PVC AUTOCLAVE MODEL

The batch reaction of polyvinyl chloride (PVC) in a pressure auto-clave is modelled by considering the various mechanisms for conversion from vinyl chloride monomer (VCM) to the polymer during the middle phase of the industrial process. A key step is to determine at what stage the droplets of VCM stop contracting because of the density difference between VCM and PVC — this is known as the 'freeze point'. A model is proposed that locates the freeze point as that point where the unfavourable energy due to wetting of the PVC by water is dominated by the energy required to compress the gel network inside the droplets. Preliminary investigations support this explanation and suggest avenues for further work. A corollary of this model is an explanation of the role of 'secondary granulating agents' in controlling the porosity of the final product.

1. Introduction

PVC (polyvinyl chloride) is an important plastic for both flexible applications — plastic coatings of cables, for example — and rigid applications, such as domestic sewer and drainage piping. It is produced by ICI Australia at two plants in Australia, one being at Laverton in Victoria.

PVC is produced in a pure powder form by ICI who supply it to manufacturers for further processing according to their particular application. For example, in flexible applications, PVC must be combined with plasticizers which give it the required mechanical properties.

Three main properties determine the various grades of PVC produced.

1. Molecular weight, i.e. the length of the polymer molecules making up the plastic. This is determined primarily by the temperature at which the batch polymerization reaction is run (between $40^{\circ}C$ and $70^{\circ}C$). The higher the temperature, the lower the molecular weight, i.e. the shorter the chains.

2. Particle size. This is determined primarily by the amount of surfactant (called 'primary granulating agent' in the trade) added initially to the reaction vessel and by agitation conditions in the reactor.

3. Particle porosity. This is crucial for the end-users since, for example, plasticizer must be able to penetrate the PVC particles. Empirically, this is determined by both reaction temperature and the addition of another surfactant — the 'secondary granulating agent' — later in the process.

The effect of temperature on molecular weight is a matter of polymerization kinetics and is well-understood. Similarly the role of the primary granulating agent in setting the particle size is fairly well-understood. The control of particle porosity, however, appears to be largely 'black magic' developed over years of plant experience. It was this aspect of the process that the MISG group addressed.

We start with an explanation of the key stages in the process (as we understand it) in Section 2, present a diagrammatic representation of the process developed by ICI (Section 3) and finally our contribution to understanding one stage in the whole process (Section 4).

2. The stages of the PVC process

PVC is manufactured in a batch process called suspension polymerization. A pressurized temperature-controlled reaction vessel called an autoclave is filled with the reactant vinyl chloride monomer (VCM) and water. Initially about 50% of the volume is VCM. The water does not take part in the reaction — it is there solely as the suspension medium. A small amount of surfactant (the 'primary granulating agent') is added initally as well as a small amount of initiator — a chemical that undergoes dissocation at a certain temperature to produce free radicals that catalyse the polymerization of VCM to PVC. The sealed autoclave is then agitated vigorously and the temperature raised to that required for the desired molecular weight. As the temperature is raised, the initiator molecules dissociate and start the polymerization process.

VCM is an organic liquid immiscible in water. If such a mixture were stirred, droplets of VCM would form, recombine, be torn apart etc. The addition of the surfactant stabilizes droplets of a certain size — essentially enough surfactant is added to form a monolayer around droplets of the desired size, around $40\mu m$ in diameter. The initial mixture can be regarded as 50% VCM in the form of droplets suspended in water. The initiator is soluble in VCM and presumably uniformly distributed throughout the drops. The solubility of VCM in water — and vice versa — is low.

The autoclaves at Laverton have a capacity of $40m^3$. The reaction is highly exothermic and so a major design feature involves removing the heat fast enough to keep the reaction at constant temperature. In addition, VCM vapour is produced so that the vessel, which is sealed, develops pressures up to 10 bar. It should also be mentioned that VCM is a highly toxic chemical. Once filled the reactor is sealed and the contents agitated until the reaction is about 90% complete. This typically takes 4–6 hours. Then the reactor is emptied, the

unconverted VCM separated from the PVC suspension, the PVC separated from the water, the PVC dried and the water cleaned and discharged to effluent.

Industrial autoclaves are typically not equipped with detailed measuring systems in such a hostile environment. Enough pressure and temperature sensors are provided for control and safety purposes but not for detailed temperature or fluid velocity profiles. Some information is available from laboratory-scale reactors in which the reaction is stopped at a given stage (by adding chemicals to halt the reaction) and the contents examined by electron microscopy (see for example, Smallwood 1986). It is from such studies that the following picture of the process has emerged.

As soon as the temperature is high enough the initiator molecules start to dissociate. Polymer molecules are formed very quickly and coil up because they are insoluble in the VCM. As more polymer molecules are formed they cluster together, trying to escape the VCM, and within 30 seconds or so have formed 'primary particles' about 0.1 μm in diameter. These primary particles can be detected by electron microscopy. Because VCM is soluble in PVC and VCM surrounds the primary particles, they are actually gel-like, made of PVC saturated with VCM. The saturated concentration of VCM in PVC is 23% by weight.

We emphasize that this is a continual process throughout the batch run — initiator molecules are continually dissociating, polymer chains formed, primary particles forming etc. On the time-scale of the run, these happen in an instant but scattered in time throughout the 6-hour period.

Once primary particles are formed, two things happen. A porous skin forms on the surface of the droplet, actually a copolymer between PVC and the surfactant. It is about 0.2–0.5 μm thick and is not thought to influence the process greatly. From electron micrographs, one can see that the primary particles aggregate to form a network — the spherical primary particles retain their identity until quite late in the process but stick together. It is the space-filling properties of this network that determines the porosity of the droplets.

After a while, the droplets themselves start to aggregate to form the final grains of the powder. Each grain has about 10 'droplets' — by now consisting of PVC gel — and is about 150 μm in diameter.

3. A 'phase diagram' for the PVC process

A key step for further progress is to change the independent variable from time to percentage conversion, i.e. the fraction of VCM that has been reacted

to PVC. Experiments with different initiators and various initiator concentrations (Smallwood, 1986) suggest that, although the time course of the process varies under different conditions, the same stages are reached at given percentage conversion values under a wide variety of conditions. For example, at 10% conversion the network has a certain morphology and the droplet a certain porosity regardless of how long it took to reach that point.

Next we use physical data to construct a 'phase diagram' showing the relative volumes of each phase in the autoclave. Since the vessel is closed, we have a constant volume system. We now describe how to construct the diagram in figure 1.

Initially, we have 50% by volume VCM in water at 0% conversion. If all the VCM were reacted, we would have only PVC and water, with PVC making up 30% by volume because of the quite large density difference between PVC and VCM — 1400 kg m^{-3} and 850 kg m^{-3}, respectively. This enables us to draw a 'tie-line' AB in our diagram under which lies the volume of total PVC and VCM for any value of conversion. A further tie-line OB starting at the origin separates the VCM volume from the PVC volume.

But not all the VCM is present as liquid — some is dissolved in the PVC. At 77% conversion, it would all be present in the dissolved gel and none as free liquid. This point is observed during plant operation as a pressure drop because of reduced PVC vapour pressure. This then allows a third tie-line OC separating the liquid VCM from that in the PVC gel.

In the absence of any other effects, the water would remain at constant volume and so a fourth tie-line DE parallel to AB represents the water phase.

The implication of the line AB is that the droplets shrink as VCM is reacted because of the density difference between PVC and VCM. At some stage, it is thought that the droplets stop shrinking, whereupon water must enter through the porous skin to make up the volume left by the reacted VCM. The point where this happens is called the 'freeze point'.

Experimental evidence for the freeze point is rather indirect. If the droplets kept shrinking all the way down line AB to point C the gel droplets would have zero porosity. But they do have a porosity — in fact, all the value in the product relies on having uniform porosity in the range 12–30% depending on the grade.

Another piece of evidence is the following. If water enters the droplets, then less water is acting as the suspension medium and the suspension will become harder to agitate. This is in fact observed and extra water is usually added during the process to prevent the suspension becoming too viscous near the
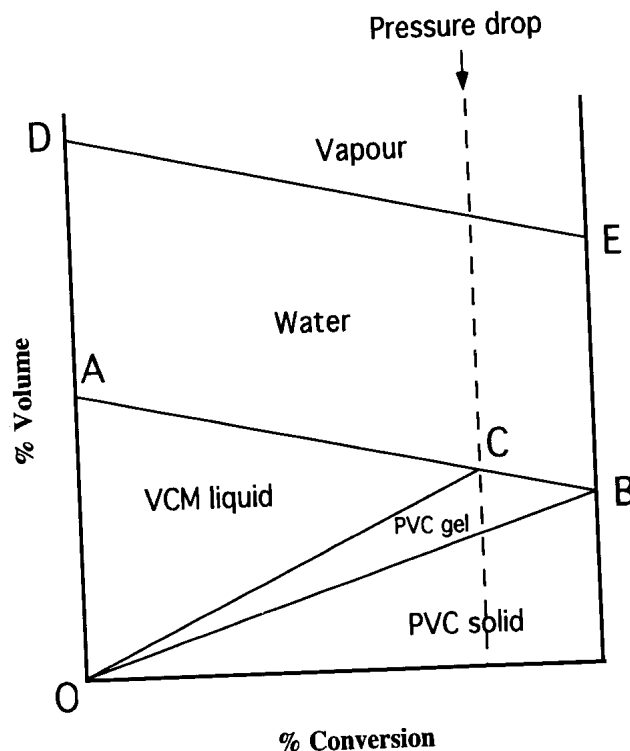
Figure 1: A 'phase diagram' of the PVC process.

point of pressure drop.

From this sort of evidence, the freeze point is thought to occur at conversions between 10 and 30%. It is not known what factors determine the location of the freeze point. The task set by ICI was to develop a model for the 'freeze point'.

Before we present the model we first explain how such information would enable predictions of the final porosity of the product — a key property that is ignored in all the literature treatments with which we are familiar (Xie *et al.*, 1991; Kiparissides *et al.*, 1994).

Growth mechanisms in the droplet

Suppose the droplet has stopped shrinking. As more VCM is converted, the network of primary particles can change through two mechanisms.

1. If VCM liquid is converted, it produces insoluble PVC (actually gel). At moderate volume fractions of primary particles, it is faster for this insoluble gel to diffuse to the existing network than to diffuse together to form

new primary particles. Thus the new PVC gel coats the existing network, thickening it up and filling in the space in the droplet. We call this 'coating growth' — it can be characterized as a process that keeps the overall network (droplet) dimensions constant and reduces the porosity by thickening the network.

2. There is another source of VCM in the droplet — that dissolved in the gel. Suppose some of this is converted — we are presuming that the initiator is present in the gel — to PVC. In the presence of excess liquid VCM, the new PVC will become saturated with VCM — the net effect is more gel. This process has the effect of swelling the network in all directions uniformly. This 'gel growth' can be characterized as a process that increases the overall network (droplet) dimensions and keeps the porosity constant (since the volume fraction inside the droplet is not altered by a uniform dilation).

We associate these two mechanisms with the two sources of VCM in the droplet — the liquid and the gel. Initially there is only liquid so coating growth must dominate. As we approach the pressure drop, gel growth must dominate. After pressure drop, only dissolved VCM is left. As this is converted the primary particles and the whole network must shrink uniformly in size because of the density difference between PVC and VCM. By the same argument as before, this reduces the 'droplet' dimensions at constant porosity. This argument implies that we need only determine the porosity at pressure drop — it is constant afterwards.

Both these processes can be represented graphically on our phase diagram (see figure 2). We assume the existence of a freeze point F on the line AB.

If we only had coating growth, the droplet volumes would stay constant, represented by the horizontal line FG. The droplet now contains gel, VCM liquid and encroaching water. From the location of the point F and hence G, we could calculate the final porosity of the product, noting that point C occurs at 34.6% volume. In the example shown, freeze occurs at 40% volume so the final porosity is given by

$$\frac{40 - 34.6}{40} = 13.5\%.$$

If only gel growth occurred, the droplets would grow at constant porosity. Since the porosity at freeze is the ratio of the vertical distance between F and OC and the height of F, by similar triangles the droplet volume must traverse a straight line formed by extending OF to the point H at pressure drop. Again, given F, H is known and the final porosity can be calculated. Clearly, gel growth produces higher final porosities than coating growth.
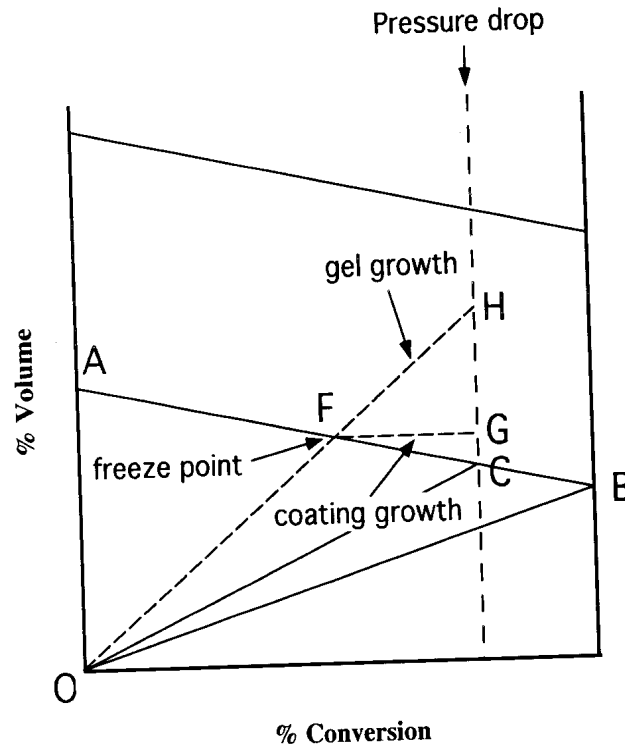
Figure 2: Growth mechanisms on the phase diagram. The region between the dashed lines FH or FG and the line FC represent water that has entered the droplets. The final porosity can be calculated from the position of points G or H — the two extreme cases.

In reality, both types of growth occur but already we can produce bounds on the location of the freeze point from experimental values of the final porosity. To illustrate this, we use the typical range of porosities of 14–30%.

4. A model for the freeze point

If there is only coating growth, we obtain a lower bound on the conversion at freeze x_f; if only gel growth, an upper bound. Using these we obtain, for a porosity of 14%,

$$0.488 < x_f < 0.692$$

and for a porosity of 30%

$$0.028 < x_f < 0.594.$$

From these bounds we conclude that, for low porosities, the freeze point must occur very late. This occurs either at high temperatures or without the addition

PVC autoclave model

of secondary granulating agent. For higher porosity, the bound is so wide as to be useless. For coating-only growth, the maximum porosity obtainable is 31% so any measured porosities higher than this hint at the reality of gel growth.

Suppose we have both processes acting — then the final volume can be expressed as

$$V = V_f \left(\frac{1 - \alpha x_{\text{final}}}{1 - \alpha x_f} \right)^{-\beta}$$ (1)

where

$$\alpha = 1 + \eta - \frac{k_g}{k_f}\eta$$

$$\beta = \frac{k_g}{k_f}\eta/\alpha$$

and where η is the ratio of VCM to PVC in the gel (here 30%) and k_f and k_g are the reaction rates in the gel and free VCM, respectively. See Appendix 1 for a derivation of equation 1. Since η is known, we just need the value of k_g/k_f to produce the final volume and hence porosity. Clearly, equation 1 interpolates between the two extreme cases considered above. For example, if $k_f = k_g$, a porosity of 14% (30%) corresponds to x_f equal to 0.68 (0.52). At typical observed porosities, it seems that the results for $k_f \geq k_g$ are fairly close to those for pure gel growth.

Percolation and aggregation models

Now we know what to do with a knowledge of the freeze point, how do we find it? When faced with a complicated particle network we thought: '*Percolation, diffusion-limited-aggregation,* fractal dimension!!'. The first hope was that as soon as a cluster spanning the droplet was formed it would be strong enough to resist the compression by water and so would determine the freeze point.

Depending on the lattice, percolation thresholds in three dimensions range from around 0.12 to 0.3 (Hughes, 1995) which looks encouragingly close to pre-conceptions of the freeze point. Unfortunately the network is not really formed by a percolation process but more by a cluster-cluster aggregation process with possibly some percolation-like process as VCM is used up outside the network.

Simulation data on off-lattice cluster-cluster aggregation (Meakin, 1984) can be summarized by

$$N = k(\frac{R}{r})^2$$

where N is the number of particles in the cluster, R is the size of the cluster (strictly a radius of gyration) and r the particle size. The exponent 2 gives a fractal dimension for the cluster. So we ask: at what volume fraction will this cluster be when it spans a droplet of diameter 40 μm and is made of particles of 0.1–1 μm in size? Taking k from figure 1 of Meakin (1984) produces estimates for the volume fraction less than 1%. This means the cluster is so wispy at the ends that it spans the droplet at a very low volume fraction.

This calculation relied on data obtained from fairly small clusters grown in a large simulation cell, which we then extrapolated to clusters of the size in the droplet. In fact, the droplet skin is present all the time and micrographs show the network growing inwards from the skin as well as inside the droplet. This would be expected to lead to a denser network — more than this we could not say in a MISG time-frame.

Since mere presence of the network did not seem to explain the freeze point, we could no longer avoid treating the mechanical strength of the network.

Wetting versus mechanical strength

Imagine a droplet filled with a network and liquid VCM. Some of the VCM is converted to PVC so the volume of the network plus liquid VCM falls. At this stage, two things can happen.

1. The network (and skin) retains its size and water enters the droplet. Water then displaces the VCM pushing it inwards towards the centre of the droplet. This costs free energy because the PVC primary particles prefer to be wet by the VCM. This is a kind of capillary effect driven by surface tension except that instead of water being sucked into a porous medium which likes being wet, here we have water forced into a porous medium (the network) which doesn't like being wet.

2. The alternative is that the network collapses against the ingress of water, thus preventing the primary particles being wet. This costs elastic free energy due to the compression of the network, including compression of the primary particles.

Both of these effects vary with the volume fraction of the network and which one occurs depends on which has the lower free energy cost at that volume fraction. For this purpose we assume that initially the capillary effect dominates so that the droplet shrinks but at some volume fraction the elastic cost becomes

too great and the droplet 'freezes' and water starts to wet the network. We estimate the work done by the capillary forces first.

We adapt a treatment of the capillary rise in powders (White, 1982). We want to interpret the free energy cost of wetting the PVC with water as a capillary pressure P_{cap} acting to crush the network. As the water/VCM interface advances, it sweeps out a volume dV. The volume of liquid VCM swept out is $(1 - \phi)dV$ where ϕ is the volume fraction of the network so the work done is $P_{cap}(1 - \phi)dV$. This must be equated to the free energy cost to obtain an expression for the capillary pressure. The free energy cost is

$$(\gamma_{PVC/water} - \gamma_{PVC/VCM})dA$$

where γ is the surface tension of the specified interface and dA is the area of PVC particles wet. This area is just $A_s \phi dV$ where A_s is the surface area of the network per unit volume of the network — for a collection of spheres this is just $3/r$ where r is the radius of the primary particles in our case. As the network thickens, we may approach something more like cylinders for which A_s is $2/r$. Putting this together we get

$$P_{cap} = (\gamma_{PVC/water} - \gamma_{PVC/VCM})\frac{A_s \phi}{1 - \phi}. \tag{2}$$

We now need to estimate the mechanical properties of the network. The closest analogue anyone could suggest was to consider the properties of open-cell foamed plastics, on which there is extensive data.

Lee White expressed his misgivings towards using the mechanical properties of foams as a model for these networks.

Typically, there are two relevant modes of collapse of such foams — at low compressions, they behave elastically; at higher compressions they yield plastically due to buckling of the foam cell walls. In each regime, the mechanical modulus of the foam can be expressed as a function of the volume fraction of the foam times the mechanical strength of the solid plastic making up the foam. This latter quantity is generally a strong function of temperature. For elastic collapse, we have

$$\text{foam modulus} = 0.05\phi^2 \times (\text{bulk modulus of solid plastic}).$$

Comparing this expression with a similar one for plastic yield, it appears that the elastic modulus is much smaller so the foam will elastically deform under the capillary pressure before it has a chance to irreversibly yield. Of course, deformation is a continuous process — consistent with the simplification of a

freeze point, we ignore any deformation until the capillary pressure exceeds the network modulus.

At this stage, we can start testing the model.

Parameter estimation and testing the model

The data of particular interest to ICI was a prediction of final product porosity versus temperature. In the absence of secondary granulating agent, the dependence is typically as given below.

Reaction temperature (°C)	% Porosity
50	30
60	23
70	14

Table 1: Porosity dependence on reaction temperature.

For each temperature, the freeze point must be estimated. To do this, we calculate the capillary pressure and the elastic modulus as a function of volume fraction (related to conversion) — where the elastic modulus dominates the capillary pressure is the freeze point. Once this is known, the porosity can be determined as shown above.

To proceed we need

1. an estimate of k_g/k_f

2. data for the bulk modulus of the PVC gel for various temperatures.

To estimate k_g/k_f, we used typical plant data for the heat production during the run. The heat comes from the reaction so the rate of heat production is an indirect estimate of the reaction rate. Field (1973) expressed the overall reaction rate in terms of a quantity α dependent solely on conversion

$$\text{rate} = \alpha(x)g(T,t)$$

where g accounts for the decay of the initiator during the run. The function α is fairly constant over a range of temperatures and initiator concentrations. It behaves approximately linearly in conversion from the start of the run to pressure drop increasing roughly fourfold over this range. Since initially there is only liquid VCM and at pressure drop only VCM in gel form, we estimate

$$\frac{k_g}{k_f} \simeq 4.$$

As noted above, the precise value of this ratio doesn't affect things much for low porosities. Apparently (Faraday, 1992), kinetic models can now be used to obtain predictions of $\alpha(x)$, so perhaps such models could refine this estimate.

No data is available on the properties of PVC swollen with VCM so we must make do with the properties of PVC with added plasticizer. It is not clear which plasticizer to choose, so at best we can obtain rough estimates.

The most important feature is that, at typical reaction temperatures, the PVC gel is well above the glass temperature so that the network is made up of rather soft material. Taking typical values for PVC with plasticizer, we get (Sears and Darby, 1982) values for the modulus around 10 MPa. The modulus is quite temperature-dependent — in one case falling about 4 MPa every 10°C. At the highest reaction temperature of 70°C, the modulus may be as low as a few MPa. In addition, at higher reaction temperatures, the molecular weight of the polymer is lower, producing even softer material.

For a given temperature, we estimate a modulus as best we can and hence calculate the capillary pressure and the elastic network modulus as a function of volume fraction, i.e. conversion. For the particle radius appearing in equation 2 we use the data of Smallwood (1986) for the primary particle diameter as a function of temperature and conversion. Some examples are shown below.

In figure 3 we can clearly see the freeze point where the elastic network pressure becomes greater than the capillary pressure — in this case, freeze occurs at about 40% conversion. For this graph and the next, we have used

$$\gamma_{PVC/water} - \gamma_{PVC/VCM} = .03 \text{ J m}^{-2}$$

and taken A_s as $3/r$. Obviously there is some freedom in the choice of values here.

In figure 4, the freeze happens much later at a conversion of around 49%. This would produce a much less porous product, in qualitative agreement with the data of Table 1. Using these figures as input to equation 1, we could then estimate the porosity of the final product.

5. Conclusions

At this stage, we must be content with qualitative success of the model. We have not been able to reproduce Table 1 with our current parameter estimates. In particular, our estimated value of k_g/k_f implies freeze must be rather late $(0.57 < x_f < 0.69)$ to give the observed porosities. But the equation to estimate network modulus — based on foams — is clearly meant to apply to much lower
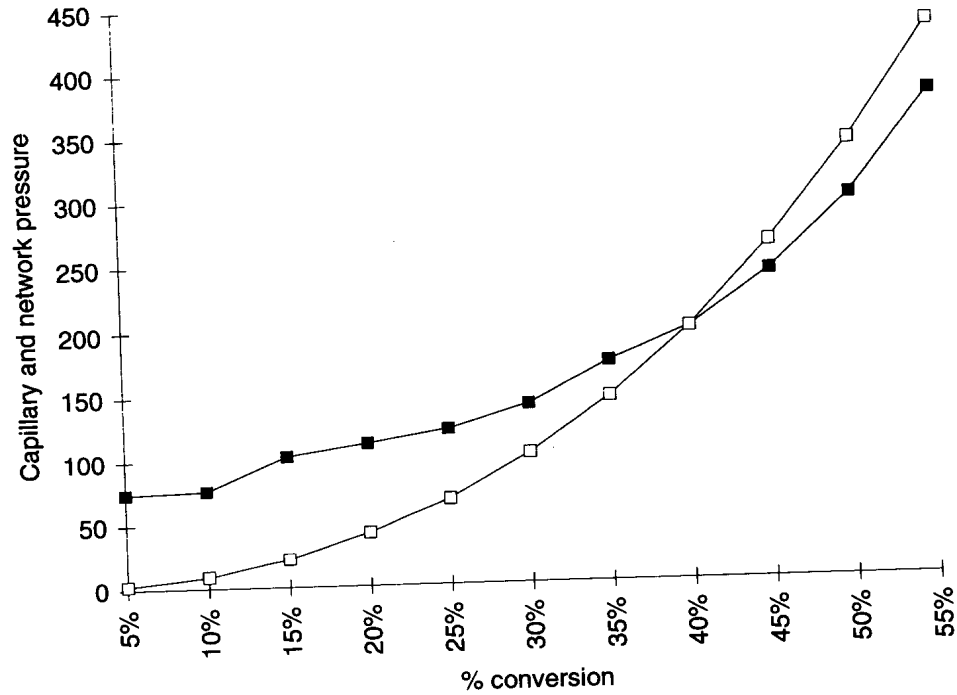
Figure 3: Capillary (■) and network (□) pressure (kPa) at 51°C. Modulus is chosen as 21 MPa.
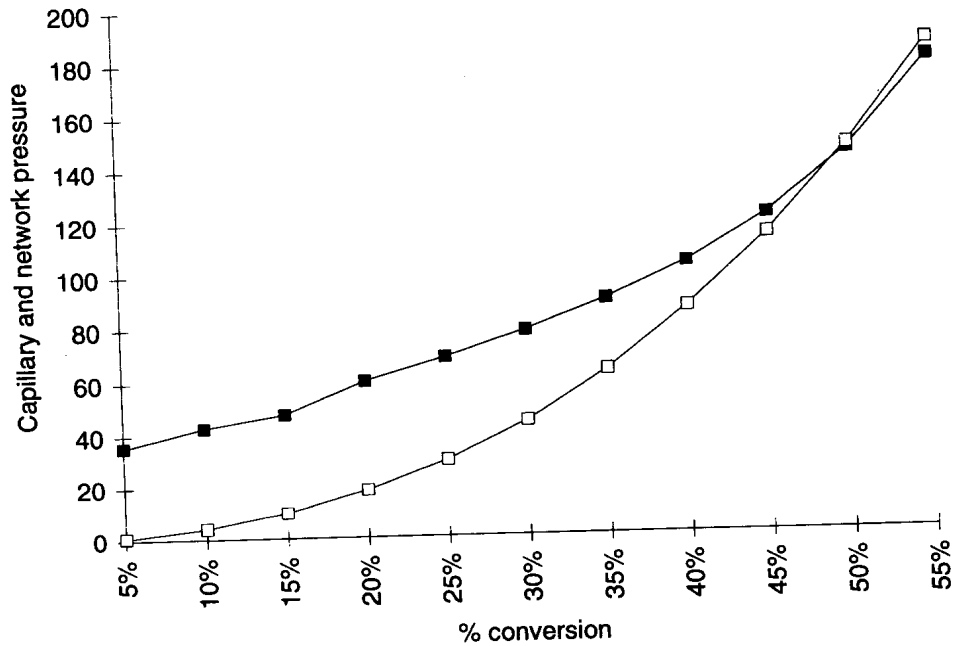

Figure 4: Capillary (■) and network (□) pressure (kPa) at 71°C. Modulus is chosen as 8 MPa.

volume fractions than this. Starting with the foam equation and using reasonable bulk modulus values, the network pressure appears to rise too slowly with volume fraction to produce freeze points at such conversion values. This agrees with the underestimation of the foam equation as ϕ approaches 1.

The chief value of the model is as a conceptual aid. Freeze occurs because of the balance between capillary forces and a network pressure. As temperature increases, the capillary forces weaken due to the (empirical) increase in primary particle size but the network pressure decreases even faster as the PVC gel rises further above its glass point and softens. Hence the freeze point occurs later and the final porosity decreases. Thus the control of porosity through reaction temperature occurs mainly through the mechanical properties of the gel.

As mentioned in the introduction, changing the temperature also changes the molecular weight of the product. In order to give independent control of the porosity, a second surfactant — the 'secondary granulating agent' — is added some time during the batch run. This addition acts to raise the porosity so that low molecular weight product can be made with a moderate-to-high porosity.

The role of this secondary granulating agent is apparently controversial. In our model, addition of surfactant acts to lower the interfacial tension at the water/VCM/PVC interface and so weakens the capillary forces. The network pressure thus can withstand the capillary pressure at lower volume fractions, freeze occurs earlier and the porosity rises. Thus the control of porosity through secondary granulating agent occurs mainly through the capillary forces.

Armed with such a picture, ICI is in a position to refine what we have done — a better treatment of the network modulus, data on the mechanical properties of PVC/VCM gel — as well as test the picture by further experiments. For example, if the secondary granulating agent is added too late, freeze would already have occurred so it should not affect the porosity. By varying the timing of addition of secondary granulating agent, inferences about the freeze point can be made.

Acknowledgements

References

A.G. Faraday, "Kinetic modelling of PVC polymerisations", (ICI Internal Report, 1992).

M.A. Field, "Prediction of optimum temperature profiles for vinyl chloride polymerisation using a mathematical model", (ICI Internal Report, 1973).

B.D. Hughes, *Random Walks and Random Environments, Vol. 2: Random Environments* (Oxford University Press, 1995, to appear).

C. Kiparissides, D.S. Achilas and E. Chatzi, "Dynamic simulation of primary particle-size distribution in vinyl chloride polymerization", *J. Applied Polymer Sci.* **54** (1994), 1423–1438.

P. Meakin, "Effects of cluster trajectories on cluster-cluster aggregation: A comparison of linear and Brownian trajectories in two- and three-dimensional simulations", *Phys. Rev. A* **29** (1984), 997–999.

J.K. Sears and J.R. Darby, *The Technology of Plasticizers* (Wiley, New York, 1982).

P.V. Smallwood, "The formation of grains of suspension poly(vinyl chloride)", *Polymer* **27** (1986), 1609–1618.

L.R. White, "Capillary rise in powders", *J. Colloid Interface Sci.* **90** (1982), 536–538.

T.Y. Xie, A.E. Hamielec, P.E. Wood and D.R. Woods, "Experimental investigation of vinyl chloride polymerization at high conversion: mechanism, kinetics and modelling", *Polymer* **32** (1991), 537–557.

Appendix 1

This calculation is a slight elaboration of one presented to the moderators by Peter McGowan.

Let the initial amount (mass) of VCM be M_0. Then at conversion x, there is an amount $M_0 x$ of PVC and an amount $M_0(1 - x)$ of VCM. Of this VCM, an amount $\eta M_0 x$ is dissolved in the PVC (here η is 0.3) leaving an amount $M_0(1 - x - \eta x)$ of free VCM.

Let the amount of PVC produced, per unit mass of VCM, be k_g in the gel and k_f in the free VCM (presumed constant). Then the fraction of new PVC

produced which is formed in the gel at conversion x is

$$\frac{k_g \eta x}{k_g \eta x + k_f(1 - x - \eta x)} = \frac{(k_g/k_f)\eta x}{1 - \alpha x}$$

where

$$\alpha = 1 + \eta - \frac{k_g}{k_f}\eta.$$

As the conversion goes from x to $x + dx$, the amount of new PVC is $M_0\, dx$ and so the amount of new PVC in the gel is

$$\frac{(k_g/k_f)\eta x}{1 - \alpha x} M_0\, dx.$$

Since the volume of the drop only grows due to the PVC being converted in the gel (gel growth), the fractional increase in the droplet volume is given by

$$\frac{dV}{V} = \frac{(k_g/k_f)\eta x}{1 - \alpha x} \frac{M_0\, dx}{M_0 x} = \frac{(k_g/k_f)\eta\, dx}{1 - \alpha x}.$$

This can be readily integrated with the freeze point as initial condition to give equation 1 in the text. It can easily be shown that it reduces to the expected expressions for the cases $k_g \rightarrow 0$ (coating growth only) and $k_f \rightarrow 0$ (gel growth only).