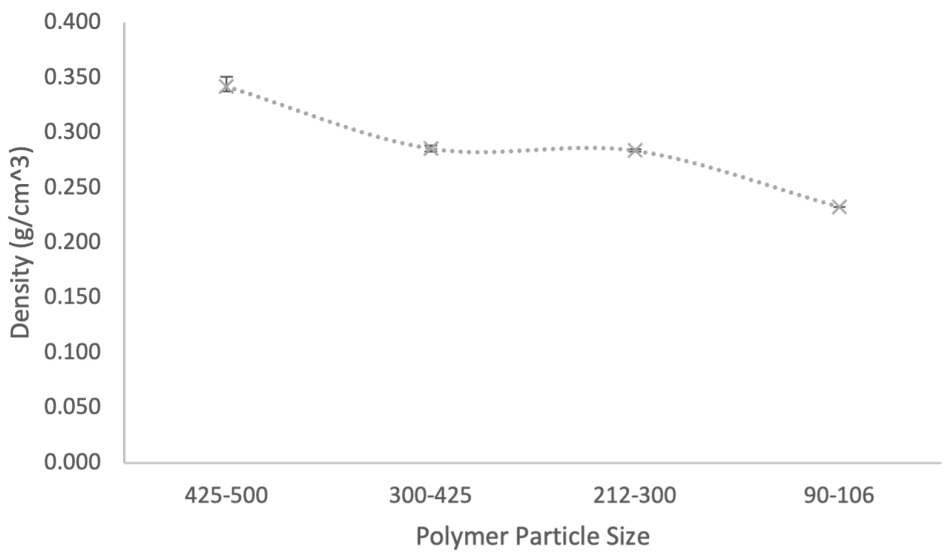

Fig. 4. Variation of Foam Density with Change in Particle Size.

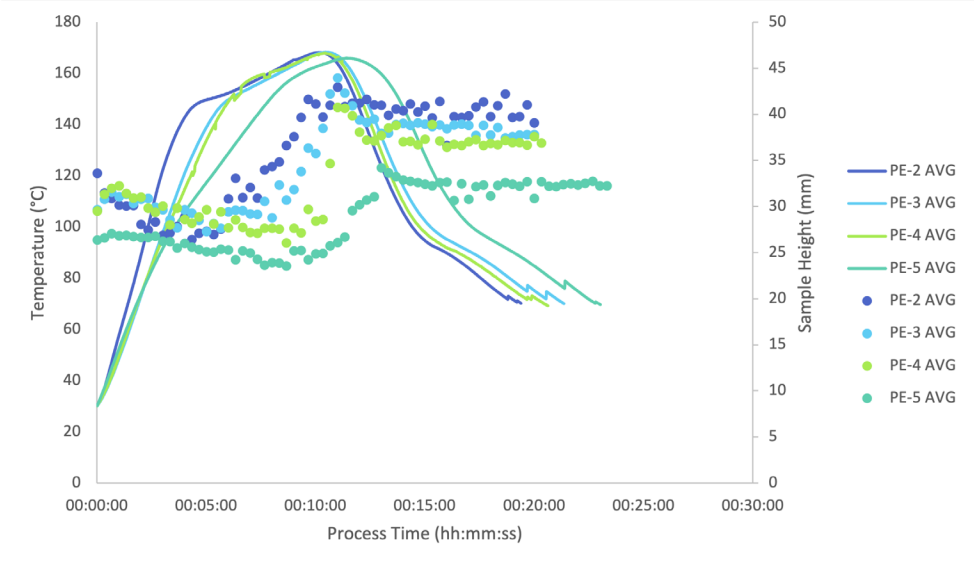

Fig. 5. Effect of MFI on the Sample Height and Melt Temperature.

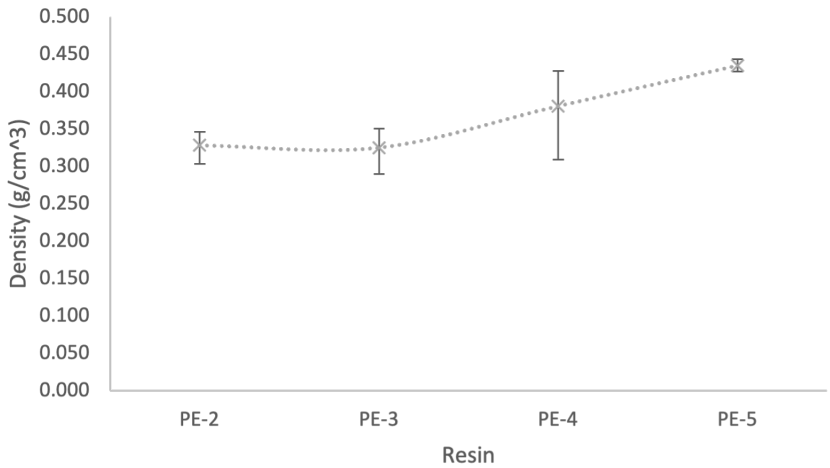

Fig. 6. Variation of Foam Density with Change in MFI.

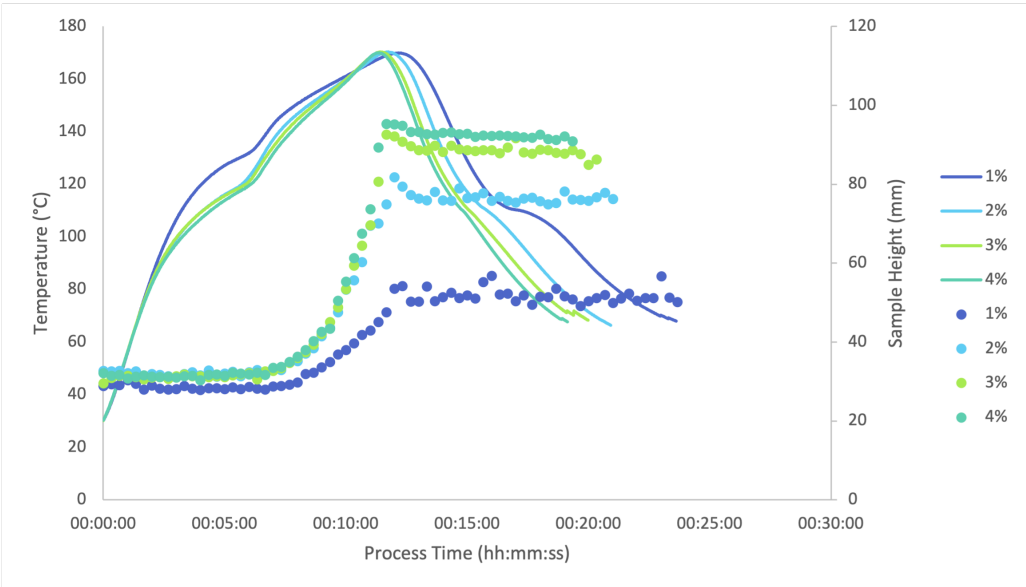

Fig. 7. Effect of CBA Concentration on the Sample Height and Melt Temperature.

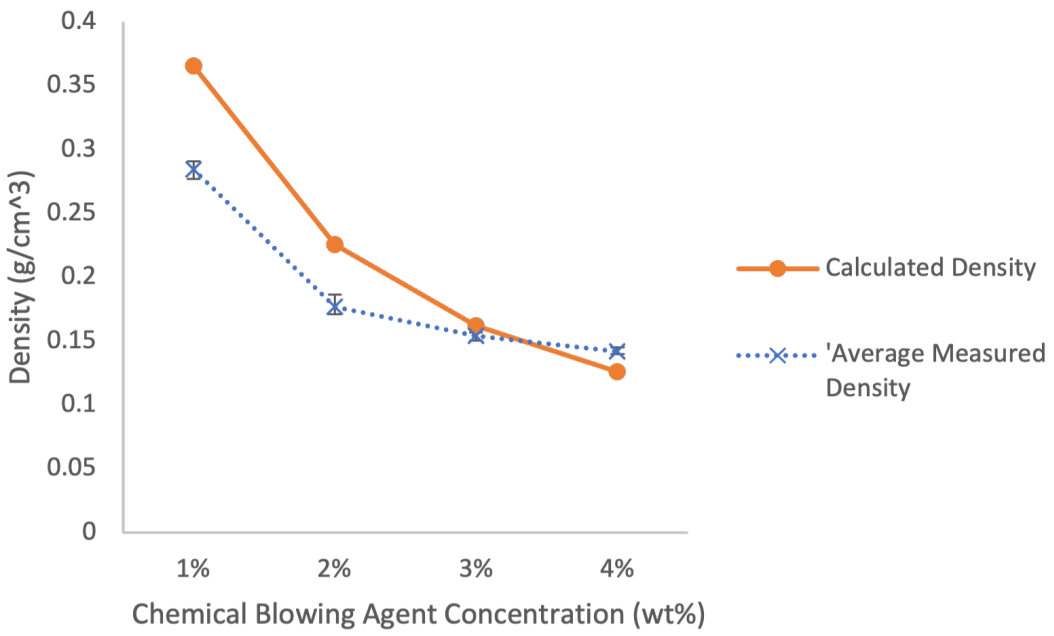

Fig. 8. Variation of Density with Change in CBA Concentration.

Mould Pressure. The melt temperature could not be obtained during the creation of the samples in this study, the removal temperature was therefore based on the time of events from the previous studies. The samples were moved from the heating oil bath to the cooling oil bath at 12 minutes. Fig. 9 shows the behaviour of foam samples produced under increasing increments of continuous vacuum conditions. It can be seen that increasing the vacuum pressure incrementally increases the height of the foam produced. Fig. 10 shows the density variation of the samples with changing vacuum pressure. It can be seen that each incremental increase in vacuum pressure decreases the density of the foam samples produced.

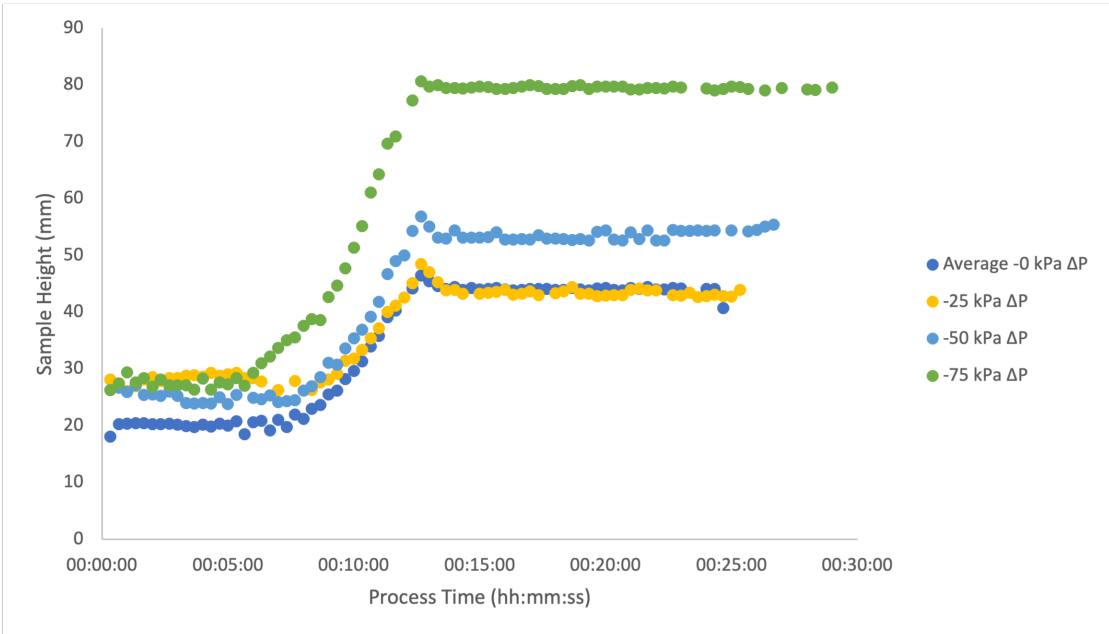

Fig. 9. Effect of Vacuum Pressure on the Sample Height and Melt Temperature.

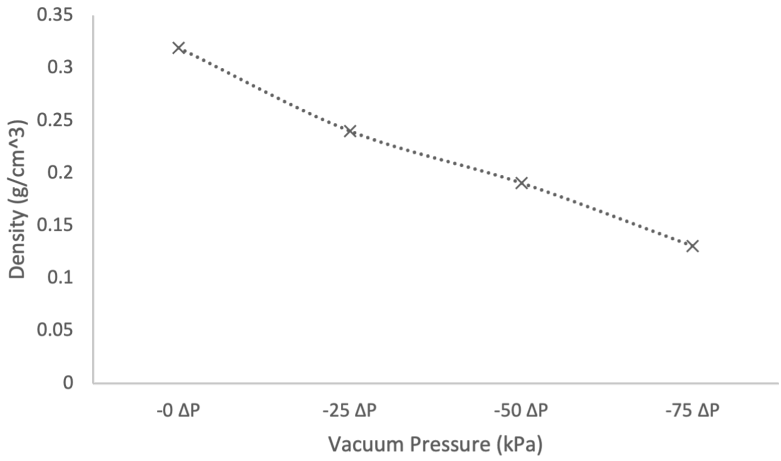

Fig. 10. Variation of Foam Density with Change in Vacuum Pressure.

The benefits of mould pressurization are demonstrated in Figures 9 and 10. However, due to health and safety concerns, further studies could not be conducted. Mould pressurisation has been successfully used for controlling densification in the past, with vacuum pressures considered to be the safest option for achieving this [4]. This could allow coarser particles to be used, potentially reducing the cost of the resin. It was though that the use of mould pressure to control densification could also remove the careful balancing act of polymer rheology properties needed to create foams in rotational moulding, meaning that higher zero shear viscosity materials with a high melt strength could be explored instead. Speeding up densification would mean that CBAs with a lower decomposition temperature would be needed to shorten cycle times. Exothermic CBAs may then perform better under the lower temperatures. Similarly, kickers could be explored to lower the decomposition temperature of the faster reacting exothermic CBAs too.

Conclusions

The aim of the work was to develop processes and procedures to enable the optimisation of foam structures for large-scale lightweight rotationally moulded multi-layer products. The objective of the work was to establish the parameters that control foam and quantify how much they effect the foam. The following key conclusions were drawn from the work:

1. A unique method using a glass oil bath to heat tests tubes containing polymer/ CBA mixtures was found to be a very successful rapid method for observing the evolution of a polymer foam structure during its production. The method allowed for sample height changes to be anlaysed, and provided samples suitable for post-moulding characterisation, such as for density analysis.
2. In order of importance, the key variables that control CBA developed foams in terms of foam density are found to be polymer rheology (0.290-0.598 g/ cm^3), mould vacuum pressure (0.131-0.319 g/ cm^3), CBA concentration (0.291- 0.134 g/ cm^3), and polymer particle size (0.227-0.351 g/ cm^3). Heating rate, cooling rate, and PST are also found to influence the foam structure, but their effects were less significant.
3. It was demonstrated that mould pressurisation could control foaming behaviour. Studies should be continued to understand how pressure applied after CBA decomposition might be used to maintain the foam structure during cooling.
4. Future work should also explore the use of mould pressurisation for speeding up the densification process, meaning that the process is no longer limited to materials that naturally densify during a standard moulding cycle. This could mean that materials that are less susceptible to cell coalescence could be used, and by the subsequent lowering of CBA decomposition temperature, cycle times could be reduced.

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