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Foam Extrusion of Rigid PVC. I. Effect of Decomposition Mode of Chemical Blowing Agent on the Foaming Characteristics and Foam Properties

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Abstract: Two chemical blowing agents with different decomposition mode, azodicarbonamide (ADCA) and sodium bicarbonate (SBC), were selected, and foaming process of rigid poly (vinyl chloride) (PVC) was investigated. At the same usage level, ADCA gave higher degrees of nucleation and growth of microbubble than SBC. Further, the decomposition mode and gas properties had a profound influence on foaming process and foam properties. ADCA exhibited high initial bubble expanding rate under ambient pressure and yielded almost round to elliptical cells with even size distribution, while SBC required some induction time for bubble expansion and yielded irregularly shaped cells with wide size distribution. Of the two chemical blowing agents, ADCA yielded foams with better mechanical properties than SBC.

INTRODUCTION

Plastic foams have been used since man began to use wood, which offered a motive to develop synthetic plastic foams. Nowadays, synthetic plastic foams are applied to diverse areas such as insulation, packaging and construction[1,2]. In general, various polymeric foams are obtained by physical or chemical blowing agents. In a chemical foaming process, the thermal decomposition mode of chemical blowing agent and the physical properties of evolved gases may play a significant role in foaming process, and they may have some influence on the foam morphology and foam properties as well. Owing to poor thermal stability of poly (vinyl chloride) (PVC), a rigid PVC foam extrusion is normally carried out at relatively low temperatures. Therfore, the polymer phase may have a viscosity high enough to exhibit the foaming characteristics of chemical blowing agent.

So far, however, most studies on the foaming process have been focused on the low melt viscosity materials. Little attention has been paid to the high viscosity models which may visualize the foaming characteristics of chemical blowing agent rather well.

This study investigates the effect of decomposition mode of chemical blowing agent on the foaming characteristics and foam properties of

rigid PVC by use of two selected chemical blowing agents, azodicarbonamide (ADCA) and sodium bicarbonate (SBC), which exhibit very different decomposition mode.

RESEARCH BACKGROUND: DECOMPOSITION MODE OF ADCA AND SBC

ADCA and SBC show very different thermal decomposition mode[3-6]. Although the composition of evolved gases and residues of ADCA vary slightly with decomposition temperature, heating rate and other environmental conditions, it was empirically established that the composition of gases evolved from ADCA is as follows: nitrogen (56 vol.%), ammonia (21 vol.%), carbon monoxide (15 vol.%) and carbon dioxide (8 vol.%). Some distinctive decomposition features of ADCA are; (i) temperature sensitive, (ii) rapid and explosive, and (iii) irreversible and exothermic (10 kcal/mole at 230°C). On the other hand, SBC evolves carbon dioxide and steam. The important decomposition features of SBC are; (i) pressure dependent, (ii) slow and erratic, and (iii) reversible and endothermic (-227 kcal/mole at 170°C).

Furthermore, physical properties of gases evolved from the two chemical blowing agents are also very different as shown in Table 1[7,8]. ADCA yields relatively inert gases which have relatively low critical temperature and low solubility in PVC, while gases evolved from SBC have relatively high critical temperature and some solubility in PVC.

EXPERIMENTS

Materials and Formulations

Materials a) Poly (vinyl chloride) (PVC); a suspension grade PVC (Korea Plastic Industry Co., Korea) was used, whose properties are as follows:

Degree of polymerization = 1000 ± 50

Bulk density = min. 0.5 g/cm^3, Volatiles = max. 0.3%

b) Chemical blowing agent; commercial grade azodicarbonamide (ADCA) and sodium bicarbonate (SBC) were used after drying in a vacuum oven at 40°C for 10 hours.

c) Nucleating agent; three nucleating agents examined are reagent grade of silica (SC), boric acid (BA) and citric acid (CA). They were ground to a fine powder (325 mesh) and dried in a vacuum oven at 70°C for 10 hours before use.

d) Thermal stabilizer; a commercially availa-

Table 1. Physical Properties of Gases Evolved from ADCA and SBC[7,8]

Evolved gas	Critical temp.(°C)	Critical press.(atm.)	Solubility in PVC S(298) in cm^3 (STP)/cm^3 bar
N_2	-147.1	33.5	0.024
NH_3	132.4	111.5	—
CO	-139.0	35.0	—
CO_2	31.3	72.9	0.480
H_2O	374.2	218.0	—

Table 2. Experimental Formulations

P = PVC + TS(2) + PA(15) + L(0.5)	P-S(0.75)
P-A(0.5)	P-S(1)
P-A(0.75)	P-S(0.75)-SC(0.75)
P-A(1)	P-S(0.75)-BA(0.75)
P-A(0.75)-SC(0.75)	P-S(0.75)-CA(0.75)
P-A(0.75)-BA(0.75)	P-A(0.375)S(0.375)-SC(0.75)
P-A(0.75)-CA(0.75)	P-A(0.375)S(0.375)-BA(0.75)
P-S(0.5)	P-A(0.375)S(0.375)-CA(0.75)

Number in parenthesis is phr
P ≡ P-base: unexpanded formulation
TS: thermal stabilizer, PA: processing aid, L: lubricant
A: azodicarbonamide, S: sodium bicarbonate
SC: silica, BA: boric acid, CA: citric acid

ble barium-cadmium type stabilizer ("Be-102", Songwoun Industrial Co., Ltd., Korea) was used without further purification.

e) Lubricant and processing aid; stearic acid and a processing aid based on poly (methyl methacrylate) ("Acryloid K-125", Rohm and Haas Co., USA) were used.

Formulations The expandable formulations investigated are listed in Table 2.

Apparatus and Experimental Procedure

Compounding The components were compounded in a super mixer (Kawada Seisakusho, Japan) to give a dry free-flowing powder. Since SBC may be decomposed above 50°C, formulations containing SBC were compounded below 45°C. After compounding for 25 minutes at 2,000 rpm, they were cooled to 15°C. A typical compounding procedure is listed in Table 3.

Measurement of Torque on a Screw The degree of microbubble nucleation in the barrel was estimated by the torque on a screw of 3/4-in-Brabender Plasti-Corder with a barrel L/D ratio of 25. The power used by the screw was measured by the torque on the suspended dynamometer, whose housing was connected by a lever arm system to a scale indicator and strip chart recorder.

Foam Extrusion Foam extrusion experiments were carried out with a conventional 1-in-single screw extruder (HanKuk JungAng Machinery Co., Korea) under various processing conditions.

The dimensions of the extruder were as follows:

Barrel: L=635 mm and L/D=25/1

Screw: L(feeding)=4D, L(transition)=16D and L(metering)=5D.

Compression ratio=2/1.

Table 3. A typical Compounding Procedure

Time (min.)	Temp. (°C) ADCA	Temp. (°C) SBC	Ingredients added
0	15	15	PVC, chemical blowing agent and nucleating agent
5	25	25	thermal stabilizer
15	50	35	processing aid and lubricant
20	70	45	Stop and cool to 15°C

The cylindrical die used for foam extrusion had dimensions of: Entrance angle=60°, L=30 mm and D=7.5 mm.

Measurement of Bubble Expansion The expanding foam process after leaving a die exit was photographed by a camera equipped with special lenses (Nikon FE-2, Sigma Zoom-Iota 80-200 mm + AML Lens).

Measurement of Foam Properties The foamed cellular morphology was examined by photomicrograph (Ortholux II, Leitz Co., West Germany). Mechanical properties such as tensile strength and compressive strength were measured by an Instron tester.

RESULTS AND DISCUSSION

Microbubble Nucleation in Extruder

Although the nucleation mechanism of microbubble from a supersaturated polymer phase has not been clearly understood, it is generally considered as a function of viscosity and surface tension among other factors. Figures 1, 2 and 3 give plots of torque against volumetric flow rate.

In a Brabender Plasti-Corder, the degree to which the energy consumption falls below the norms established by the unexpanded formulation is indicative of the degree of microbubble nucleation in the extruder because the dissolved or nucleated microbubbles may play as a lubricant[9]. Comparing with unexpanded formulation, two expandable formulations gave a substantial torque reduction which was more prominent with for-

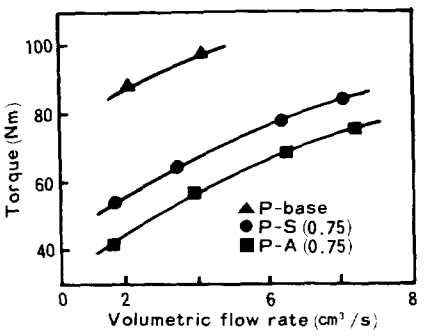


Fig. 1. Torque versus volumetric flow rate at 170°C.

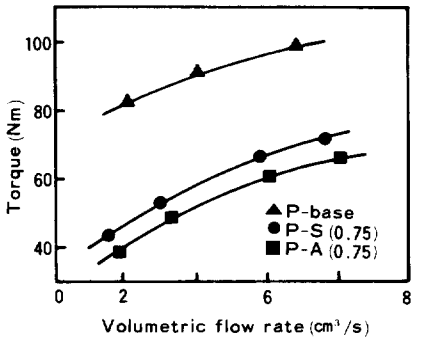


Fig. 2. Torque versus volumetric flow rate at 175°C.

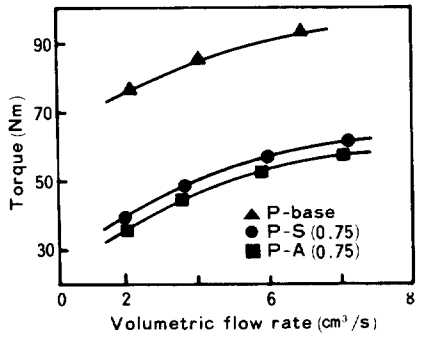


Fig. 3. Torque versus volumetric flow rate at 180°C.

mulation including ADCA than the formulation including SBC. ADCA decomposes exothermically in a specific temperature range, while SBC decomposes endothermically over a wide range of temperatures. Further, the decomposition of ADCA is irreversible and explosive while SBC decomposes reversibly and erratically. This may result in that, under high pressures, part of the microbubbles nucleated from ADCA may exist as an irreversible dispersion state in the barrel, whereas most of the microbubbles nucleated from SBC will be dissolved in the polymer phase in equilibrium state. Therefore, ADCA gave greater torque reduction in the barrel than SBC.

Microbubble Growth in a Short Cylindrical Die

When the nucleated microbubbles have reached a certain minimum size, they will continue to grow until the pressure inside them is in equilibrium with the external pressure as a result of diffusion process.

Plots of reduced viscosity versus apparent

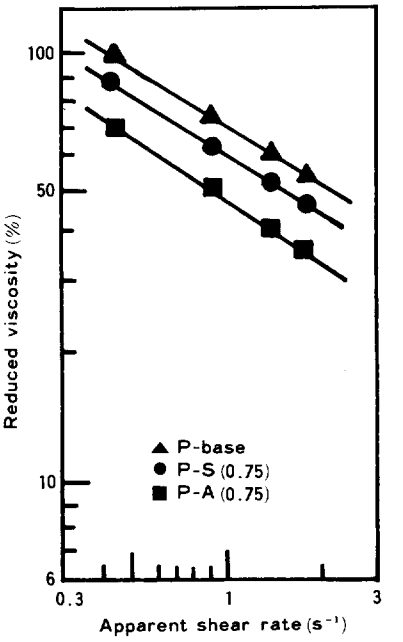


Fig. 4. Viscosity curves of three formulations at 170°C by a die with L/D 4.

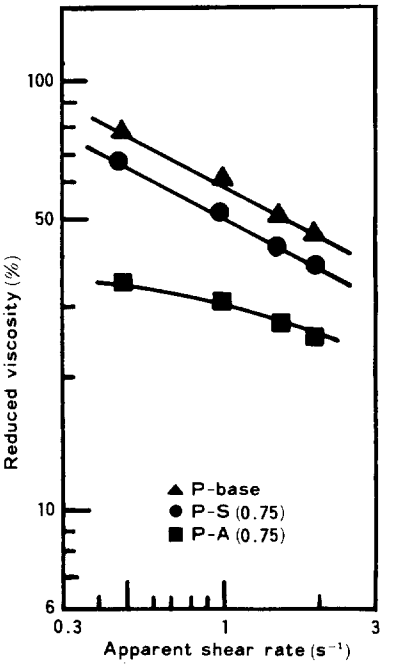


Fig. 5. Viscosity curves of three formulations at 175°C by a die with L/D 4.

shear rate are given in Figures 4, 5 and 6. The

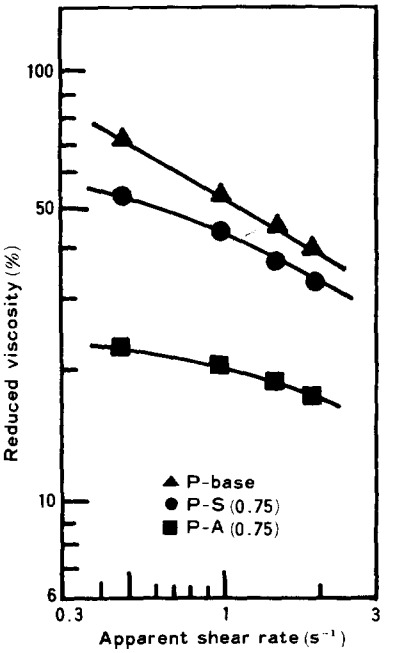


Fig. 6. Viscosity curves of three formulations at 180°C by a die with L/D 4.

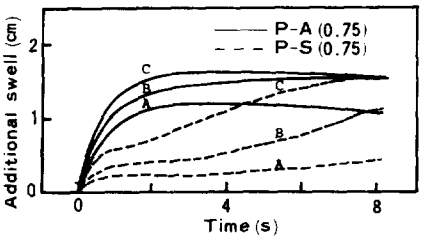


Fig. 7. Additional extrudate swell by bubble expansion versus time after leaving the die exit at 170°C (A = 0.356, B = 0.574 and C = 0.788 cm^3/s).

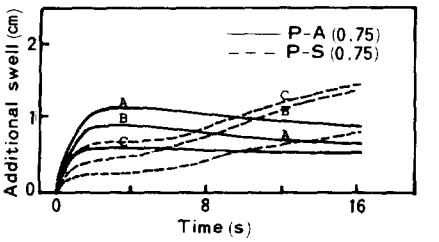
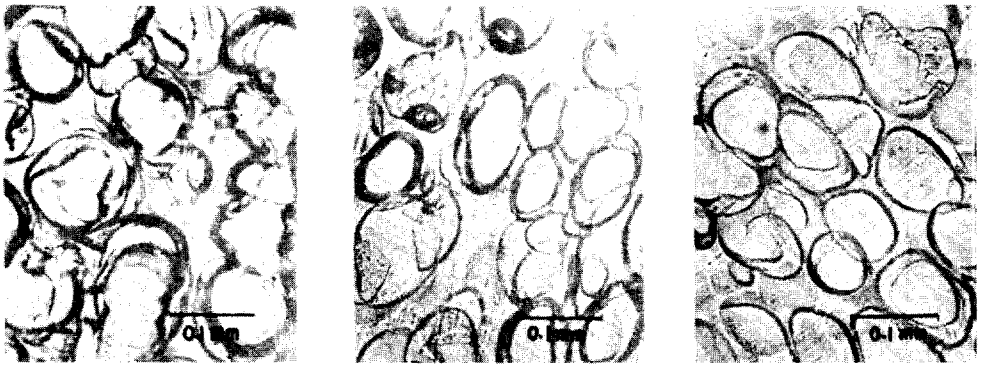


Fig. 8. Additional extrudate swell by bubble expansion versus time after leaving the die exit at the volumetric flow rate of 0.356 cm^3/s (A = 170°C, B = 175°C and C = 180°C).

reduced viscosity was calculated by dividing the measured viscosity by the viscosity of the unexpanded formulation at 170°C and at the apparent shear rate of 0.356 s^{-1}. In general, inclusion of chemical blowing agent lowered viscosity, which may be originated from the plasticizing effect of microbubble[10-14]. At the same usage level, ADCA gave greater viscosity reduction than SBC. Further, deviation of viscosity curve from straight line was also more pronounced with ADCA than with SBC. Since such viscosity reduction and deviation may indicate phase separation by microbubble growth they may be closely related to decomposition mode and physical properties of evolved gases. As the decompostion of SBC is erratic, and evolved gases have relatively high critical temperature and some solubility to PVC, SBC will exert low blowing pressure. On the other hand, as ADCA decomposes explosively, and evolves relatively inert gases, it will yield higher blowing pressure than SBC. In consequence, in the formulation with ADCA, microbubble growth may be accelerated due to the synergistic effect through a chain action. That is, the high blowing pressure and the localized reduction of viscosity and surface tension by decomposition exotherm will promote microbubble growth, and the promoted microbubble growth may reduce the mixture viscostiy in return, which may, alternatively, offer more favorable conditions for microbubble growth. Therefore, ADCA gave greater viscosity reduction than SBC. Further, in case of the formulation containing ADCA, the deviation began at lower temperatures and kept deviating up to higher shear rates since ADCA requires lower temperature and higher shear rate to suppress microbubble growth due to the chain action. However, the deviation was gradually diminished with the increase of shear rate because an increase of external pressure may lead to a less chance of microbubble growth.

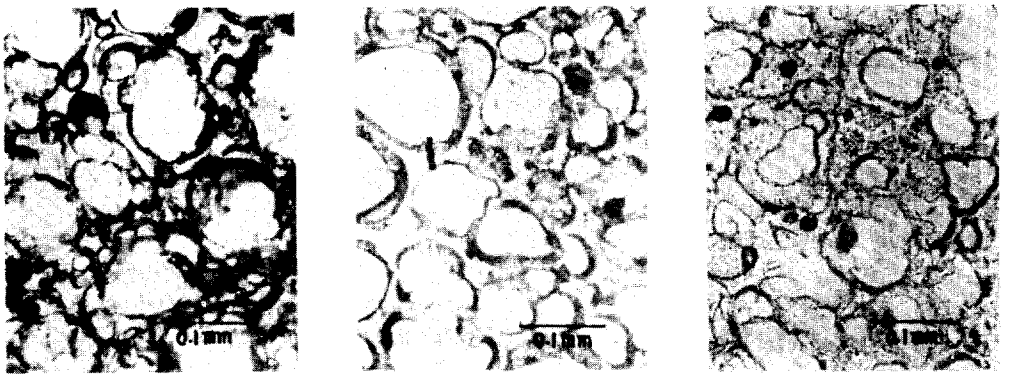
Bubble Expansion After Leaving a Die Exit

The effects of decomposition mode of chemical blowing agent on the bubble expanding behavior after leaving the die exit are shown in Figures 7



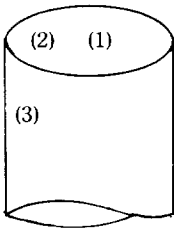
(1) (2) (3)

Fig. 9. Foamed cellular morphology of a foamed product by ADCA (density = 0.40 g/cm^3).



(1) (2) (3)

Fig. 10. Foamed cellular morphology of a foamed product by SBC (density = 0.39 g/cm^3).



(1) Cross-sectional view of core part of foam.
(2) Longitudinal view of middle part of foam.
(3) Longitudinal view of shell part of foam.

and 8. ADCA yielded a high bubble expanding rate under the atmospheric pressure, while SBC required a little induction time for bubble expansion. In a foam extusion, bubble expanding rate will be controlled by complex factors such as blowing pressure, nucleation density, medium viscosity and medium elasticity[15-17]. This suggests that bubble dynamics be strongly dependent on chemical blowing agent type as well as processing conditions. The magnitude and rate of bubble expansion were generally increased as volumetric flow rate was increased, because it reduces viscosity and increases elasticity. Further, the nucleation density will be increased due to enhanced mixing and localized heating.

On the other hand, the effect of extrusion temperature on bubble expansion appeared to be

rather ambiguous. That is, in case of SBC, bubble expansion was promoted with temperature up to 180°C over the whole volumetric flow rate range observed. In case of ADCA, however, the extent of bubble expansion was decreased with temperature at low volumetric flow rates (below 0.4 cm^3/s). Further, at high temperatures (above 180°C), a slight shrinkage was observed even at high volumetric flow rates. This may be ascribed to the different decomposition mode of two chemical blowIng agents tested. The decomposition exotherm of ADCA may partially lower the viscosity of polymer phase because of poor thermal conductivity of polymer. Moreover, ADCA decomposes explosively at a critical temperature range. Therefore, the gas expanding force may exceed the gas holding strength of polymer phase resulting in some collapses and coalescences of cells. On the contrary, since SBC decomposes endothermically and exerts relatively low blowing pressure, the bubble expansion by SBC was increased with the increase of extrusion temperature even at low volumetric flow rates.

Foamed Cellular Morphology

The photomicrographs of foamed products obtained from ADCA and SBC are shown in Figures 9 and 10. ADCA gave more uniform cells than SBC since the bubble growth will take place uniformly in a well dispersed state due to high initial bubble expanding rate. On the other hand, since SBC reguires a little induction time for bubble expansion, a viscosity gradient may be built up by cooling of the shell part during bubble expanding, which may cause a diffusion of gases from the shell part to the core part. As a result, ADCA yielded more uniform cells with narrower size distribution than SBC.

It is noted that there is a distinct morphological difference in cells. Owing to high blowing pressure, bubble expansion by ADCA will be completed before the inner pressure of the bubble is in equilibrium with the ambient pressure, while the bubble expansion by SBC may have some time lag. As a result, while ADCA gave almost round to elliptical cells due to even distribution of bubble

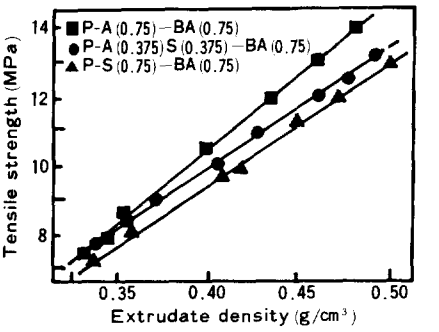


Fig. 11. Tensile strength versus density of the extrudate.

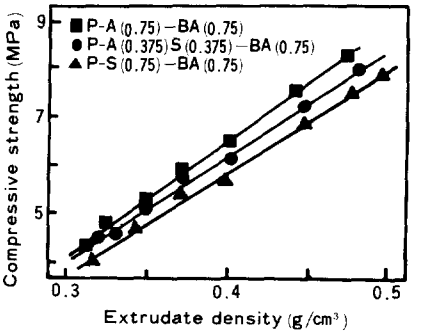


Fig. 12. Compressive strength versus density of the extrudate.

growth time, SBC gave irregularly shaped cells due to wider bubble growth time distribution causing coalescence of neighboring cells.

Mechanical Properties of Foamed Products

The tensile strength and the compressive strength were plotted against the density of foamed products in Figures 11 and 12. Foamed products by ADCA showed higher tensile and compressive strengths than those by SBC. Since foams with spherical cells can yield greater load carrying ability than those with flattened cells as a result of more uniform stress distribution possible in the configuration, the better mechanical properties of foams from ADCA is obviously obliged to the enhanced uniformity of cells. As a rule, the higher initial bubble expansion rate yielded the more uniformly foamed products with better mechanical properties.

CONCLUSIONS

1. At the same blowing agent concentration, ADCA gave greater reduction in both Brabender torque and viscosity than SBC. To suppress the phase separation in the die by microbubble growth, ADCA required lower temperatures and higher shear rates than SBC.

2. While ADCA exhibited high initial bubble expanding rate after leaving die exit, SBC required some induction time for bubble expansion.

3. ADCA yielded almost round to elliptical cells with even size distribution whereas SBC yielded irregularly shaped cells with wide size distribution. Of the two chemical blowing agents, ADCA gave foamed products with better mechanical properties than SBC.

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