

## **The Effect of Additives on Microcellular PVC Foams: Part 1 - Effect on Processing and Microstructure**

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### **SUMMARY**

The effect of the presence of commonly used additives on the processing and structure of microcellular PVC foams was investigated. It was found that the presence of additives leads to a polydisperse cell structure with large variations in cell sizes. The solubility of carbon dioxide in the additives and in the lubricants was found to be lower than in the PVC matrix. The presence of additives showed no adverse effect on the overall foam growth dynamics. It appears that target reductions in density of PVC can be achieved at lower processing temperatures when additives and processing aids are present.

### **INTRODUCTION**

Microcellular polymers are a novel class of polymer foams that offer the possibility of replacing solid polymers in applications where the full strength of the solid polymers is not needed. This is especially true for many PVC products used in the building and construction industries, where bearing a load is not the primary function of the product. Microcellular PVC foams with a reduction in density of 10% to 40% could be used in many applications, leading to a significant reduction in materials and transportation costs. Given the large volume of PVC products used in construction<sup>(1)</sup>, a potential for significant cost savings exists. A brief review of microcellular foams and their potential has been presented by Kumar<sup>(2)</sup>.

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reported by Kumar and Weller<sup>(3)</sup>. In that study a rigid PVC formulation especially prepared to be free from additives was used, and it was shown that microcellular PVC foams with relative densities of 0.1 and higher can be produced. Recently Matuana et al.<sup>(4)</sup> have reported tensile and impact data on microcellular PVC foams. These studies have established the basic feasibility of producing microcellular PVC. However, it is well known that PVC processing employs a large number of additives and process aids. In order to harness the potential represented by the family of microcellular PVC foams, it is first necessary to determine how the additives and processing aids commonly used with PVC affect the processing, structure and mechanical properties of microcellular PVC foams. This study was undertaken to answer these questions. In part 1 of this investigation the effect of additives on the processing and microstructure of microcellular PVC foams is presented. In Part 2, the effect of these parameters on the tensile behaviour will be presented.

## BACKGROUND

The addition of additives and plasticizers to "virgin" PVC resin is known to decrease the effective glass transition temperature of the PVC blend and alter the blend behaviour to a sufficient extent that it can be extruded, calendared or injection moulded without severe thermal degradation<sup>(5)</sup>. The transition temperature at which segmental polymer chain sliding motion may occur is defined as the effective glass transition temperature of the plasticized polymer blend. A combined theoretical and experimental analysis of the plasticization of PVC by several industrially significant plasticizers was reported by Beimes and Burns<sup>(6)</sup>. A wide range of material properties can be achieved in PVC through specifically selected combinations of plasticizers and processing aids. Because of the enormous flexibility this provides to designers, approximately 75% of the total volume of plasticizers used in commercial plastic products is used in the production of PVC articles<sup>(5)</sup>. In the solid state microcellular foam process, the PVC blends used in this study included precompounded additives and processing aids. To these precompounded materials a soluble gas, carbon dioxide, was added to the matrix. The gas acts as a plasticizer. In fact, one theory of plasticization concludes that a gas should function as the most efficient plasticizer due to its small size and minimal interaction with the polymer<sup>(5)</sup>.

The solid state microcellular process has been described<sup>(2,7)</sup> as a two-stage process. The first stage corresponds to the introduction of blowing gas into the polymer at temperatures below the glass transition temperature

when the specimen is surrounded by subcritical gas at high pressure. In equilibrium, a specimen exposed to these high surface gas concentrations will acquire a uniform gas concentration throughout the polymer specimen. The presence of the blowing gas acts on the polymer as a significant plasticizing agent as well as working as the driving force for bubble nucleation and growth.

The second-stage corresponds to the heating of the gas-polymer mixture thereby inducing bubble nucleation followed by growth. Bubble nucleation and the rate of bubble nucleation are most sensitive to local gas concentration and polymer temperature. After nucleation has occurred the growth rate is limited by the rate at which gas diffuses from the gas saturated bubble wall into the bubble as well as the manner in which the bubble wall accumulates and dissipates the stress associated with growth. Due to the presence of the gas in the polymer the glass transition temperature is significantly depressed and the gas-polymer mixture behaves as a rubbery viscoelastic-viscoplastic solid. In solid state microcellular systems, because the polymer is very stiff, surface tension effects are negligible compared to the elastic-plastic stresses in the bubble wall. This material behaviour has a significant impact on the observed process dynamics of solid state microcellular systems that is distinctly different from the dynamics of a non-Newtonian polymer melt.

A technique for large scale production of microcellular foam sheets has been developed in which a roll of polymer film can be converted to a roll of microcellular foam<sup>(7,8)</sup>. The solid state processing technique has the unique advantage that it can produce very thin microcellular foamed parts of carefully tailored microstructure. In practice, this technique is most applicable to modified vacuum thermoforming operations and continuous sheet fabrication processes. Thick microcellular parts can and have been produced using the batch process and very novel structures are possible<sup>(2,9)</sup>. A limitation of this process is the time required for diffusion of the blowing gas into the polymer which increases as a function of the part thickness, decreases as temperature increases, and varies substantially for different gas-polymer systems.

In the study by Kumar and Weller<sup>(3)</sup> the effect of foaming temperature and time upon steady microcellular foam structure was examined for a single initial gas concentration within the PVC matrix prior to foaming. For the rigid PVC blend examined in that study, a monodisperse closed cell structure was observed over a wide range of foaming temperatures. At temperatures exceeding the glass transition temperature of the PVC matrix the nature of the structure changed from closed cell to a combination of both closed and open cells. The reason for this behaviour transition has

mechanism present in solid state microcellular systems<sup>(7)</sup>.

This paper presents a two factor experiment designed to both qualitatively and quantitatively determine the effect of additives upon steady state foam structure in the PVC-CO<sub>2</sub> system. The two factors examined are PVC blend composition and foaming temperature. A single set of gas saturation boundary conditions was used in the experimental protocol. These conditions are therefore considered fixed parameters in this study. Dynamic foam growth response data was also recorded.

### EXPERIMENTAL

The PVC blends used in this study were provided by ALCOA Building Products. The generic compositions of the three blends investigated are given in Table 1. The experiment was designed such that a direct comparison of the foams produced from PVC-A, PVC-B, and PVC-C formulations would reveal significant effects of additives upon foam structure produced by the solid state microcellular process. Because PVC-B and PVC-C only differ in the type of lubricant (stearate) used direct comparison of PVC-B and PVC-C foams should reveal foam structure sensitivity to the type of lubricant selected. The glass transition temperature of the virgin PVC resin was approximately 80°C. The approach taken was to compare foams produced using a typical standard industrial polymer

**Table 1 Compositions of PVC blends (all quantities are in phr - parts per hundred resin by weight)**

Sample	PVC-A phr	PVC-B phr	PVC-C phr
PVC	100	100	100
Stabilizer	0.8	1.5	1.5
Wax	1.0	1.0	1.0
Stearate	1.25	0.5	1.0
Processing aid 1	0.7	0	0
Processing aid 2	0.3	0	0
Impact modifier	5	0	0
Oxidized PE	0.2	0	0
Titanium dioxide	0.2	0	0
Calcium carbonate	10	0	0
Type of stearate	Calcium	Pentaerythritol adipate	Calcium

with as little additive concentration as possible while still maintaining the minimum required processability required by the extrusion process used to produce the specimens. Thus PVC-A is an approximation of a standard polymer blend used in a building products manufacturing process. The blends identified as PVC-B and PVC-C were formulated to approximate, as closely as possible, to the virgin PVC resin. The stabilizer and wax used in the blend were completely immiscible in the PVC matrix. Blends containing wax and stabilizer alone could not be satisfactorily processed on the extruder without burning the formulation. Consequently a lubricant was added to enhance extrusion processability.

A twin screw extruder was used with a 15.24 cm (6 inch) extrusion die to produce 1.52 mm (0.060 inch) thick extruded PVC sheet for each of the three PVC blends. Specimens 3.17 cm (1.25 inch) square were prepared from the extruded sheet. The prepared specimens were placed in a pressure vessel that was maintained at 40°C and pressurized with 6 MPa carbon dioxide gas. The specimens remained in the pressure vessel until an equilibrium gas concentration level was attained. Once equilibrium with the carbon dioxide gas was attained the specimens were removed in lots of three for foaming at different foaming times. A specimen was immersed for a predetermined length of time then removed and quenched in ambient temperature water.

The internal structure of the foams produced was examined using SEM micrograph images taken from the centre of the foam specimen. The centre of the foam was exposed by first quenching the foam in liquid nitrogen and then snapping the brittle foam specimen. The specimens were then coated with gold-palladium (AuPd) and SEM photographs were taken of the foam structure at 1500X magnification. The bulk foam void fraction was determined using an Archimedes water displacement technique to first measure the bulk foam density. Void fraction was then inferred directly from the density measurements.

### RESULTS AND DISCUSSION

Figure 1 shows the uptake of carbon dioxide in the three PVC blends. Equilibrium values are shown in Table 2. It can be seen that all specimens reach equilibrium at approximately the same time, indicating that the diffusion rate of carbon dioxide was not significantly affected by the presence of additives. Figure 2 presents the equilibrium gas concentration level for each of the PVC blends (PVC-A, PVC-B, and PVC-C) when each blend is exposed to carbon dioxide at 6 MPa and 40°C. The low additive concentration PVC blends (PVC-B and PVC-C) absorbed more carbon

Figure 1 Carbon dioxide uptake as a function of time at 40°C

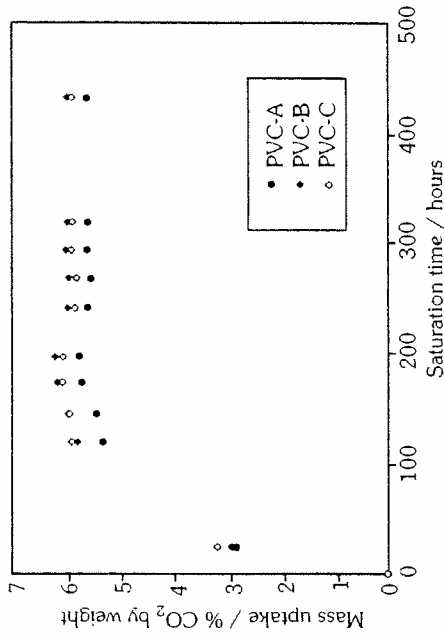
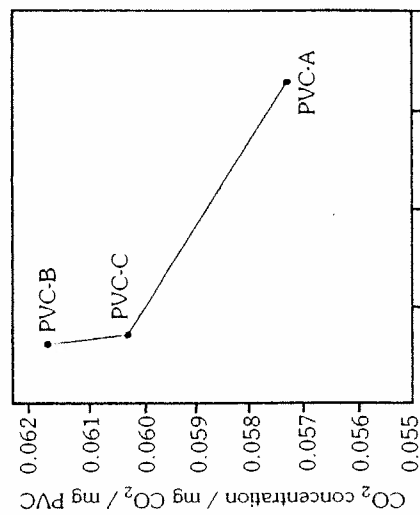


Table 2 Equilibrium gas concentration after exposure to carbon dioxide at 6 MPA and 40°C

PVC Blend	Gas concentration at equilibrium mg CO <sub>2</sub> / mg (PVC blend)
PVC-A	0.0573
PVC-B	0.0618
PVC-C	0.0603

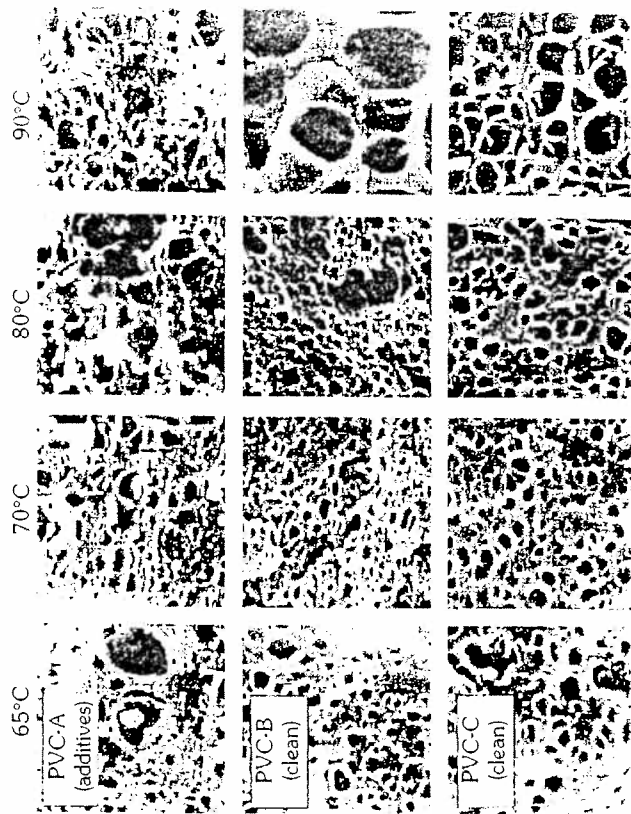
Figure 2 Equilibrium gas concentration as a function of additive concentration



dioxide than the PVC blend containing a higher weight percentage of additives (PVC-A). This suggested that the solubility of carbon dioxide in the additives of the blend was significantly lower compared to the solubility of carbon dioxide in PVC resin.

Figure 3 shows a matrix of SEM micrographs of the steady state foam structure produced as a function of blend composition and foaming temperature. Row 1 of Figure 3 shows foams produced using the PVC-A, the blend with high additive concentration. Several observations can be made as follows: firstly, a large variation in the cell diameter distribution is observed. That is, the cells present in the foam are strongly polydisperse in their distribution. Secondly, it appeared that a substantial open cell content was present. Finally, secondary phase particles are clearly observable. These distinct secondary phase particles were probably the impact modifier in the PVC-A blend. It was also observed from Figure 3 that the foam structures produced from PVC-B and PVC-C blends at low additive concentrations were virtually identical though the cell sizes were:

Figure 3 Steady state PVC foam structure. The rows are associated with a single polymer blend: row 1: PVC-A, row 2: PVC-B, and row 3: PVC-C. The columns are associated with different glycerin foaming bath temperatures according to the temperatures quoted at the head of the columns



significantly different at 80 and 90°C. There was a relatively small variation in cell size distribution (the cells were essentially monodisperse) and the foam structure is composed of closed cells. The only difference between the two blends is the type of lubricant used in the blend and a small variation in lubricant concentration. It appeared that the PVC-A structure was little affected by the foaming temperature, whereas PVC-B and C seemed to indicate significantly higher cell sizes when foamed above the T<sub>g</sub> of the resin. At 90°C foaming temperature, the micrographs for PVC-B and C showed evidence of ruptured cells indicating an indeterminate amount of open-cell content in these foams. Also a comparison of the cell structures formed after steady state expansion at 90°C shows that the average cell size is in the order PVC B > C > A. It was noted that this was in the reverse order of stearate concentration i.e.: 0.5, 1.0 and 1.25 phr respectively. It was hypothesized that increased stearate concentrations caused higher extensional viscosity leading to small cells or affected the surface tension.

However, other factors influence cell size. The final cell size is strongly influenced by bubble nucleation. The presence of TiO<sub>2</sub> and CaCO<sub>3</sub> in the PVC-A formulation provide sites for heterogeneous nucleation. Due to the very large number of cells present, the increase in void fraction as foaming temperature increased (cf. Figure 8) was accompanied by only a very small increase in average cell size for PVC-A. Put another way, the available gas was shared by all the bubbles that survived, and the larger the bubble density, the smaller the average size. Thus, in addition to the possible effect of stearate concentration, the smaller cell size of PVC-A was likely to be due to a higher cell density relative to PVC-B and C which appeared to be a direct result of increased heterogeneous nucleation from the relatively high concentration of particulate additives. It is also possible that heterogeneous nucleation may be enhanced by the immiscible lubricant. However, further work is required to fully investigate the effect of lubricant type and concentration.

Bulk void fraction of a foam is used to quantify the extent of foam growth. The void fraction of a foam is defined as the ratio of the volume occupied by the foam cells to the total volume occupied by the foam. The bulk foam growth is a geometrically dependent response because for the initial gas concentration profiles examined in this study (approximately uniform throughout the polymer excluding a thin gas depleted region on the specimen surfaces), foam growth begins near the specimen edge and propagates inward toward the specimen centre as thermal energy propagates inward from the surfaces exposed to the heated glycerin bath.

Figures 4 to 7 present the dynamic void fraction growth response at 65°C, 70°C, 80°C, and 90°C respectively for the single gas saturation level examined in this paper. From these data, the steady state void fraction as a function of foaming temperature has been plotted in Figure 8 for the three PVC blends. At all foaming temperatures no significant difference in bulk void fraction response is observed in the foams produced using either PVC-B or PVC-C. Interestingly, for a foaming temperature of 65°C the foam void fraction of PVC-A is approximately 10% higher than that of PVC-B and PVC-C. Also, to produce a foam with a void fraction of 0.4 the blend with additives can be processed at 65°C, while the other blends need to be foamed at approximately 75°C. In other words, for a given reduction in PVC density, the blend with higher additive concentration (PVC-A) can be foamed at a lower temperature. As the foaming temperature increased the difference between the bulk void fraction produced by PVC-A and both PVC-B and C steadily decreased. Preliminary results indicate that a direct correlation between the effective glass transition temperature of the PVC blend as a function of carbon dioxide level is responsible for this effect. From the void fraction data in Figures 4 to 7 it is evident that for all PVC blends and temperatures steady state foam structure is achieved in approximately one minute for the 1.52 mm (0.060 inch) thick specimens used in this study. The data also

Figure 4 Dynamic foam growth response of blends equilibrated with carbon dioxide at 6 MPa and 40°C then immersed in a glycerin bath at 65°C

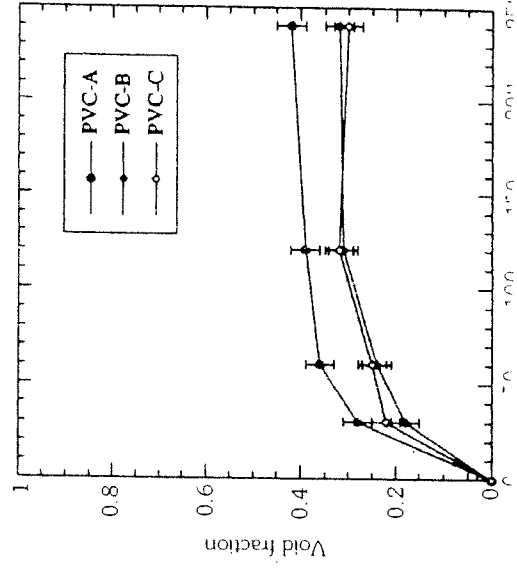


Figure 5 Dynamic foam growth response of blends equilibrated with carbon dioxide at 6 MPa and 40°C then immersed in a glycerin bath at 70°C

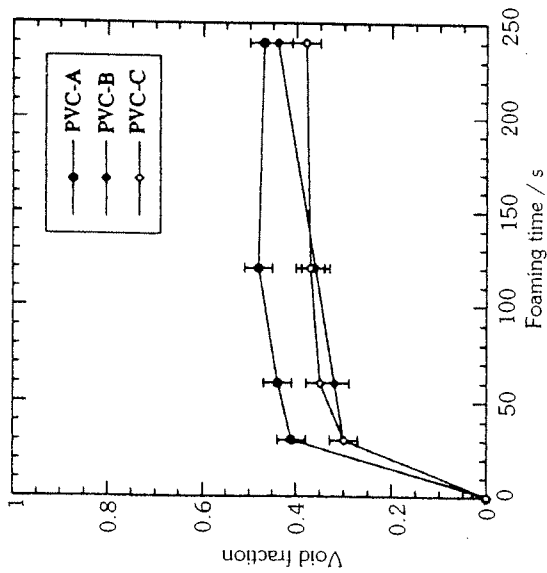


Figure 7 Dynamic foam growth response of blends equilibrated with carbon dioxide at 6 MPa and 40°C then immersed in a glycerin bath at 90°C

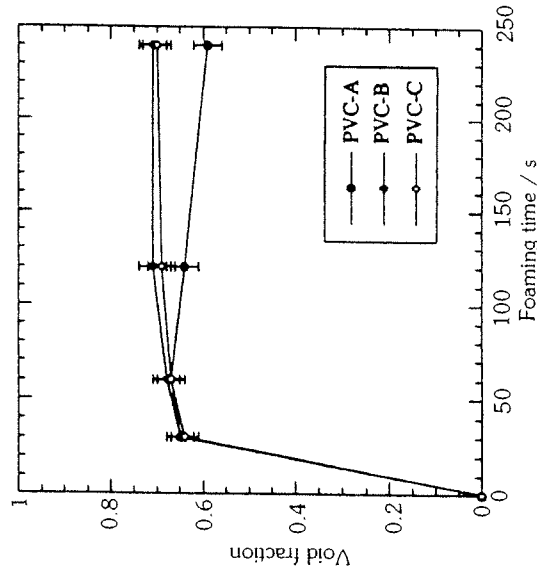


Figure 6 Dynamic foam growth response of blends equilibrated with carbon dioxide at 6 MPa and 40°C then immersed in a glycerin bath at 80°C

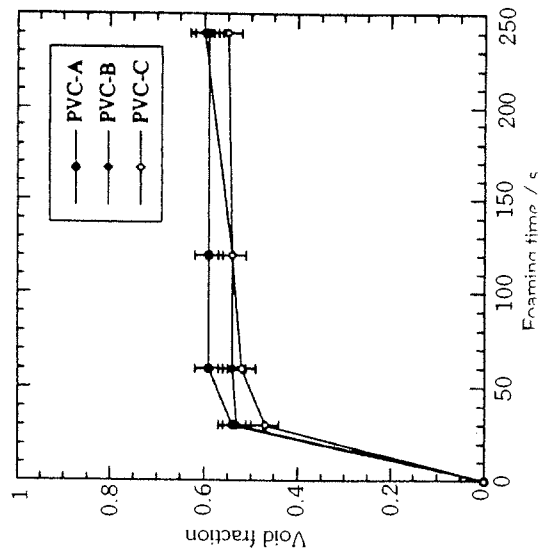
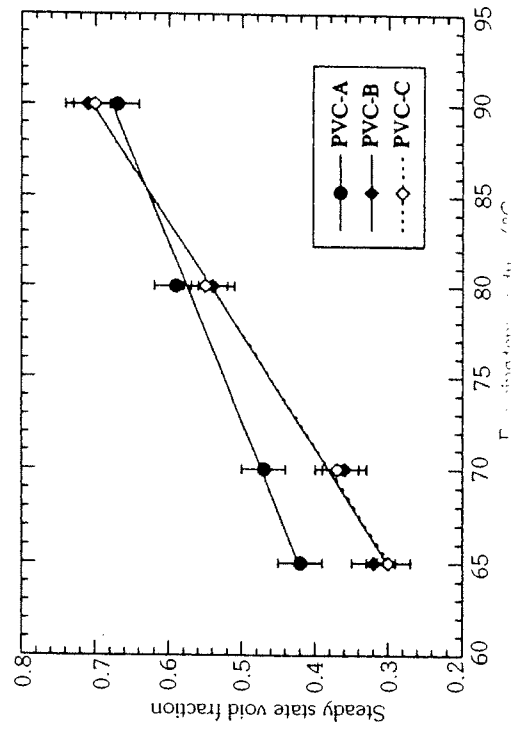


Figure 8 Steady state void fraction as a function of foaming temperature for the three PVC blends



indicates that the expanded foams are relatively stable over the immersion time considered in this work. The one exception is the PVC-A formulation at 90°C (Figure 7). Here it is suggested that the higher additive concentration may contribute to gradual collapse of the foam due possibly to a greater propensity for diffusion gas loss.

### CONCLUSION

A number of conclusions can be drawn from the experimental program presented in this paper. First, the presence of high additive concentrations leads to a solid state foam with both open and closed cells and a large variation in cell sizes. In contrast, PVC resins with minimal additive loading produce solid state microcellular foams where the cells are closed and the cell size variance is small. Second, the type of internal lubricant used in the blend does not appear to have a significant effect on the foam structure. Third, the carbon dioxide solubility of the PVC blend is directly correlated with the composition of the blend and the solubility of the carbon dioxide within each of the blend components. Finally, the foam growth data shows that the presence of additives may allow target reduction in PVC density to be obtained using lower foaming temperatures. The presence of additives did not show any adverse effects on the microcellular processing of PVC though may affect foam stability at elevated temperatures.

### ACKNOWLEDGEMENTS

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