

THE EFFECT OF ADDITIVES ON PVC SOLID STATE MICROCELLULAR FOAMS

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Abstract

The presence of plasticizers and processing aids at concentrations normally present in a wide range of commercial PVC product blends is demonstrated to significantly alter both the cell type and cell structure produced by the solid state microcellular process.

This paper presents results for a screening level experimental program specifically designed to identify whether the plasticizers and additives significantly alter the foam structure.

It was determined that high concentrations of plasticizers and additives produce a polydisperse cellular structure with visible evidence of open cell content. Whereas, the foam structure produced using "neat" (but processable) PVC was monodisperse and composed of closed foam cells. These "neat" PVC foams exhibited foam structure similar to that produced in other thermoplastic systems when the polymer blend was composed of a single base polymer and minimal additional plasticizers and processing aids (for example, the extensively studied polycarbonate-carbon dioxide system).¹

Introduction

In the early 1990's the sale of PVC products was only exceeded by the sale of LDPE products (Carley, 1991). Of the total volume of PVC used roughly 60% was used in the building and construction products industry. In many of the products produced in this industry a significant fraction of the PVC used in the product is not used in a load (or stress) bearing capacity. The strength of a material is directly correlated to the bulk structure of the foam. Therefore, as long as the material strength is not drastically compromised the solid PVC can be replaced by a PVC foam. Replacing solid PVC with a PVC foam has two immediate practical benefits: 1) reduced direct material costs, and 2) reduced shipping costs. Therefore, the potential for significant dollar savings exists.

The addition of plasticizers to "neat" PVC resin are known to decrease the effective glass transition temperature of the PVC blend and alter the blend behavior to a sufficient extent that it can be extruded, calendered, or injection molded without severe thermal degradation (Sears and Darby, 1982). 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. An combined theoretical and experimental analysis of the plasticization of PVC by several industrially significant plasticizers was given by Beimes and Bums (1986). 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 75% of the total volume of plasticizers used in commercial plastic products are used in the production of PVC articles (Sears and Darby, 1982). In the solid state microcellular foam process the PVC blends used in this study will have pre-existing plasticizer, additive, and processing aid levels. To these pre-existing levels a soluble gas is added to the matrix, carbon dioxide in this paper. The gas acts as an additional 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 plasticized polymer (Sears and Darby, 1982).

The solid state microcellular process has been described commonly as a two-stage process. The first stage corresponds to the introduction of blowing gas to the polymer at temperatures below the glass transition temperature of the gas-free polymer. Gas is introduced into the polymer by diffusion when the specimen is surrounded by subcritical gas at high pressure. In equilibrium, a specimen exposed to these the high surface gas concentrations will acquire a uniform weight percent 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 to 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 behavior 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.

The solid state processing technique has the unique advantage that it can produce very thin microcellular foamed parts of carefully tailored microstructure. In practice, the technique is most applicable to modified vacuum thermoforming operations and continuous sheet fabrication process (Kumar and Schirmer, 1995). Thick microcellular parts can and have been produced using this technique and very novel structures are possible. A limitation of this technique is the time required for diffusion of the blowing gas into the polymer which increases as a function of

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the part thickness, decreases as temperature increases, and varies substantially for different gas-polymer systems.

Investigation of the polyvinylchloride (PVC)-carbon dioxide system was first reported by Kumar and Weller in 1993 (Kumar and Weller, 1993). The PVC blend used in their study was provided by the BF Goodrich Company. In the research of Kumar and Weller 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 stage two foaming. For the BF Goodrich blend examined in their 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 behavioral transition has been identified as being directly coupled to a self regulating foam growth mechanism present in solid state microcellular systems by Holl (1995).

This paper presents a two factor experiment designed to both qualitatively and quantitatively determine the effect of plasticizers and additives upon steady foam structure in the PVC-CO₂ system. The two factors examined are PVC blend composition and foaming temperature. A single set of gas saturation boundary conditions were used in the experimental protocol. These conditions are therefore considered fixed parameters in this study. Dynamic foam growth response data was also collected during the study.

The experiment was designed such that a direct comparison of the foams produced by PVC-A, PVC-B, and PVC-C would reveal significant effects of plasticizers and additives upon foam structure. Because PVC-B and PVC-C only differ in the type of internal lubricant used direct comparison of PVC-B and PVC-C foams will reveal whether or not the foam structure is sensitive to the type of internal lubricant selected.

Experimental

An experimental program is defined in this paper which examines the correlation between polymer blend and steady foam structure. The interrelationship between polymer blend, foaming temperature, and foaming time is examined. Three PVC blends were formulated for a comparative study of the effects of plasticizers and additives upon the microstructure produced in the solid state microcellular PVC production process. The glass transition temperature of the "neat" PVC resin is approximately 80°C. The approach taken was to compare the foams produced using a standard polymer blend with those produced by two other PVC blends that were processed to be as "neat" as possible while still maintaining the minimum required processability required by the extrusion process used to produce the specimens.

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 are formulated to approximate, as closely as possible, "neat" PVC resin. The stabilizer and wax used in the blend are completely immiscible in the PVC matrix. The blend containing wax and the stabilizer alone could not be processed on the extruder without burning the formulation. An internal lubricant was added to the "neat" blends 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. Square specimens 3.17 cm (1.25 inch) on edge were prepared from the extruded sheet. The prepared specimens were placed in a pressure vessel that was maintained at 40°C and then the vessel was 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 and then removed and quenched in room temperature water.

The internal structure of the foams produced was examined using SEM micrograph images taken at the center of the foam. The center of the foam was exposed by first quenching the foam in liquid nitrogen and then snapping the brittle (-70°C) thermoplastic foam. The specimens were then coated with gold-palladium (AuPd) and SEM photographs were taken of the foam structure at 1500X magnification.

The bulk foam structure was quantified by inferring the bulk void fraction of the foam using an Archimedes method water displacement technique to first measure the bulk foam density. Void fraction was then inferred directly from the density measurement.

Results and Discussion

Table I presents the equilibrium gas concentration level for each of the three PVC blends (PVC-A, PVC-B, and PVC-Q when each blend is exposed to carbon dioxide at 6 MPa and 40°C. The "neat" PVC blends (PVC-13 and PVC-Q absorbed more carbon dioxide than the PVC blend containing a high weight percent plasticizers and additives (PVC-A). Figure I shows the correlation between the weight percent of total plasticizers and additives and the PVC blend carbon dioxide solubility. This suggests that the solubility of carbon dioxide in the plasticizers and additives of the blend is very low when compared to the solubility of carbon dioxide in PVC resin.

Figure 2 shows a matrix of SEM micrographs of the steady state foam structure produced as a function of blend composition and foaming temperature. Row I of Figure 2 shows foams produced using the PVC-A, the blend with high plasticizer and additive concentration. Three observations can be made from PVC-A foams shown in Figure 2. First, a large variation in the cell diameter distribution is observed. That is, the cells present in the foam are strongly polydisperse in their distribution. Second, a substantial open cell structure is present. Finally, second phase particles are clearly observable. These distinct second phase particles are most likely the impact modifier in the PVC-A blend.

The internal lubricant is not completely miscible in the PVC matrix and therefore may create advantageous heterogeneous foam cell nucleation sites. The foam structures produced by both of the "neat" PVC-blends (PVC-13 and PVC-Q are virtually identical. The only difference between the two blends is the type of internal lubricant used in the blend with a small variation in the amount of lubricant. Therefore, it is observed that the type of internal lubricant has virtually no effect on foam structure at the concentrations examined in this paper. Heterogeneous nucleation may be enhanced by the immiscible internal lubricant. However, this effect cannot be resolved from the results presented in this paper.

From Figure I it is clear that the carbon dioxide solubility in the internal lubricant is much lower than the solubility of carbon dioxide in the PVC matrix.

Two observations for the foam structures produced using PVC-13 and PVC-C can be made. First, a small variation in cell size is observed in the foams produced (the cells are monodisperse). Second, the foam structure is composed of closed cells. The general structure of the foams shown in Figure 2, for all foaming temperatures, is summarized in Table 2.

The rate at which a bulk foam specimen achieves a steady foam structure is a useful specimen geometry dependent processing characteristic. 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 gas-filled 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 center as thermal energy propagates inward from the surfaces exposed to the heated glycerin bath. See Holl (1995) for a detailed description of the dynamics associated with this phenomenon.

Figure 3 (a) through (d) present the dynamic void fraction foam growth response at 65 °C, 70 °C, 80 °C, and 90 °C for the single gas saturation level examined in this paper. For a foaming temperature of 65 °C the steady foam void fraction of PVC-A is significantly higher than that of PVC-B and PVC-C at lower steady foaming temperatures. At all steady foaming temperatures no significant difference in bulk void fraction response is observed in the foams produced using either PVC-B or PVC-C. As the steady foaming temperature is increased the difference between the bulk void fraction produced by PVC-A and both PVC-B&C steadily decreases. 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. This effect will be presented in a subsequent paper. For all PVC blends and temperatures steady foam structure is achieved in approximately one minute for the 1.52 mm (0.060 inch) thick specimens used in this study.

Conclusions

Several 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 high open cell content and a large variation in cell sizes. In contrast, "neat" PVC resins produce solid state microcellular foams characteristic of those seen in other "neat" gas-polymer solid state system (i.e. polycarbonate-carbon dioxide) where the cells are closed and the cell size variance is small.

Second, the type of internal lubricant used in the blend has no significant quantifiable effect on 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.

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Table 1. Equilibrium gas concentration for three PVC polymer blends exposed to carbon dioxide at 6 MPa and 40°C.

	Polymer Blend		
	PVC-A	PVC-B	PVC-C
Gas Concentration mg (CO ₂)/mg (PVC Blend)	0.0573	0.0618	0.0603

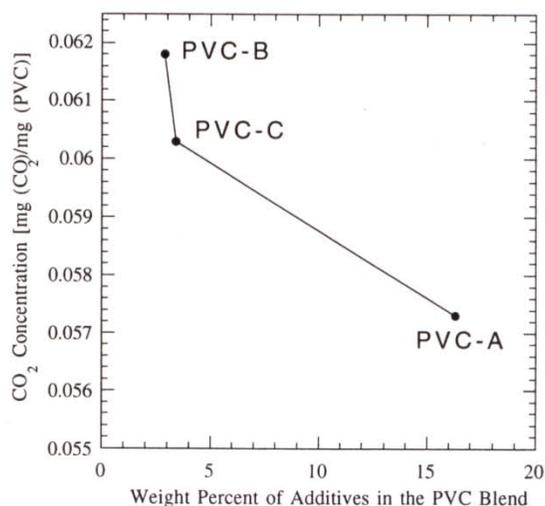


Figure 1 Equilibrium gas concentration level as a function of percent plasticizer and additive concentration.

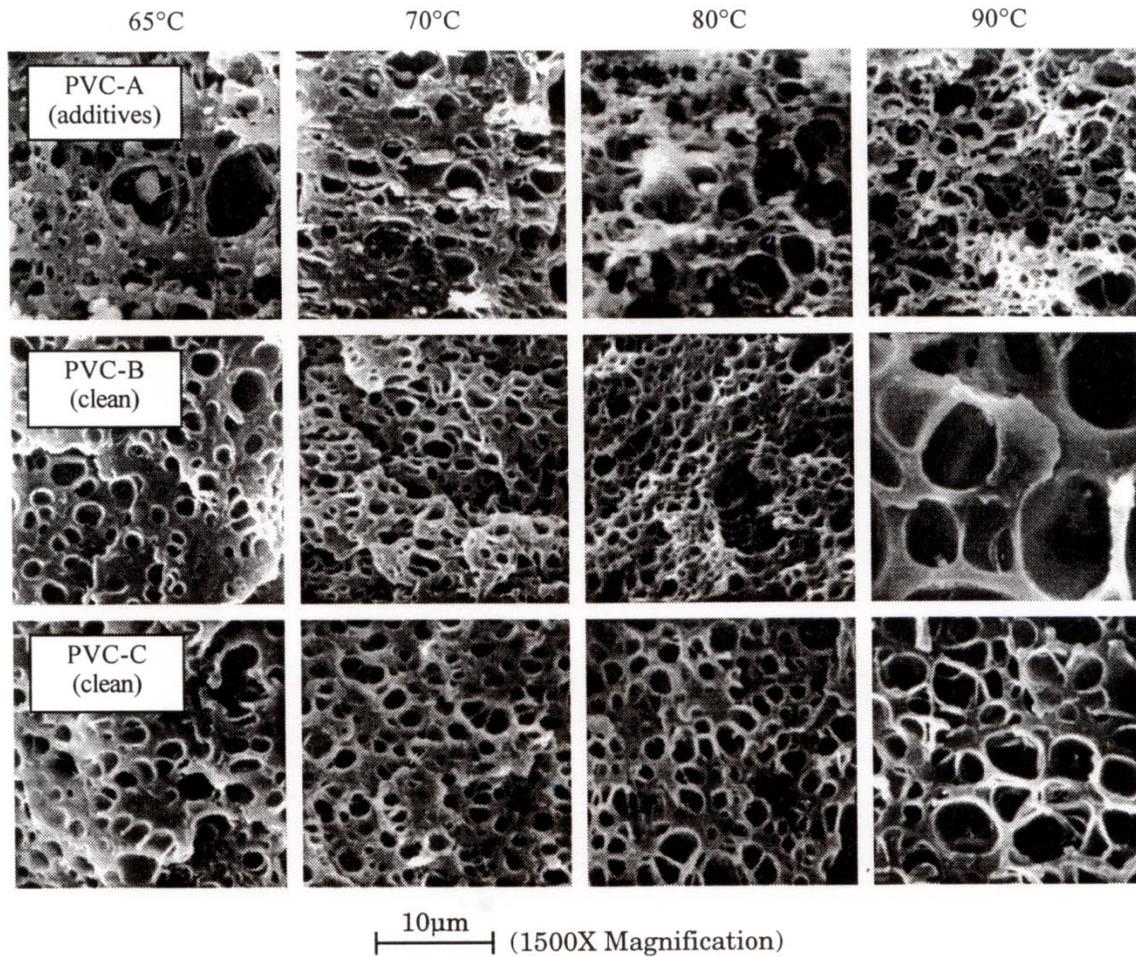
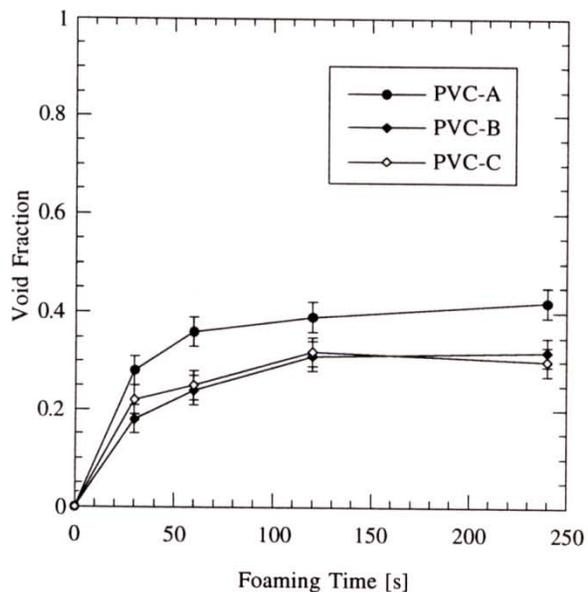


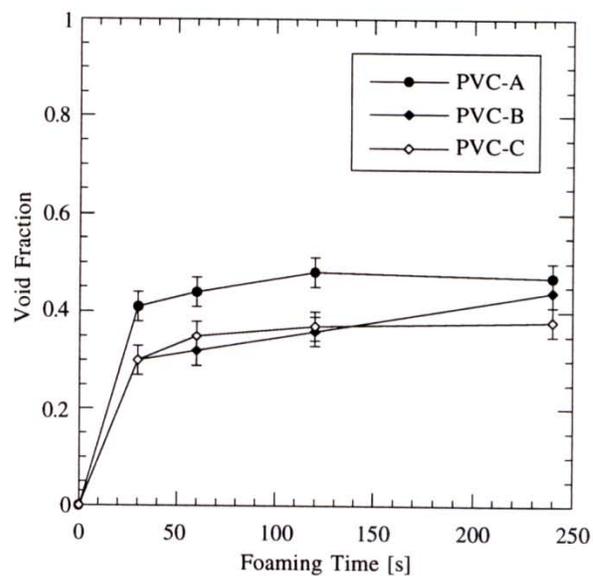
Figure 2 Steady state PVC foam structure. The rows are associated with a single polymer blend: row 1: PVC-A, row 2: PVC-B, and row 3: PVC-C. The columns are associated with different glycerin foaming bath temperatures: column 1: 65°C, column 2: 70°C, column 3: 80°C, and column 4: 90°C.

Table 2. Qualitative evaluation of foam steady state foam structure.

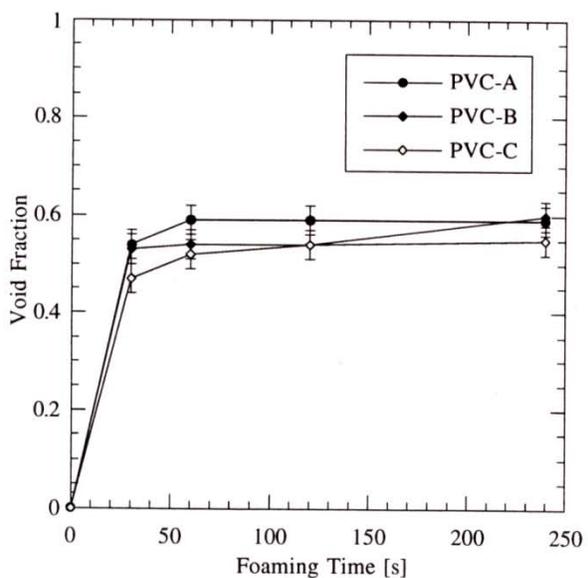
Polymer Blend	Foam Structure	
	Cell Type (open or closed cells)	Cell Size Distribution (mono or polydisperse)
PVC-A	closed & open cells	polydisperse
PVC-B	closed cells	monodisperse
PVC-C	closed cells	monodisperse



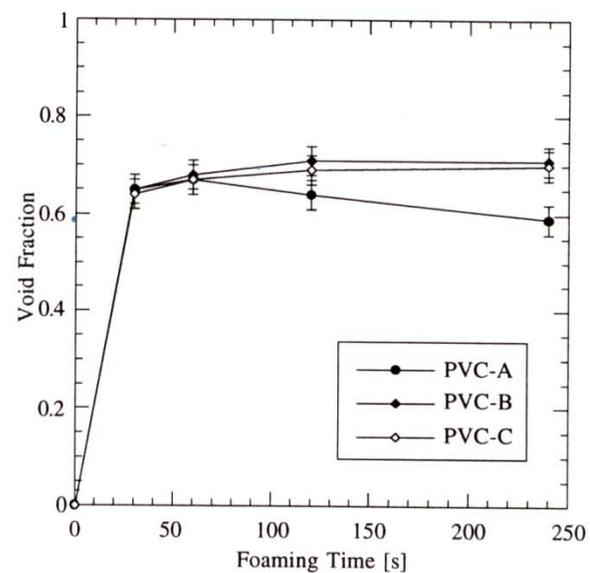
(a)



(b)



(c)



(d)

Figure 3 Dynamic foam growth response of three PVC polymer blends equilibrated with carbon dioxide at 6 MPa and 40°C and then immersed in a heated glycerin bath with temperature: (a) 65°C, (b) 70°C, (c) 80°C, and (d) 90°C.

Keywords: microcellular plastics, PVC foams, thermoplastic foams.