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硬質 PVC의 發泡押出 II.
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Foam Extrusion of Rigid PVC. II. Effects of Processing Additives and Processing Parameters on Foam Processing

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Abstract: The effect of several processing additives and processing parameters on the foam extrusion of rigid poly(vinyl chloride) (PVC) was investigated. The metallic thermal stabilizer played a role as auxiliary nucleating agent and promoted decomposition of ADCA. Additional nucleating agent had little effect on cell size and distribution. Two acidic nucleating agents, citric acid and boric acid, promoted decomposition of ADCA and SBC. They lowered foaming temperature and enhanced foaming efficiency. The decomposition of ADCA was promoted almost in proportion to acidity of nucleating agent. An increase of temperature increased cell size but decreased cell frequency, but an increase of shear rate increased cell number along with cell size. A decrease of die L/D ratio enhanced foaming efficiency and increased cell size.

INTRODUCTION

Incorporation of gases into polymeric materials has long been attempted to produce synthetic plastic foams. The first commercial synthetic plastic foam was a sponge rubber, introduced in 1910's. Over the last two decades, emphasis has been given to develop foams meeting the diverse reguirements of practical importance, and a considerable progress has been made in manufacturing techniques[1-3]. Recently, poly (vinyl chloride) (PVC) foams have been developed with a significant commercial importance.

PVC foams, in general, can be classified into rigid type and plasticized flexible type. The plasticized flexible PVC foams have widely been used to manufacture artificial leather, carpet underlay, flooring materials, etc.. However, the inclusion of a large amount of plasticizers gives such drawbacks in product properties as low service temperature and poor strengths. Moreover, the low molecular weight plasticizer tends to migrate to the surface in the long term.

On the other hand, rigid PVC foam without any plasticizer may exhibit better properties of service temperature, flammability and strengths. Such rigid PVC foams possess a strong potential for building materials, housings for electric or electronic eguipments, and substitutes for wood.

Although several processing additives are indispensable to rigid PVC foam processing, few systematic studies on the effect of such additives

Table 1. Physical Properties of Three Nucleating Agents Tested[4]

Nucleating agent	Chemical structure	Chemical nature	Melting temp. (°C)	PH of 0.1 N aq. solution
Silica	SiO_2	Inert	—	Neutral
Boric acid	HO-B-OH OH	Volatile with steam	171	5.2
Citric acid	CH_2COOH HO-C-COOH CH_2COOH	Highly hygroscopic	153	2.2

have been disclosed. In this study, several usual processing additives such as thermal stabilizer and nucleating agents were chosen, and their effect on the foam processability of rigid PVC was investigated. Some important properties of three nucleating agents tested are listed in Table 1[4]. In addition, the effect of processing parameters on the foamed cellular morphology was also examined.

EXPERIMENTS

Materials and Formulations

Materials The materials are described in Part I of this series[5].

Formulations In addition to the expandable formulations for processability described in Part I of this series[5], another type of formulations was prepared for thermal analysis and shown in Table 2.

Apparatus and Experimental Procedure

Compounding The compounding procedure is described in Part I of this series[5].

Thermal Analysis The effect of processing additives on the thermal decomposition of ADCA and SBC was examined by use of differential scanning calorimeter (DSC, Perkin Elmer, USA) along with thermogravimetric analyzer (TGA, Perkin Elmer, USA). The scan rate was 15°C/min in both cases.

Foam Extrusion Foam extrusion procedure is described in Part I of this series[5].

Measurement of Foam Morphology The foamed cellular morphology was examined by scanning electron microscope (SEM, Hitachi Co., Japan).

Table 2. Experimental Formulations for Thermal Analysis

M≡PVC+TS(5)+PA(15)	M-S(5)-SC(5)
M-A(5)	M-S(5)-BA(5)
M-A(5)-SC(5)	M-S(5)-CA(5)
M-A(5)-BA(5)	PVC-A(5)
M-A(5)-CA(5)	PVC-S(5)
M-S(5)	

Number in parenthesis is phr
M: unexpanded formulation for thermal analysis
TS: thermal stabilizer, PA: processing aid
A: azodicarbonamide, S: sodium bicarbonate
SC: silica, BA: boric acid, CA: citric acid

RESULTS AND DISCUSSION

Effect of Processing Additives on the Decomposition of ADCA and SBC

For the prediction of foam processability, the effect of usual processing additives on the decomposition temperature of ADCA and SBC was examined by differential scanning calorimeter (DSC), and the results are given in Table 3.

The onset decomposition temperature measured was 232°C for ADCA and 165°C for SBC, and PVC resin had little effect on the decomposition of the two chemical blowing agents tested. The metallic thermal stabilizer activated the decomposition of ADCA, but it had little effect on the decomposition of SBC.

It can be seen from the table that the decomposition of ADCA was promoted almost in proportion to the acidity of nucleating agent. That is, boric acid lowered the onset decomposition temperature of ADCA from 189°C to 173°C and citric acid lowered it from 189°C to 165°C. Boric

Table 3. Effect of Processing Additives on the Decomposition Temperature of ADCA and SBC

Temp. (°C) / Sample code	From	To	Onset	Max.	Temp. (°C) / Sample code	From	To	Onset	Max.
ADCA	214	241	232	236	SBC	147	192	165	167
PVC-A(5)	218	246	230	240	PVC-S(5)	152	183	162	172
M-A(5)	180	227	189	208	M-S(5)	151	199	169	186
M-A(5)-SC(5)	182	230	191	207	M-S(5)-SC(5)	153	186	165	174
M-A(5)-BA(5)	168	210	173	183	M-S(5)-BA(5)	137	178	144	162
M-A(5)-CA(5)	160	210	165	176	M-S(5)-CA(5)	150	180	—	—

acid was also an effective promoter for SBC and it lowered the onset decomposition temperature from 169°C to 144°C. However, the effectiveness of citric acid on SBC was somewhat ambiguous, which may result from its hygroscopic nature. That is, steam evolved from SBC may be readily hydrated by hygroscopic citric acid. The inert silica, however, had little effect on the decomposition of two chemical blowing agents.

To evaluate the effect of processing additives on the foaming efficiency of ADCA and SBC, the of SBC of weight loss by the evolution of gaseous products was measured by thermogravimetric analyzer (TGA), and the results are shown in Figures 1 and 2.

The order of increasing the foaming efficiency was citric acid, boric acid and silica for ADCA and boric acid, citric, and silica for SBC.

Effect of Processing Parameters on a Rigid PVC Foam Extrusion

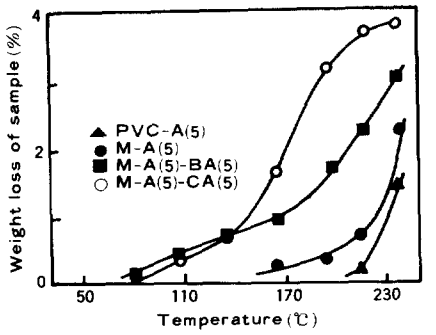

Fig. 1. Effect of processing additives on the fomaing efficiency of ADCA (the scan rate was 15°C/min).

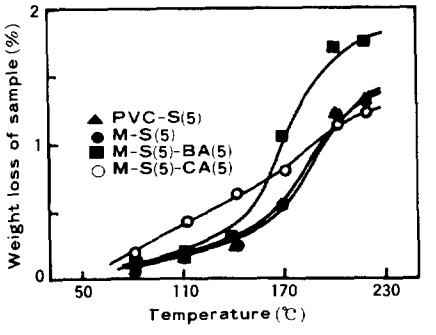

Fig. 2. Effect of processing additives on the foaming efficiency of SBC (the scan rate was 15°C/min).

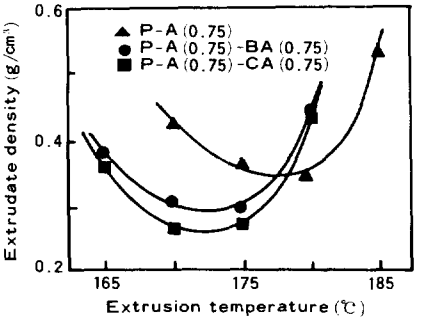

Fig. 3. Effect of processing additives on the foaming by ADCA ($Q = 0.7$ cm^3/s).

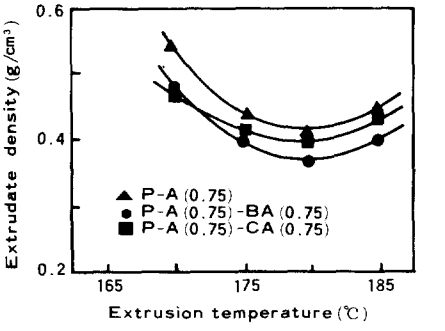

Fig. 4. Effect of processing additives on the foaming by SBC ($Q = 0.7$ cm^3/s).

Processing Additives Figures 3 and 4 show the effect of processing additives on foaming temperature and foaming efficiency at the volumetric flow rate of 0.7 cm^3/s.

Unlike foaming processes of polyethylene, polypropylene and polystyrene, nucleating agents-tested on the foaming of rigid PVC exhibited no significant effect on cell size and distribution[6-8]. This can be ascribed to the fact that the metallic thermal stabilizer particles which are finely dispersed in the polymer phase may play a role as auxiliary nucleating agent because of high specific heat and high thermal conductivity[6,7]. Nevertheless, the two acidic nucleating agents, boric acid and citric acid, enhanced foaming efficiency of two chemical blowing agents. On the whole, the trends of foaming temperature and foaming efficiency in foam extrusion approximately agreed with those in thermal analysis within the experimental error. However, the observed extrusion temperature for optimum foaming was generally a little lower than the predicted value by thermal analysis, which may be due to enhanced contact of processing additives with chemical blowing agent in the barrel.

For each formulation, there exists a temperature range giving the maximum foaming efficiency. Below this temperature range, the foaming efficiency is low because of low blowing pressure of chemical blowing agent and high viscosity of polymer phase. Above this temperature range, however, the collapse and coalescence of cells reduce the foaming efficiency. Therefore, it is evident that the maximum foaming efficiency will be attained at a unique balance of gas holding strength of polymer phase and blowing pressure of chemical blowing agent.

Mixed Chemical Blowing Agents of ADCA and SBC Figure 5 represents the effect of mixed

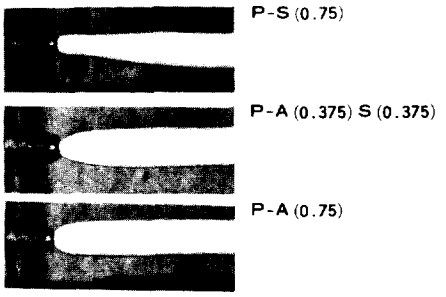

Fig. 5. Effect of mixed chemical blowing agents of ADCA and SBC on the bubble expansion rate at 175°C (Q = 0.574 cm^3/s).

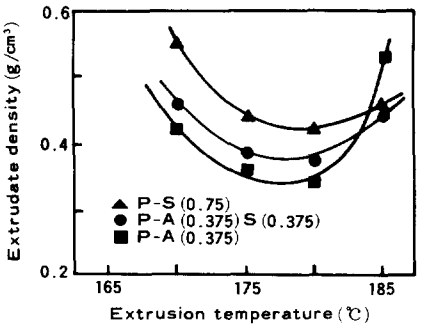

Fig. 6. Density variations with extrusion temperature showing the effect of metallic thermal stabilizer (Q = 0.7 cm^3/s).

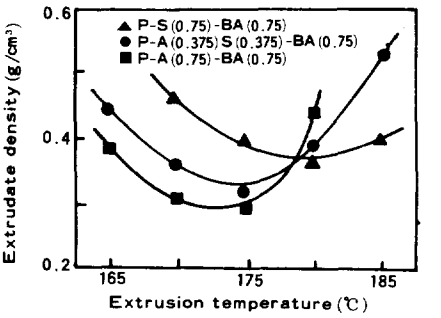

Fig. 7. Density variations with extrusion temparature showing the effect of boric acid (Q = 0.7 cm^3/s).

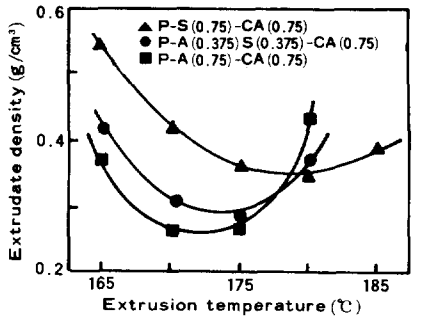

Fig. 8. Density variations with extrusion temperature showing the effect of citric acid (Q = 0.7 cm^3s).

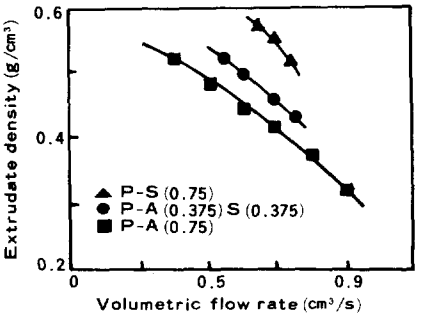

Fig. 9. Density variations with volumetric flow rate showing the effect of metallic thermal stabilizer at 170°C.

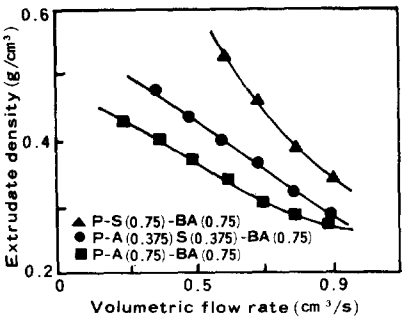

Fig. 10. Density variations with volumetric flow rate shwoing the effect of boric acid at 170°C.

chemical blowing agents of ADCA and SBC on the bubble expanding behavior after leaving die exit.

As shown in the figure, combined use of two chemical blowing agents exhibited almost an intermediate bubble expanding behavior of ADCA and SBC.

Extrusion Temperature and Volumetric Flow Rate Density variations with extrusion temperature and volumetric flow rate are shown in Figures 6 to 11. Foaming efficiency of two chemical blowing agents was generally increased with temperature due to decreases in both viscosity and surface tension as well as due to enhanced decomposition of chemical blowing agent. However, above a critical temperature, foaming efficiency was decreased with temperature because of cell collapse before stabilization. Uniformity of cells and foaming efficiency were enhanced as volumetric flow rate increased due to better mixing and reduced viscosity.

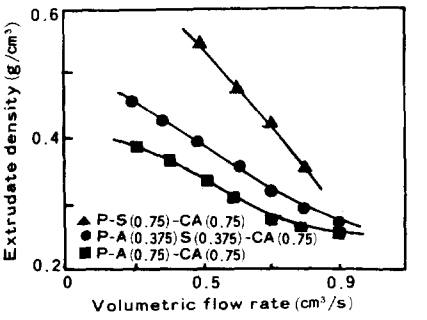

Fig. 11. Density variations with volumetric flow rate showing the effect of citric acid at 170°C.

Of the two chemical blowing agents tested, ADCA exhibited wider leverage of volumetric flow rates for processability while SBC showed a wider processable temperature leverage. However, in terms of general appearance of foamed product, ADCA favored relatively high volumetric flow rates and low extrusion temperatures for the optimum foaming conditions, while SBC favored relatively low volumetric flow rates and high extrusion temperatures. In addition, ADCA was more efficient than SBC, and processing additives had a significant influence on the foaming temperature and foaming efficiency.

The effect of extrusion conditions on the foamed cellular morphology is shown in Figure 12. The samples were obtained from ADCA (P-A(0.75)) by use of a long capillary die (L = 80 mm and D = 4 mm).

An increase of extrusion temperature increased cell size but decreased cell number, which may be obliged to decreases in both viscosity and gas solubility[9-12]. That is, with the increase of extrusion temperature, coalescence of neighboring cells will be pronounced due to both viscosity reduction and increased blowing pressure. An increase of shear rate, however, increased the cell number along with cell size[9,10]. The increase of cell number is clearly attributable to the enhanced mixing and a localized viscosity reduction by viscous heating.

Combined use of the two chemical blowing agents showed almost additivity with respect to processable conditions but gave a slightly syner-

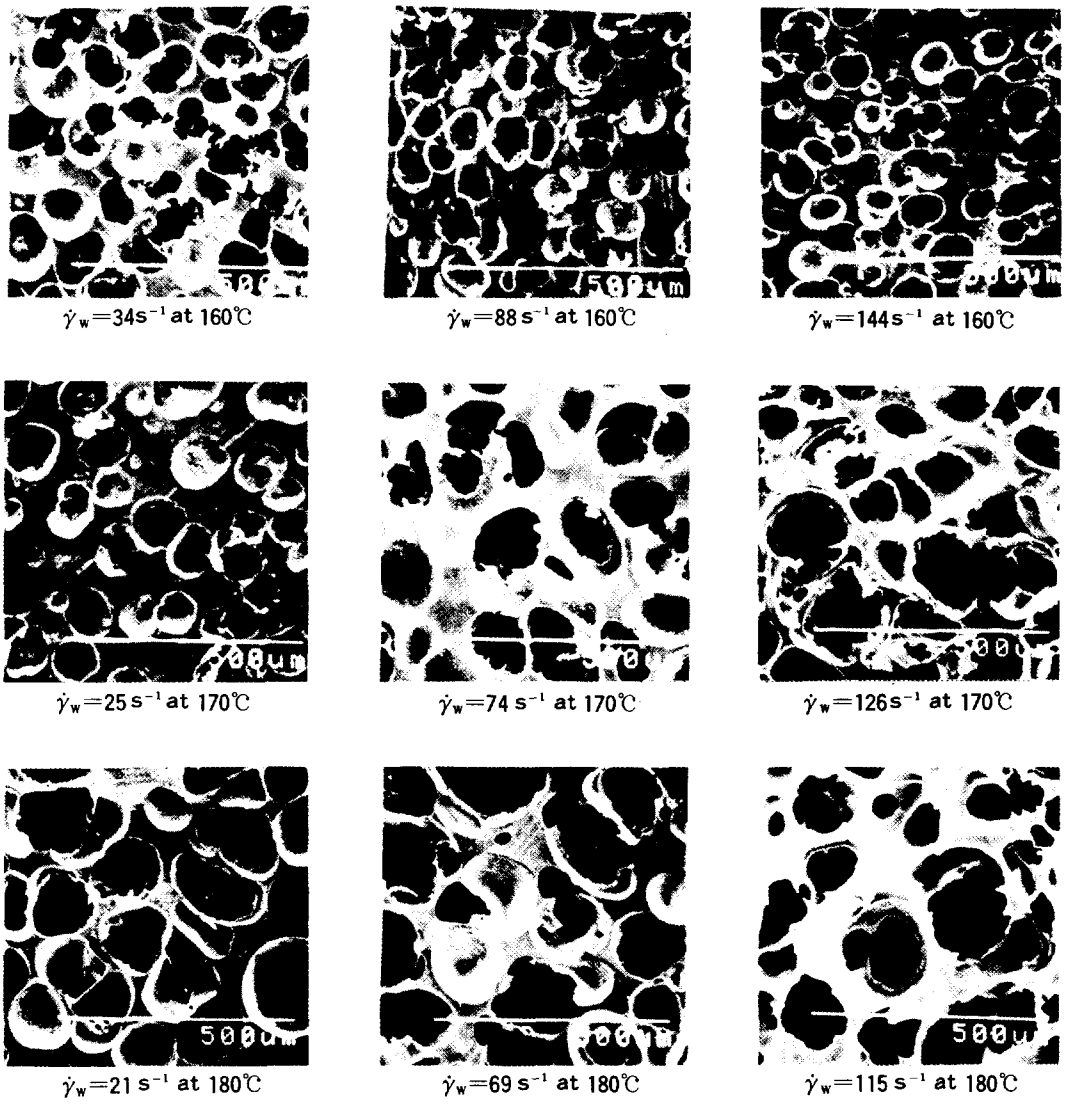

Fig. 12. Effect of extrusion temperature and shear rate on the foamed cellular morphology.

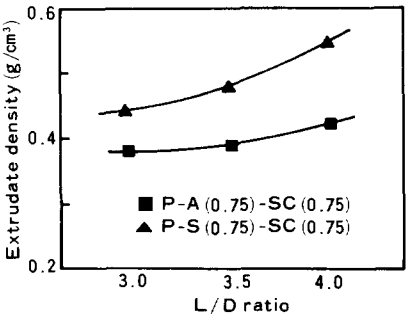

Fig. 13. Effect of die L/D ratio on the foaming efficiency of ADCA and SBC (Q=0.7 cm^3/s at 170°C).

gistic effect on the foaming efficiency. The synerism may be ascribed to the fact that SBC can act as a nucleating agent for ADCA[13].

Die L/D Ratio Density variations of extrudate with die L/D ratio are given in Figure 13.

Since a polymer has a decaying memory, elasticity will increase, at constant volumetric flow rate, with the decrease of the residence time of the polymer in the die. Moreover, the external pressure set up in the die will be diminished with the decrease of die L/D ratio. Therefore, foaming efficiency was increased with the decrease of die

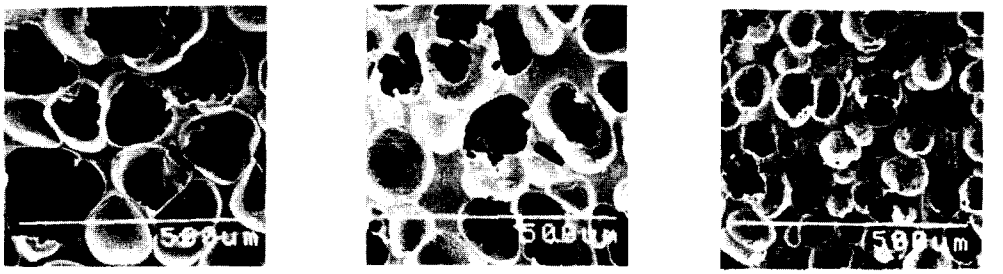

Fig. 14. Effect of die L/D ratio on the cellular foamed morphology.

L/D ratio due to both increased elasticity and decreased external pressure. A careful observation of the figure also reveals that the effect of die L/D ratio on foaming efficiency was more pronounced with SBC than with ADCA, which might be obliged to pressure sensitive decomposition mechanism of SBC.

The effect of die L/D ratio on the foamed cellular morphology is shown in Figure 14. The samples were prepared by extruding an expandable formulation (P-A (0.75)) with three cylindrical dies of different L/D ratios (D=0.4 mm, L/D=20, 15 and 13.5).

In general, average cell size was increased with the decrease of die L/D ratio due probably to the increased elasticity and due to the decreased external pressure. In case of ADCA, average cell diameters measured from foamed products obtained at similar processing conditions (about 88 s^{-1} at 165°C) were 97 μm, 150 μm and 183 μm for the die L/D ratios of 20, 15 and 13.5, respectively.

CONCLUSIONS

1. The metallic thermal stabilizer played a role as auxiliary nucleating agent and promoted decomposition of ADCA. Additional nucleating agent had little effect on cell size and distribution.
2. Two acidic nucleating agents, citric acid and boric acid, promoted decomposition of ADCA and SBC. They lowered foaming temperature and enhanced foaming efficiency. The decomposition of ADCA was promoted almost in proportion to acidity of nucleating agent.
3. ADCA exhibited wider leverage of volumetric flow rates for processability, while SBC showed a wider processable temperature leverage.
4. An increase of temperature increased cell size but decreased cell frequency, but an increase of shear rate increased cell number along with cell siz. A decrease of die L/D ratio enhanced foaming efficiency and increased cell size.

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