Effects of silicon surfactant in rigid polyurethane foams

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Abstract. The rigid polyurethane foams (RPUFs) have been fabricated from high functional crude 4,4'-di-phenylmethane diisocyanate (CMDI) and polypropylene glycols (PPGs) for a wide range of surfactant concentration with an environmentally friendly blowing agent (HFC 365mfc). Cream time, gel time, and tack-free time increased with the addition of surfactant. Foam density decreased rapidly to a minimum at 0.5 pphp (part per hundred polyol) surfactant due to the increased blowing efficiency with surfactant. Surface tension rapidly decreased to an asymptotic value at 2 pphp surfactant. In accordance with this, cell size decreased and closed cell content increased rapidly to constant values at low surfactant concentrations (<1 pphp). The decrease of cell size was accompanied by the decrease of thermal conductivity to give a linear relatiohship between the two implying that the series model of heat transfer is applicable.

Keywords: *thermal properties, rigid polyurethane foam (RPUF), cell structure, compression strength, thermal conductivity*

1. Introduction

Polyurethanes (PUs) are used as coatings, adhesive, sealants, elastomers (CASE), and fibers as well as flexible, semi-rigid and rigid foams [1–3]. Among them, rigid PU foams (RPUFs) have closed cell structure with low thermal conductivity, high compression strength, low density, high strength-to-weight ratio, and low moisture permeability [2–4]. Consequently, RPUFs finds such applications as insulations of refrigerators, freezers, piping, tanks, ship building, and LNG cargos [5–8].

The foaming can be done by one shot or two shot methods. In one shot method, all materials are put into a mixing cup and mixed homogeneously before they are poured into a mold. In the two shot method, isocyanate is added to the mixture at the second stage. The foaming can be carried out with a physical blowing agent, chemical blowing agent, or with a mixture of the two [5]. In physical blowing, reactions between isocyanate and polyol produce polyurethane linkages with the emission of heat of reaction. Then, the blowing agent vaporizes and the gas trapped in the closed cells of the foam [9]. Typically, thermal conductivity of the blown gas is very low. This, with small closed cell structure gives extremely low thermal conductivity of the RPUFs. In chemical blowing, water (most widely used blowing agent) reacts with isocyanate to form unstable carbamic acid which immediately decomposes into an amine and carbon dioxide [2, 10, 11]. Recently, many of the conventional blowing agents such as monofluorotrichloromethane (R11) and difluorodichloromethane (R12) have been suggested to contribute to the depletion of the stratospheric ozone layer and the use has been regulated in many countries. Consequently, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane foam [12–14]. Water can in part replace such environmentally hazardous blowing

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agents. However, the excessive use of water causes a negative pressure gradient due to the rapid diffusion of CO_2 through the cell wall causing cell deformation [2, 3, 15, 16].

The kinetics of RPUF formation mainly depends on the rates of blowing and gelling reactions, which on the other hand are respectively governed by an amine and a tin catalyst [4, 6]. On the other hand, the properties of the foam mainly depend on the type of polyol such as functionality and hydroxyl value, and type and amount of surfactant, and blowing agent. To reinforce the foam, composites with particle, clays and fiber have been considered [17–21].

As far as the present authors are concerned, systematic investigations of the effects of surfactant on various properties of RPUF are sparse, perhaps except those blown with water [7, 22].We synthesized various types of RPUFs from CMDI and polypropylene glycols (PPGs) with an environmentally friendly physical blowing agent, viz. HFC 365mfc ($CF_3CH_2CF_2CH_3$), with a potential target application of insulation panel of LNG cargo where high compression strength as well as thermal insulation is highly desired. The effects of silicon surfactant concentration on the performances of the foams have been extensively analyzed in terms of reactivity, cell morphology, surface tension, and mechanical and thermal properties of the foams.

2. Experimental

2.1. Raw materials

Two types of PPG having hydroxyl value (OHV, mg KOH/g of sample) of 450 and 400 (HR-450P and KR-403) were provided by Korea Polyol Co (Korea). The CMDI was provided by Huntsman (Suprasec-5005), HFC 365mfc by Solvay Chemicals (Belgium), and Polycat-8 as foaming catalyst by Air Products. Silicon surfactant (B 8404) known to augment the closed cell content thus providing improved thermal insulation was provided by Goldschmidt. PPGs were dehydrated before use at 90°C for 24 h in a vacuum oven. Other chemicals were used as received.

2.2. Preparation of samples

The rigid foams were synthesized by one shot method. All raw materials were first put into a mix-

Table 1. Formulation to synthesize the RPUFs

Components	Compositions [g]
HR-450P	80
KR-403	20
Polycat-8	1
B 8404	Variable (0, 0.2, 0.5, 1.0, 2.0, 5.0 pphp)
HFC 365mfc	10.1
CMDI	116.9
Index	110

HR-450P; hydroxyl value 450, Initiator; glycerin and sucrose + PO
KR-403; hydroxyl value 400, Initiator; toluene diamine + PO

ing vessel (Utra-Turrox T-50, Ika-Werke) and mixed for 30 s at 7000 rpm. Then the mixtures were discharged to an open mold (200×200×200 mm) and the foam cake was cured for 1 week at room temperature. The NCO index (isocyanate equivalents/polyol equivalents) was fixed at 1.10. The basic formulations are given in Table 1.

2.3. Characterizations

Density of the foam was measured according to ASTM D 1622 with sample size of 30×30×30 mm (width×length×thickness), and an average of at least five measurements was taken to report. The density distribution [%] was calculated according to 100×(maximum density-minimum density)/average density.

The closed cell content was determined by an air pycnometer following ASTM D 2850 with specimen dimension 50×50×25 mm. Thermal conductivity was measured using HC-074 (Laser Comp) according to ASTM C 518. The cell morphology was observed under a scanning electron microscope (SEM, HITACHI S3500N). Samples were cryogenically fractured in liquid nitrogen and gold sputtered before they were scanned in the free rising direction. Mechanical properties at room temperature were measured using a Universal Testing Machine (Ametek, Lloyd). Compression strength was determined by ASTM D 1621 at a crosshead speed of 3.0 mm/min with the sample dimension of 30×30×30 mm [7]. The force required for 10% deformation based on the original thickness has been taken as the compression strength of the foam. The surface tension was measured using Tensiometer K 100 (Kruss) according to ASTM D 1331 based on bubble pressure.

Table 2. Reactivity

|	Without silicone surfactant	With silicone surfactant
Cream time [s]	57	60~62
Gel time [s]	180	198~206
Tack-free time [s]	220	240~250

3. Results and discussion

3.1. Kinetics of foam formation

Kinetics of the foam formation is followed by the cream time, gel time and tack-free time [4, 6, 10]. The cream time corresponds to the start of bubble rise and hence color of the mixture becomes cream-like from dark brown due to the introduction of bubbles. Gel time is the starting point of stable network formation by intensive allophanate crosslinks as well as urethane. At the tack-free time, the outer surface of the foam loses its stickiness and the foam can be removed from the mold. Table 2 shows that cream time, gel time and tack-free time increase with increasing surfactant concentration, implying that the surfactant reduces diffusion across the interfaces. The PPGs are incompatible with CMDI and the reaction mixtures are heterogeneous. For this reason surfactants should carry high surface activity to act as a nucleation supporter and good emulsifying ability for the raw materials and blowing agents [3].

3.2. Foam density and density distribution

Density is a most important parameter to control the mechanical and thermal properties [23] of closed cell foams [2, 3]. With increasing surfactant concentration, foam density decreases asymptotically to a small minimum at 0.5 pphp, beyond which the increase is marginal (Figure 1). Similar results were obtained by Krupers *et al.* [22] who reported that average foam height increases, i.e., density decreases with the addition and increasing amount of fluorosurfactant. This implies that the blowing efficiency is increased with the addition of surfactant by supporting the ability to create nuclei and augmenting the stability of the foams. It seems that the surfactant in excess is not interposed at the interfaces and rather increases the heterogeneity of the system.

Foam density decreases along the bubble rising direction i.e., from bottom to top due to the gravity
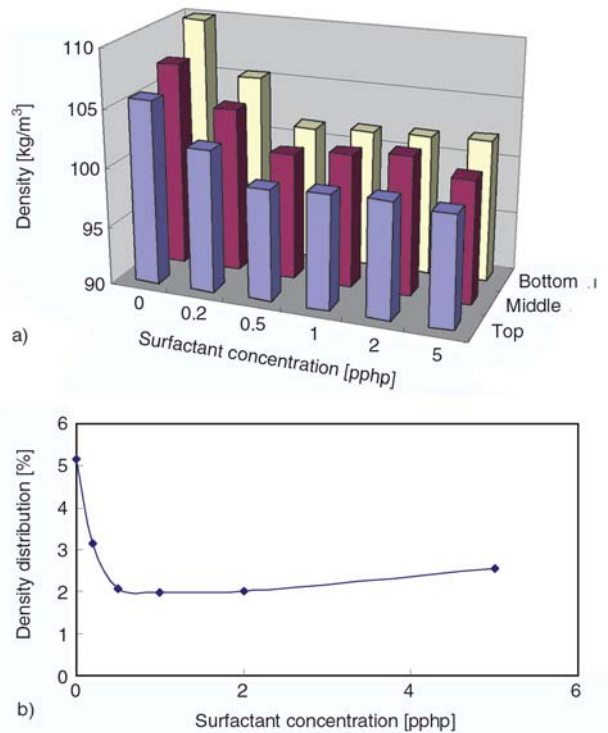

Figure 1. Densities (a) and density distributions (b) of the RPUFs vs. surfactant concentration

effect giving rise to great compression at bottom. The density distribution along the rise direction also shows similar surfactant dependence as density, i.e., the density variation shows a minimum at 0.5 pphp surfactant.

3.3. Surface tension and cell morphology

The exothermic heat of reaction causes the super-saturation of the reactive mixture resulting in phase separation into gas, followed by diffusion into the nuclei which are small air bubbles entrapped during the mixing of raw materials [24]. Then the nuclei grow into bubbles and spherical cells by adopting
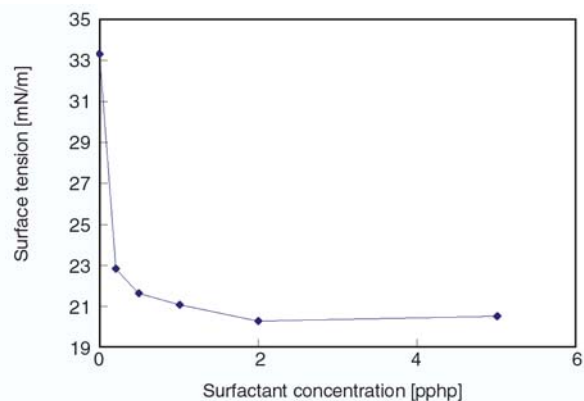

Figure 2. Surface tensions of the RPUFs vs. surfactant concentration

more gases or by coalescence with neighboring ones. As the blow ratio increases the spherical bubbles are eventually separated by the cell membrane and become polyhedral.

The surface tension of the polyol for various surfactant concentrations are shown in Figure 2 which shows that the surface tension decreases rapidly to an asymptotic value at 2 pphp. The asymptotic value of surface tension is approximately 2/3 of the surfactant-free value.

SEM micrograph shows that the foams consist of cells of spherical and polyhedral shape (Figure 3). Cell size (Figure 4) decreases rapidly to an asymptotic value of about 140 μm with the addition of surfactant. Cell size as small as 100 μm was also reported with fluorosurfactant [22]. On the other hand, the closed cell content (Figure 5) increases asymptotically with increasing surfactant concentration due to the decrease in surface tension. The increase of closed cell content is accompanied by
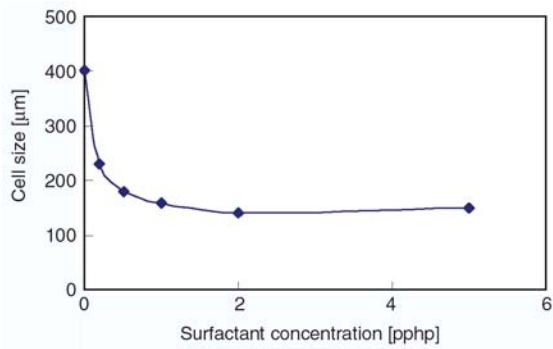

a)   0 pphp

b)   0.2 pphp

c)   0.5 pphp

d)   1.0 pphp

e)   2.0 pphp

f)   5.0 pphp
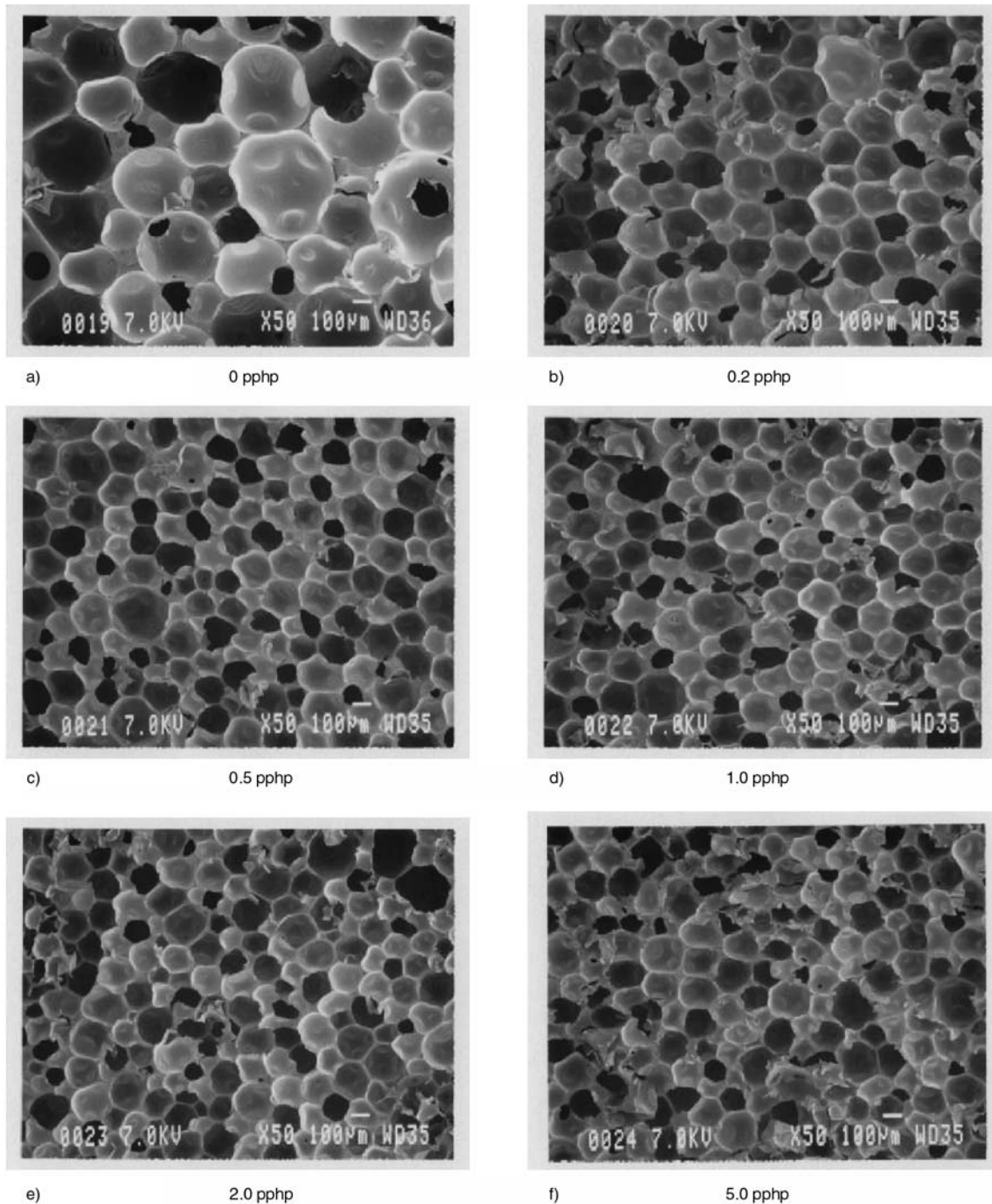
Figure 3. SEM micrographs of the RPUFs vs. surfactant concentration

Table 3. Porosities of the RPUFs

Surfactant [pphp]	0	0.2	0.5	1	2	5
Porosity [%]	89.6	89.2	90.0	90.3	89.6	89.7
Closed porosity [%]	63.3	82.8	84.3	84.7	84.1	84.6
Open porosity [%]	26.3	6.4	5.7	5.6	5.5	5.1

Porosity was calculated using the resin density of 980 kg/m^3

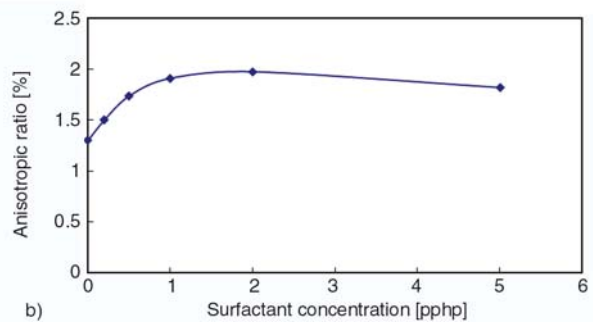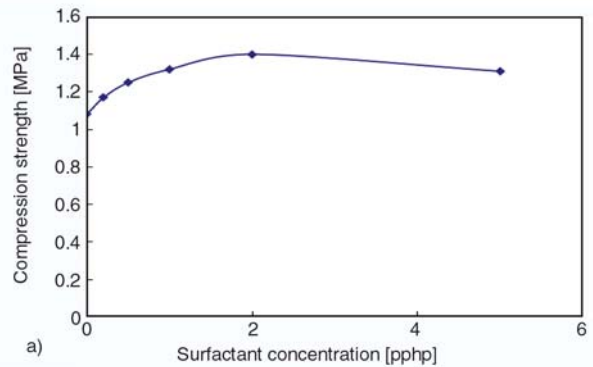**Figure 4.** Cell size of the RPUFs vs. surfactant concentration
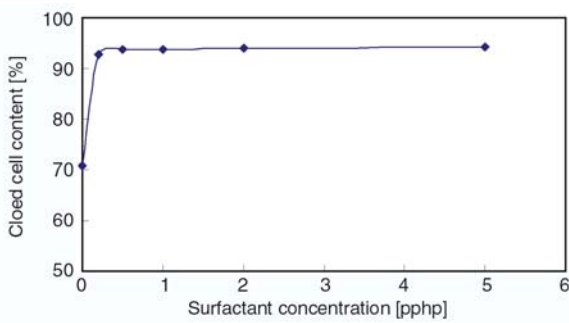
Figure 5. Closed cell contents of the RPUFs vs. surfactant concentration

Figure 6. Compression strengths (a) and strength anisotropies (b) of the RPUFs vs. surfactant concentration

the increase of closed porosity while the full porosity is kept almost constant (Table 3). This implies that closed cell content and porosity as well as the cell size are closely controlled by the amount of surfactant being added.

3.4. Compression strength

The compression strength is closely related to the dimensional stability of closed cell foams. As the temperature goes up, gas pressure inside the cell increases, and the pressure difference relative to the atmospheric pressure becomes great. If the foam is to be dimensionally stable under these conditions, the compression strength must be greater than the pressure rise [2]. The minimum compression strength of 0.1 MPa is generally recommended for closed cell foam [6].

The compression strength of our foam is greater than 0.97 MPa (perpendicular). In contrast to the density decrease, strength and its anisotropy (strength ratio of parallel to perpendicular direction) smoothly increases with increasing concentration of surfactant with a maximum at 2 pphp (Figure 6). An earlier work showed simultaneous decreases of compression strength with increasing surfactant concentration [7]. It seems that the compression strength is closely related to the closed cell content and cell size when the density variation is insignificant

3.5. Thermal conductivity of the foam

Heat conduction through the closed cell foams can be approximated by a series model which is composed of polymer walls and gas cells in series [25].

Conductive heat flux (*q*) through the composite wall is given by Equation (1):

$$q = \frac{\Delta T}{R} \tag{1}$$

where ΔT is the temperature drop across the foam and *R* is the conduction resistance given by the following Equation (2):

$$R = \sum_{i=1}^{n} \left(\frac{X_{W,i}}{k_W} + \frac{X_{G,i}}{k_G} \right) \tag{2}$$

Here $X_{W,i}$ and $X_{G,i}$ are the cell wall thickness and cell dimension, and *n* is the number of polymer walls, respectively. For uniform cells, wall thickness ($X_{W,i}$) and cell dimension ($X_{G,i}$) are constant to give Equation (3):

$$R = n \left(\frac{X_W}{k_W} + \frac{X_G}{k_G} \right) \tag{3}$$

In the typical closed cell foam, the polymer walls occupy 3–6 volume% of the foam. In addition, the conductivity of the polymer is much greater than that of the blowing gas. So, the first term, viz. polymer wall resistance can be neglected to give Equation (4):

$$R = n \left(\frac{X_G}{k_G} \right) \tag{4}$$

The above simple analysis shows that the thermal insulation of closed cell foams increase linearly with the number of closed cells, i.e., effect of insulation increases as the cell size decreases [26].
The thermal conductivity of our foam rapidly decreases to an asymptotic value at 1pphp surfac-
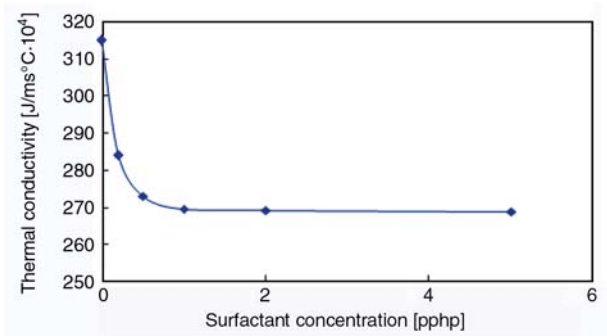
Figure 7. Thermal conductivities of the RPUFs vs. surfactant concentration
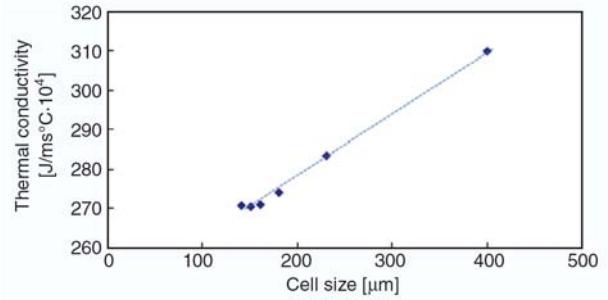
Figure 8. Thermal conductivities vs. cell size for the RPUFs

tant (Figure 7). The decrease is mainly due to the decreased cell size as analyzed above. To confirm this, the relationship between the thermal conductivity and cell size is plotted in Figure 8 which shows a straight line for a broad range of cell size. This implies that the series model is applicable where the wall resistance can be considered for small cells.

4. Conclusions

The RPUFs have been fabricated from CMDI and PPGs as a function of surfactant concentration with an environmentally friendly blowing agent (HFC 365mfc). Cream time, gel time, and tack-free time increased with the addition of surfactant due to the increased stability of reaction mixture and rising bubbles.
Foam density and density distribution decreased rapidly to a minimum at 0.5 pphp surfactant due to the increased blowing efficiency in the presence of surfactant. Surface tension of the foam rapidly decreased to an asymptotic value at 2 pphp surfactant, implying that the reaction mixture is saturated at this concentration.
In accordance with the decreased surface tension, cell size decreased and closed cell content increased rapidly to constant values at low surfactant concentrations (<1 pphp)).
The decrease of cell size was accompanied by the decrease of thermal conductivity, and a linear relatiohship between the two was held for a broad range of cell size. Simple analysis based on series model also gave the same result assuming the resistance of cell wall is negligible except the small cells.

Acknowledgements

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