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# Polyurethane foam growth in Air Void Analyzer

W. Brostow\*, G. Granowski and N. Hnatchuk

The authors have used an Air Void Analyzer (AVA) designed for concretes and applied it to polymeric foams. Similarly as with air voids in concretes, there is a kinetic process of foam cell formation and growth. Good results have been obtained for polyurethane foams. There seems to be no limitation in using AVA for other polymeric foams formation.

**Keywords:** Foams, Air Voids Analyzer, Bubble size distribution, Polyurethanes

## Introduction and scope

The process of concrete formation takes time. This formation begins when a clinker consists mainly of  $6\text{CaO}-4\text{Al}_2\text{O}_3\cdot\text{FeO}\cdot\text{SiO}_3$ , monocalcium aluminate  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  and calcium dialuminate  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , reacts with water, clinker forms a complex hydrated product that is cementitious. As discussed in a classical text by Kingery and his colleagues,<sup>1</sup> calcium silicate hydrate is formed, but also calcium hydroxide. The latter reacts with carbon dioxide from the air as well as with water, so that calcium carbonate is formed. The formed gel phase contains pores between gel particles. The relatively large pores are created by the excess water present. Moreover, there are relatively large pores created by the excess water present. In service, the cement is subjected to consecutive thawing and freezing cycles. As long as the voids (pores, air bubbles) are relatively small, they enhance the durability of concrete made from the cement. The ice formed in the voids during freezing expands into adjacent 'empty' voids, so that the material is not damaged. By contrast, large voids weaken the cement and the concrete is made from the cement.

Since void sizes and their probability distribution are important for that reason, ASTM standard C 457 has been developed, 'Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete'.<sup>2-5</sup> The standard is limited to the spacing factor, the maximum distance from any point in the cement paste to an air-void boundary and the specific surface, and the ratio of the surface area of the air voids to their volume. An apparatus called an Air Void Analyser (AVA) needs been developed for concretes by Germann Instruments A/S in Copenhagen.

In the AVA apparatus, the air bubbles entrained in a mortar sample (removed from fresh concrete) are transferred to a blue release liquid while the mortar is stirred. That liquid needs to have viscosity within a certain range and be hydrophilic. Provided that these two conditions are met, the bubbles released from the mortar retain their original size; they neither coalesce nor disintegrate into smaller bubbles. The apparatus has a column of water above the release liquid; the bubbles rise through that column; larger bubbles rise faster

(Stokes' law). Those bubbles are collected under an inverted and submerged buoyance pan attached to a sensitive balance. As a consequence of the accumulation of bubbles in the top of the pan, the apparent mass of the pan decreases; water is displaced by air. The apparent mass of the pan is recorded over time and the size distribution of the collected air bubbles calculated. Given that size distribution, the spacing factor and the specific surface defined in ASTM C 457 are calculated.

There is no ASTM standard regarding measurement of void sizing, void probability distribution, or gas formation in chemical foam formation. However, our analysis of the above process led to a simple conclusion: the AVA apparatus should be usable also for polymeric foams, such as polyurethane foams, poly(vinyl chloride) foams, styrofoam, polyimide foams and microcellular foams. The authors have been working on polyurethanes (PUs)<sup>6,7</sup> and also on polycarbonate (PCarb).<sup>8,9</sup> They have now created foams based on PUs and on PCarb and analysed them using the AVA apparatus. The results are reported below.

## Experimental

### Principle of the AVA apparatus

The principle of the AVA apparatus for determining the air void quality in fresh concrete has been described above. The high viscosity of the analysis liquid slows down the initial rise of the bubbles and provides a measurable separation in time between the arrival at the top of the column of bubbles of different sizes. The change in buoyancy is measured as a change in weight and is recorded as function of time.

An earlier version of the method became available during the second half of the 1980s and was used by Dansk BetonTeknik as a method for fast subjective evaluation of the fineness of an air void system. It was soon documented that mixtures of glycerol and water were well suited for the purpose. The method was qualitative and subjective and had limited application. Subsequent improvements led to the technique we now use. The void size distribution may be calculated based on simple measurements of the released amount of air through recordings of the volume of air, which has risen related to time elapsed.

The AVA provides data such as the spacing factor, specific surface, size distribution of air voids under 2mm, histogram of air voids under 2mm, as well as

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calculates the percentage of air void content in concrete and in cement paste. More importantly, for concrete engineers, one obtains also the percentage of air void content with diameters  $< 300 \mu\text{m}$ .

### Polyurethane materials formation

Polyurethanes are any type of polymer containing a urethane linkage,  $-\text{NH}-\text{CO}-\text{O}-$ . Polyurethanes (PUs) are formed by reacting isocyanates with compounds that have an active hydrogen, such as diols, in the presence of a catalyst. Since there are many compounds containing active hydrogens and many different diisocyanates, the number of polyurethanes that can be synthesised is also large. The specific properties of the PUs can be tailored to a specific need by combining the appropriate compounds. PUs can exist as both rigid and flexible foams, also as coatings or adhesive materials. Since polyurethanes come in so many forms and can have a wide variety of properties, they are also used in many different applications. The applications involving PUs include apparel, appliances, automotive, building and construction, wood-based composites, electronics, flooring, furnishing, marine, medical, and packaging. Rigid PUs can be used for insulation, like thermal barriers for refrigerants and in flotation devices for marine equipment, while flexible PUs are used for cushioning applications including carpet bedding, furniture interiors, and packaging peanuts.<sup>10,11</sup>

Polyurethanes are mostly thermosets, as a consequence, they are hard to melt and reprocess and can therefore have the disadvantage of being non-recyclable.

### Materials used in testing

The materials used were: Germann Instruments AVA-3000 instrument, 220 mL of AVA Blue Release Liquid (glycol), 20 mL of FibreGlast 625 (A side), 20 mL of FibreGlast 624 (B side), mixing rod, and three 25 mL non-reactive cups.

### Test procedure

At the outset of the research, the following procedure for testing was established:

- (i) The PU epoxies are separately poured into 25 mL non-reactive containers.
- (ii) The authors set the syringe to 2 mL more than the volume that is planned to be tested.
- (iii) They pour the PU components into the syringe in a 50:50 volume ratio to the planned volume. Note that for the mixing of PU components with glycol requires the ratio to be a multiple of 1:1:'x' (PU-A:PU-B:glycol) by volume ratio, where 'x' is the volume of the glycol added before mixing.
- (iv) They thoroughly mix the components together and attach to the base of the riser column.
- (v) They inject the sample from a syringe into the bottom of a riser column filled with glycol and water. The mixture is stirred for 30 s to release PU droplets. The liquid prevents the PU droplets from coagulating together. The expanding PU droplets then rise through the liquid at rates dependent on their size and enter a column of water above the glycol.
- (vi) The PU droplets rising through the column of water are collected under a submerged dish, which is attached to a balance. The balance records the buoyancy of the dish as a function of time.

In the early stages of the measurement, the size distribution of the PU droplets arriving under the dish ranges from a few millimeters down to a few micrometers. As time continues, the PU droplets gradually get smaller, but the droplets in the dish continue to expand because of the PU foam reaction.

The measurement procedure continues for 25 min – assumed to be an appropriate time period to give the air parameters comparable to those obtained by the ASTM C457 standard with acceptable accuracy. The 25 min is preprogrammed into the device and the user cannot change the end time. However, the test does have an end early condition and will end if the scale reads no weight change for 2 min. The data sheet for Fibre Glast PU foaming resin provided a cream time of 58 s, a gel time of 155 s and a tack free time of 225 s, totalling to approximately 7 min of foam reactivity. Thus, the adoption of 25 min provides ample time to collect data.

### Materials tested

A series of tests were conducted with various volumes and mixture ratios of PU components and the blue release liquid, as listed in Table 1. Critical time is defined as the maximum of the change of mass with respect to time. Test duration is defined as the maximum time the computer kept collecting data – typically 2 min of zero change of buoyancy on the dish.

The data in Table 1 tell us that the average critical time is 6 min. with a 1 min standard deviation. The average test time duration is 18 min with a 3 min standard deviation. The reaction time of 7 min, stated earlier, coincides with the critical time for reaction one sees in the AVA results. The use of the AVA can provide additional data in the reaction time that goes unnoticed by the ASTM designation D7487. This means that we can expand the definition of foaming time to include gas formation during static volume growth. Sample 9 is excluded from the average. In sample 9, with 2 mL PU, and the ratio of 33% PU and 66% Glycol, the glycol largely inhibits the PU epoxy reaction, thus minimising gas formation. Thus sample 9 does not have a critical time.

**Table 1** Samples investigated

Sample number	Sample	Critical time (min)	Test duration (min)
1	1mlA+1mlB	3	17
2	1mlA+1mlB	6	23
3	1mlA+1mlB+1mlG	6	19
4	1mlA+1mlB+1mlG	6	16
5	1mlA+1mlB+1mlG	6	19
6	1mlA+1mlB+1mlG	7	18
7	1mlA+1mlB+2mlG	5	15
8	1mlA+1mlB+3mlG	4	14
9	1mlA+1mlB+4mlG	?	6
10	2mlA+2mlB	7	19
11	2mlA+2mlB	6	21
12	2mlA+2mlB+1mlG	7	17
13	2mlA+2mlB+1mlG	8	20
14	2mlA+2mlB+2mlG	8	22
15	2mlA+2mlB+3mlG	8	17
16	2mlA+2mlB+4mlG	7	14

Key: A: part A of PU compound; B: part B of PU compound; G: blue release liquid (glycol).

## Results and discussion

First, the authors present changes in mass with time for all 16 samples in Fig. 1.

The curves seen in Fig. 1 reveal that PU foams have a Gaussian growth rate. The best data with a well-defined bell curve pertain to samples 10–14, where 4 mL of PU with a ratio PU/liquid greater than 66 vol.-% is used.

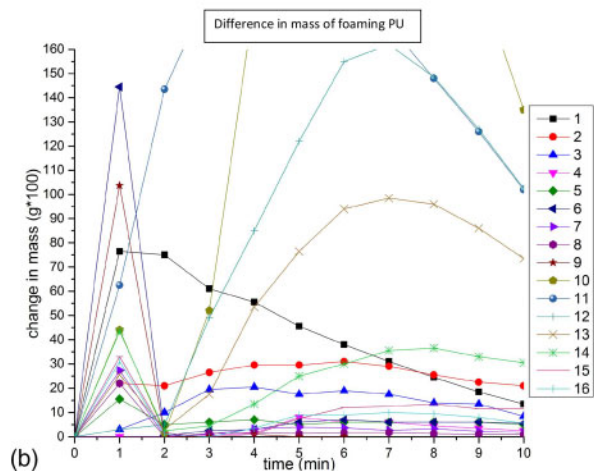
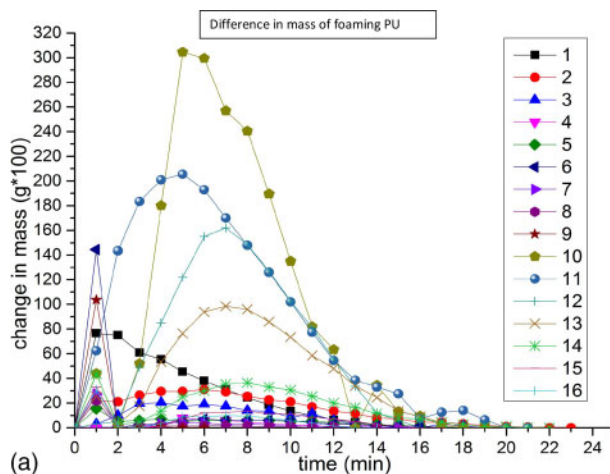
Looking at the compositions <4 mL of PU or a volume ratio <66% to glycol, the change in mass as a function of time becomes very small and loses the Gaussian reproducibility.

The spike at the 1 min mark for several samples is attributed to extraneous bubbles introduced into the riser column from the initial injection of PU/G-solution. The extraneous anomaly was omitted when calculating the average critical time.

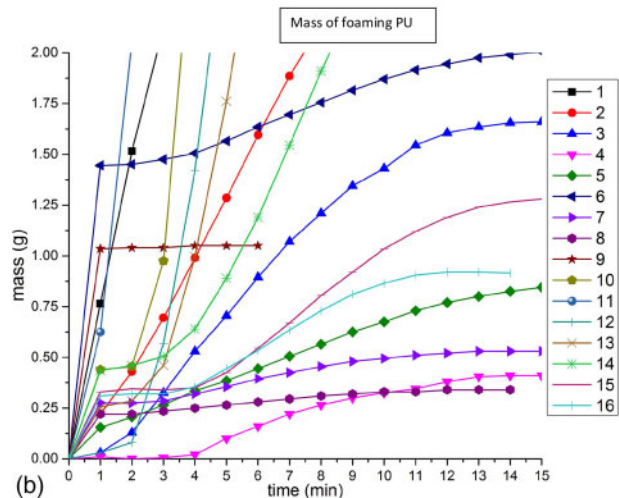
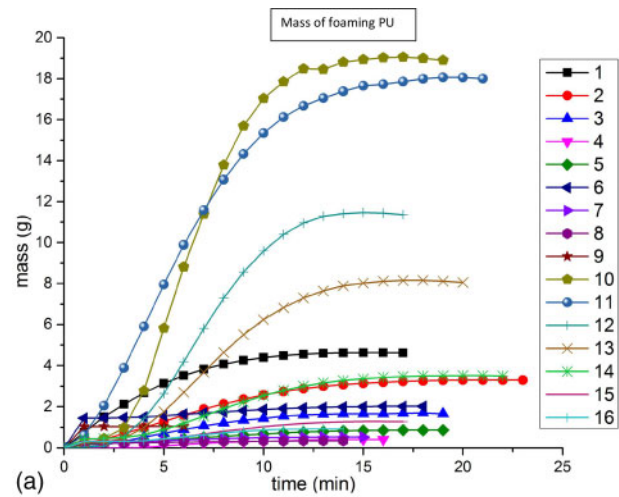
In Fig. 2, the authors show the total mass of foaming PU as a function of time.

Figure 2a reveals that PU foam samples 10–13, with 2 mL of the A component, provide significant changes, a clear correlation with time.

Comparing samples 1 and 10, we see that the increase of the initial volume from 2 to 4 mL caused a buoyancy change from 4 to 19 g. Thus, doubling the initial volume caused a 475% increase in mass displacement. This reveals a positive non-linear trend in gas formation;



1 a Changes in mass with time of PU foams as provided by the AVA machine, b a windowed graph of change in mass of PU-foam as provided by the AVA computer to show the smaller changes in data



2 a Curves of the mass of expanded PU foams collected by the dish, b a windowed graph of mass of PU-foam to show the smaller changes in data

as the initial volume of PU increases, the final volume of the foam is even greater. Nevertheless, a maximum expansion limit could not be attained with the current AVA instrument; PU mixtures with volumes larger than 2 mL will cause the buoyancy pan to lift off the scale.

Since in Fig. 2a, there is ‘crowding’ of curves at the bottom of the diagram, with low perspicuity, an enlarged part of the diagram is provided in Fig. 2b. Samples 14–16 provide curves comparable in shape to samples 2–8. A PU:G ratio of 2:1 with increasing concentration of G mitigates the PU reaction, thus negating the 475% mass displacement and inhibiting the PU reaction in general.

In Fig. 2b, sample 9 has an almost horizontal slope after the 1-min mark and a short process duration. In samples 15 and 16, the mass displacement is <10% of the displacement established by sample 10. In samples 6–8, the mass displacement is <25% of the displacement seen for sample 1.

The authors have noted above a broad range of applications of polyurethanes. Colombo and Hellman<sup>12</sup> create ceramic foams by creation of polymeric foams followed by high temperature pyrolysis in an inert atmosphere. The resulting foams have outstanding strength, mechanical and thermochemical durability, as well as applications related to their electromagnetic

properties provided by fillers. The durability was verified by static and cyclic exposure to 1200°C in air. The direct foaming procedure of Colombo and Hellman is advantageous compared to other techniques of creation of ceramic foams.

## Conclusions

Utilising an instrument designed to calculate air voids in fresh concrete does provide quantitative data in PU foam curing. The AVA apparatus can deliver repeatable and accurate results for determining the reaction rate and duration for a small volume of foaming polymers that are not soluble in glycol or water. In addition, the data acquired can correlate the per cent expansion from initial volume to final volume based on buoyant displacement.

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