# Mathematical Modeling of the Porosity of Suspension Poly(vinyl chloride)

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*A mathematical model that describes the effect of conversion and polymerization temperature on the porosity of suspension poly(vinyl chloride) is proposed. The model considers that the packing of the primary particles that develop in the polymerizing drop begins at a conversion at which the particles become motionless. The model considers the morphology of the primary particles as a group of particles with a particular sphericity that form a network whose porosity decreases as conversion increases. Furthermore, the model considers the effect on porosity of the desorption of residual monomer and the difference in contraction and deformation between the pericellular membrane and the network of particles. The model contains three parameters that are estimated from data reported in the open literature. The agreement between experimental data and the theoretical predictions of the model are satisfactory.* *AIChE J,* 50: 3184–3194, 2004

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## Introduction

To a great extent, the usefulness of poly(vinyl chloride) (PVC) depends on a key feature of this material—its porosity. PVC can be used to manufacture a wide range of products such as pipes, bottles, and films, among many other applications, because it can absorb numerous different additives that make it suitable for diverse end-use applications. Furthermore, PVC can be made with different combinations of molecular weight, porosity, particle size distribution, and bulk density to match as much as possible the requirements of the end-use application.

The porosity of a specific PVC grade can also have significant impact on its processing and stripping, which has encouraged researchers to study in detail the complex physicochemical phenomena that occur along the polymerization of vinyl chloride monomer (VCM), leading to the development of porosity. Because the suspension process is by far the most common process for manufacturing PVC, many studies have collected abundant data and facts related to the phenomena involved in the development of the porosity of suspension-PVC (S-PVC). Through these, several variables have been found to have a significant influence on the development of porosity in S-PVC, that is, temperature of polymerization, conversion, agitation rate, and type and concentration of suspending agent (Johnson, 1980; Lewis and Johnson, 1981; Ormondroyd, 1988; Smallwood, 1986). Nevertheless, although extensive experimental work has been performed and abundant data is available, the mechanism by which porosity arises in S-PVC is not completely understood and only a few models have been proposed to explain and describe quantitatively the development of the final porosity of S-PVC (Kelsall and Maitland, 1983). The purpose of the present work is to propose a new model that predicts the effect of polymerization variables such as conversion and polymerization temperature on the final porosity of

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S-PVC. The model is based on a mechanism that intends to explain how different parameters such as conversion and polymerization temperature and simple morphological parameters interact to build the inner structure of S-PVC and thus its porosity.

## VCM Suspension Polymerization Overview

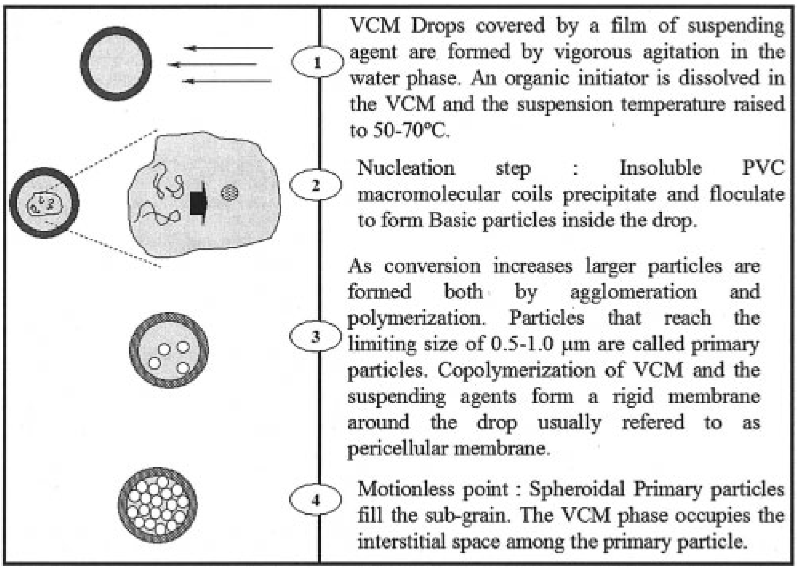
S-PVC is produced by blending VCM and water in an agitated reactor. The vigorous agitation of the mixture forms a suspension of VCM droplets in water that is stabilized by one or more suspending agents. The latter act by forming a film in the water/organic interface that lowers the interfacial tension, prevents excessive coalescence of the drops, and ultimately controls its size. An organic initiator or mixture of initiators that migrates to the VCM phase and distributes through the monomer drops is added to the suspension, which is then heated to the temperature required to attain the desired molecular weight of the S-PVC. Typical polymerization temperatures range from 50 to 70°C. At such temperatures the initiator decomposes at a rate given by its Arrhenius parameters and produces free radicals that trigger the polymerization of VCM. If some initiator remains dispersed in the aqueous phase, it will decompose progressively through the reaction time, but will have no significant influence on either the polymerization kinetics or the polymer final properties. Because this process occurs in each of the VCM droplets, suspension polymerization can be considered to occur in a legion of microreactors, one for each droplet. However, the initiator may not be distributed evenly among all the drops and therefore a certain distribution of conversion and properties among the PVC particles may occur. Unlike most polymers, PVC cannot be dissolved by its own monomer, although it can imbibe VCM. As a consequence, two phases are present in the bulk and in the suspension polymerization of VCM: a monomer phase, which consists mainly of VCM, and a polymer phase composed of PVC and VCM in thermodynamic equilibrium with the monomer phase. The weight fraction of PVC in the polymer phase in equilibrium with the monomer phase is a function of temperature. Because the initiator can be present in both phases, the polymerization of VCM occurs in the monomer phase and in the polymer phase according to a well-studied kinetic mechanism (Kiparissides et al., 1997).

The main reaction that generates dead polymer in the free-radical polymerization of VCM is that of transfer to monomer. Therefore, several PVC macromolecules are formed from each initial initiator radical. Not being soluble in its own monomer, PVC macromolecules precipitate, forming coils very close to each other, because the transfer reaction time is much shorter than the time it takes the macromolecules to diffuse away, according to calculations performed by several researchers (Rance and Zichy, 1981). As a consequence, the coils tend to flocculate and form so-called *basic particles*, with a diameter that has been estimated around 0.01–0.02 $\mu$m (Allsopp, 1981; Rance and Zichy, 1981). The latter step can be considered the nucleation step of a process of growth of PVC particles in each droplet both by agglomeration and by polymerization.

Further agglomeration of basic particles as polymerization proceeds forms larger particles, named *domains* or *granules*, whose size is between 0.1 and 0.2 $\mu$m. According to experimental evidence the process of particle agglomeration and growth within the VCM suspension drops ceases when particles reach a limiting size of 0.5–1.0 $\mu$m. These particles are usually called *primary particles*. At high conversions primary particles pack and interknit inside the polymerized drop, forming a structure with interstitial space that determines the porosity of the particle referred to as a *subgrain*. Several authors have studied and acknowledged the importance of the inner structure of the subgrains on the porosity of S-PVC. According to Allsopp (1981) the porosity of S-PVC is a measure of the interstitial space and the degree of porosity depends on how primary particles pack in the subgrain. He shows experimental evidence of the effect of temperature and agitation rate on porosity and remarks the fact that porosity decreases as conversion increases. The latter fact was observed experimentally by Zerfa and Brooks (1996) who, in a series of experiments, collected data that show how porosity decreases with conversion and suggest that the fusion of the primary particles in the subgrain, as well as its shrinking at high conversion, caused the observed decrease of porosity as conversion increases. Cebollada et al. (1989) also obtained data from pilot suspension polymerizations that show how porosity decreases with conversion and how porosity is affected by different suspension agents.

The influence of the partition coefficient of the suspending agent on porosity was previously proposed by several authors (Cheng, 1981; Cheng and Langsam, 1984; Nilsson et al., 1985; Sarkar and Archer, 1991). However, these theories explain only partially the effect on porosity of suspending agents that are not soluble in the organic phase, such as poly(vinyl alcohol)s (PVAs) of high degree of hydrolysis and some celluloses. Furthermore, this theory cannot explain the effect of suspending agents used as porosity promoters or porosizers that are not soluble in either phase, such as PVA of degree of hydrolysis in the range 40–60% (Törnell, 1988; Törnell and Uustalu, 1982). The effect of the latter suspending agents on S-PVC porosity and other properties was researched by Ormondroyd (1988) and Nilsson et al. (1985), among other investigators. Suspending agents and porosizers are also responsible for an important morphological feature of S-PVC, that is, a membrane that wraps S-PVC grains, usually called *pericellular membrane*. In addition to controlling the coalescence of the drops, suspending agents copolymerize in the interface of the drop, with VCM forming the pericellular membrane (Davidson and Witenhafer, 1980). This structure becomes stronger and more coherent as conversion increases by adsorbing more PVA from the aqueous phase, as discussed by Allsopp (1981) and observed experimentally by Zerfa and Brooks (1996). Both the concentration of the suspending agent and its chemical nature play a crucial role in the formation of the pericellular membrane and in the development of porosity (Ormondroyd, 1988; Sarkar and Archer, 1991).

Some studies have suggested that the interfacial activity of the suspending agent is closely related to the development of porosity in S-PVC and propose that high porosity is the result of lowering the contractional force generated by the interfacial tension, which tends to pack the particles more closely in the subgrain (Nilsson et al., 1985). Nilsson and co-workers acknowledge that, although suspension agents with high interfacial activity usually lead to high porosity S-PVC, these can affect other factors that also have influence on porosity, such as the attachment of PVC primary particles to the drop interface as well as the rheology of the interface and thus the shear rate



1 VCM Drops covered by a film of suspending agent are formed by vigorous agitation in the water phase. An organic initiator is dissolved in the VCM and the suspension temperature raised to 50-70°C.

2 Nucleation step : Insoluble PVC macromolecular coils precipitate and floculate to form Basic particles inside the drop.

3 As conversion increases larger particles are formed both by agglomeration and polymerization. Particles that reach the limiting size of 0.5-1.0 μm are called primary particles. Copolymerization of VCM and the suspending agents form a rigid membrane around the drop usually refered to as pericellular membrane.

4 Motionless point : Spheroidal Primary particles fill the sub-grain. The VCM phase occupies the interstitial space among the primary particle.

**Figure 1. Suspension PVC primary particle formation mechanism.**

within the droplet that would modify the coagulation of the primary particles. The concentration of suspending agent will control not only the porosity of the resin, but also the degree of drop protection provided initially to the suspension. Partially polymerized drops or subgrains may remain as individual units or agglomerate to form the components of the final S-PVC powder called *grains*. The following section is devoted to the proposal of a physical mechanism for the development of porosity in S-PVC, based on the evolution of the particulate structure of the S-PVC subgrains caused by polymerization.

## Grain Structure Formation Mechanism

The experimental evidence reviewed above allows us to reach three important conclusions regarding the suspension polymerization of VCM. First, spheroidal particles that reach a limiting size are generated in the droplet at low conversion. Next, these particles tend to fuse or interknit as conversion increases, forming a structure with interstitial space that determines the porosity of the subgrains. Finally, these particles are wrapped by a rigid membrane. Thus, early in the formation of the subgrain structure the polymer phase is formed by PVC particles that grow in number and in size up to a limiting diameter. This growth should reach a limit at a conversion such that all the drop volume is filled with polymer particles that constitute the polymer phase, whereas the monomer phase is totally contained in the interstitial pores of the primary particles. The stages of the transformation of the initial monomer droplet up to this point are shown in Figure 1. At this conversion, the packed primary particles are constrained by the pericellular membrane, and can therefore be considered motionless. When this event is reached the following condition holds

$$\frac{\varepsilon_0}{1+\varepsilon_0}\,\mathrm{VPVC}_m = \mathrm{VVCM}_m \tag{1}$$

where $\mathrm{VPVC}_m$ and $\mathrm{VVCM}_m$ are, respectively, the volumes of the PVC and VCM phases at the conversion, such that primary particles become motionless; and $\varepsilon_0$ is the porosity of the subgrain, defined as the ratio of the volume of the pores ($V_\phi$) among the primary particles to the total volume of the drop (particles and pores). If the volume of the particles is $V_p$, then

$$\varepsilon_0 = \frac{V_\phi}{V_\phi + V_p} \tag{2}$$

Because $X_f$, the weight fraction of polymer in the polymer phase in thermodynamic equilibrium with the VCM phase, is a function of temperature only and can be estimated by several independent correlations (Schmidt et al., 1994), the volume of the polymer phase, and therefore of the primary particles, is given by

$$\mathrm{VPVC}_m = \frac{X_m m}{X_f \rho_{f\mathrm{PVC}}} \tag{3}$$

where $m$ is the total mass of the subgrain, $X_m$ is the conversion at which primary particles become motionless (which will hereafter be referred to as *motionless point*), and $\rho_{f\mathrm{PVC}}$ is the density of the PVC phase.

On the other hand, the volume of the monomer phase is given by

$$\mathrm{VVCM}_m = \frac{m}{\rho_{\mathrm{VCM}}}\left(\frac{X_f - X_m}{X_f}\right) \tag{4}$$

where $\rho_{\mathrm{VCM}}$ is the density of the monomer phase. The conversion at which the motionless point is reached can be obtained by combining Eqs. 2, 3, and 4, as follows

$$X_m = \frac{X_f}{1 + \dfrac{\rho_{\mathrm{VCM}}}{\rho_{f\mathrm{PVC}}}\left(\dfrac{\varepsilon_0}{1-\varepsilon_0}\right)} \tag{5}$$

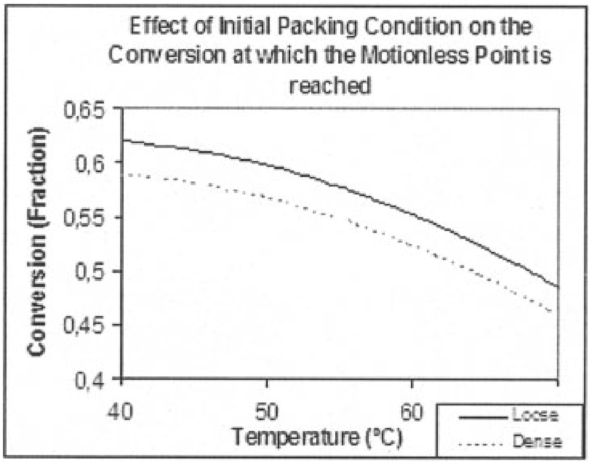


**Figure 2. Effect of the value of the initial packing condition (loose or dense) on the conversion at which primary particles cease their motion in the droplet at different temperatures.**

In Eq. 5, $X_f$ and the densities of the polymer and monomer phases are a function of temperature only. With respect to porosity $\varepsilon_0$, it has been established that packed spherical particles have a porosity that varies between 0.36 and 0.4, depending on its packing conditions, irrespective of size (Yu and Standish, 1991). Spherical particles with loose random packing have a porosity of 0.4, whereas densely random packed spheres have a porosity of 0.36. The packing porosity of nonspherical particles can be calculated from its sphericity $\psi$. The sphericity of a particle is a shape factor defined as the ratio of the surface area of a sphere having a volume identical to that of the particle to the actual surface area of the particle. Yu and Standish (1991) obtained the following equation that relates the porosity of nonspherical particles to its sphericity

$$\varepsilon_0(\psi, \alpha) = \alpha^{15.521\psi^{3.853} - 14.521\psi^{4.342}} \tag{6}$$

where $\alpha$ is the porosity of spherical particles at a given initial packing condition. Equation 5 shows that the packing of primary particles in the subgrain at the motionless point depends only on the initial packing condition, on the shape factor of the primary particles, and on temperature. Figure 2 depicts the effect of the initial packing condition on the motionless conversion in a wide range of polymerization temperatures. The looser the initial packing, the lower the conversion at which the motionless point is reached at constant temperature. Similarly, the lower the sphericity of the primary particles, the higher the conversion at which the motionless point is reached at constant temperature, as is seen in Figure 3. Nevertheless, the sphericity of the primary particles should be close to 1 according to electron microscopy photographs of S-PVC taken under different polymerization conditions, which show that subgrains are filled with nearly spherical particles (Allsopp, 1981; Smallwood, 1981).

As will be seen later, the conversion at which the motionless point is reached exerts a substantial influence on the final porosity of S-PVC.

## Effect of High Conversion on Porosity

Up to the motionless point, which according to Eq. 5 is reached at conversions that range from 0. 4 to 0. 62 depending on the polymerization temperature, the polymer phase gains mass and volume as PVC forms and VCM is absorbed by the polymer phase to keep the thermodynamic equilibrium between both phases. Beyond the motionless point, most of the polymer is produced in the polymer phase, that is, in the primary particles. If the inner subgrain structure remained identical to that of the motionless point at higher conversions, the primary particles formed up to that point would just increase their volume and so would both subgrains and grains, whereas the porosity would remain constant. Experimental evidence (Mariasi, 1986) shows that is not the case. S-PVC grains reach a maximum in size at conversions close to 0.1 and shrink slightly thereafter. Furthermore, scanning electron micrographs of sections of S-PVC particles taken at different conversions (Smallwood, 1981) show that primary particles interknit increasingly with conversion and that the higher the conversion, the lower the free space within the subgrain. This evidence allows us to deduce that the polymer formed beyond the motionless point fills the pores set at the motionless point and the porosity of the subgrains decreases as conversion increases, which is confirmed by experimental data (Cebollada et al., 1989; Zerfa and Brooks, 1996). The fact that primary particles interknit, forming a network instead of just growing as tangential spheres as polymerization increases, suggests that the pericellular membrane is strong enough to constrain the growth of the polymer phase and therefore that of the subgrain, although the pericellular membrane may deform as the subgrain shrinks.

At the motionless point the porosity of the subgrain is a function of the sphericity of the primary particles only, according to Eq. 6. That porosity will decrease as conversion increases and the new polymer fills the pores. Therefore, according to Eq. 2 the porosity $\varepsilon$ beyond the motionless point can be expressed as

$$\varepsilon = \frac{V_{\phi0} - V_p}{V_{\phi0} - V_p + V_{pt}} \tag{7}$$

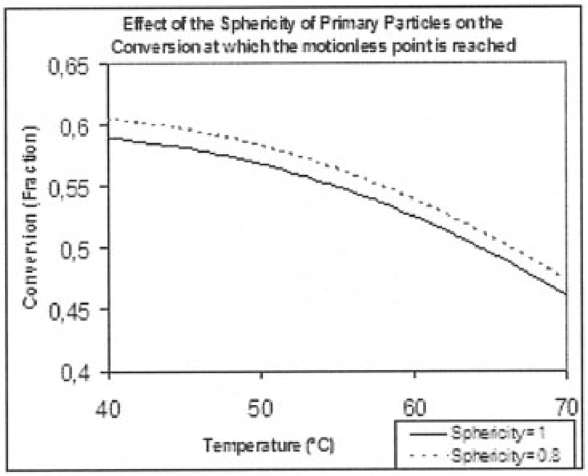


**Figure 3. Effect of the sphericity on the conversion at which primary particles cease their motion in the droplet at different temperatures.**

where $V_{\phi 0}$ is the volume of the pores at the motionless point, $V_p$ is the volume of the polymer phase formed between the motionless point and conversion $X$, and $V_{pt}$ is the overall volume of the polymer phase in the particle. According to Eq. 2, $V_{\phi 0}$ can be expressed as

$$V_{\phi 0} = \left(\frac{\varepsilon_0}{1 - \varepsilon_0}\right) V_{p0} \tag{8}$$

where $\varepsilon_0$ is the porosity of subgrains of mass $m$ and $V_{p0}$ is the volume of the polymer phase, both at the motionless point. It should be noticed that $\varepsilon_0$ is a function of both the sphericity of the primary particles and the initial packing condition $\alpha$. On the other hand, $V_p$ and $V_{p0}$ can be readily expressed as

$$V_p = \frac{(X - X_m)m}{X_f \rho_{f\mathrm{PVC}}} \tag{9}$$

and

$$V_{pt} = \frac{Xm}{X_f \rho_{f\mathrm{PVC}}} \tag{10}$$

If $V_{\phi 0}$, $V_p$, and $V_{pt}$ in Eq. 7 are replaced by Eqs. 8, 9, and 10, the following expression is obtained after simplifying

$$\varepsilon = 1 - \frac{(1 - \varepsilon_0) X}{X_m} \tag{11}$$

Equation 11 describes how the volume fraction of pores in the subgrain decreases as conversion increases from the motionless point at a given temperature.

The interknitting or fusion of the primary particles lasts while there are two phases. When the monomer phase depletes, the growth of the polymer phase stops and further polymerization only causes shrinkage of the whole subgrain structure while the volume fraction porosity of the subgrain remains constant. The depletion of the monomer phase occurs when the overall conversion $X$ equals the equilibrium polymer fraction $X_f$, or critical conversion. Therefore, Eq. 11 is valid only up to the critical conversion $X_f$. Beyond $X_f$, the volume fraction of pores remains constant, given that the whole structure only shrinks, and therefore all the geometrical proportions of the inner structure of the subgrain remain constant.

Although Eq. 11 describes how the volume fraction of pores in the subgrain behaves, it is an incomplete picture of the porosity of PVC. First of all, the porosity of PVC is usually measured as empty volume in the subgrain per unit mass, rather than as volume fraction. In addition to this, Eq. 11 does not consider the fact that the porosity of industrial interest is that resulting after stripping the resin of residual VCM. Finally, according to experimental evidence, the porosity of the subgrain is a consequence of not only the pores, but also of cracks in the structure formed by the primary particles (Smallwood, 1986).

## Effect of VCM Desorption and Pericellular Membrane Stiffness on Porosity

Despite the morphological importance of $\varepsilon$, the most important and applied definition of porosity in the PVC industry is

$$\phi = \frac{V_{emp}}{mp} \tag{12}$$

where $\phi$ is the empty volume of the particles per unit mass of PVC, $V_{emp}$ is the empty volume of the subgrain, and $m_p$ is the mass of the subgrain after the residual VCM is desorbed. It is important to remark that $V_{emp}$ and $V_\phi$ may be different. As residual VCM is desorbed, the polymer phase shrinks and the pericellular membrane may shrink, deform, or both, also experiencing a volume reduction. The same phenomenon occurs as conversion increases beyond the critical conversion $X_f$. However, the shrinkage experienced by the network of primary particles may not be equal to the reduction experienced by the volume contained in the pericellular membrane. This generates cracks in the network of primary particles with a volume that, if added to that of the pores, amounts to $V_{emp}$, the total empty space in the subgrain. Figure 4 illustrates this mechanism and shows the different volumes that should be considered to calculate $\phi$. The pericellular membrane envelope may experience a contraction because of shrinkage or deformation that ranges from a volume equal to that of the primary particles network after the residual VCM is stripped to no contraction at all. In the former case, that of maximal contraction, the volume of the primary particles network $V_{pp}$ at conversion $X < X_f$ can be expressed as

$$V_{pp} = \frac{mX}{\rho_{\mathrm{PVC}}(1 - \varepsilon)} \tag{13}$$

Combining Eqs. 13 and 11 yields

$$V_{pp} = \frac{mX_m}{\rho_{\mathrm{PVC}}(1 - \varepsilon_0)} \tag{14}$$

If no contraction at all is experienced by the pericellular membrane, its inner volume $V_s$ will equal that of the polymer phase at the motionless point, which remains constant until the critical conversion $X_f$ is reached. Therefore

$$V_S = \frac{mX_m}{X_f \rho_{f\mathrm{PVC}}(1 - \varepsilon_0)} \tag{15}$$

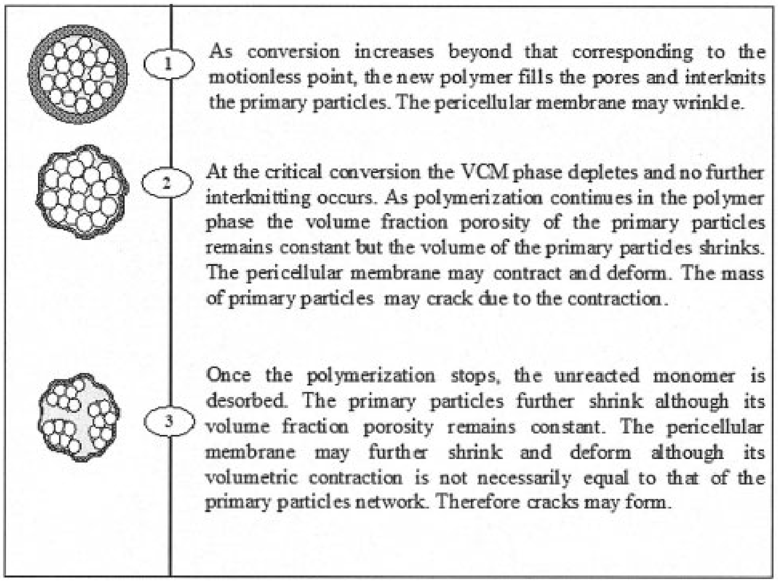
If $\lambda$ is the fraction of maximal possible contraction actually experienced by the pericellular membrane, then $V_{emp}$ can be expressed as

$$V_{emp} = V_S - \lambda(V_S - V_{pp}) - \frac{mX}{\rho_{\mathrm{PVC}}} \tag{16}$$

If $V_s$ and $V_{pp}$ are replaced by Eqs. 14 and 15, an expression for $\phi$ can be readily obtained

$$\phi = \frac{X_m}{X(1 - \varepsilon_0)}\left(\frac{1 - \lambda}{X_f \rho_{f\mathrm{PVC}}} + \frac{\lambda}{\rho_{\mathrm{PVC}}}\right) - \frac{1}{\rho_{\mathrm{PVC}}} \tag{17}$$

Equation 17 provides a relationship between the porosity of PVC based on weight and temperature and conversion. $\lambda$, the fraction of volume reduction of the pericellular membrane, accounts for the



1. As conversion increases beyond that corresponding to the motionless point, the new polymer fills the pores and interknits the primary particles. The pericellular membrane may wrinkle.

2. At the critical conversion the VCM phase depletes and no further interknitting occurs. As polymerization continues in the polymer phase the volume fraction porosity of the primary particles remains constant but the volume of the primary particles shrinks. The pericellular membrane may contract and deform. The mass of primary particles may crack due to the contraction.

3. Once the polymerization stops, the unreacted monomer is desorbed. The primary particles further shrink although its volume fraction porosity remains constant. The pericellular membrane may further shrink and deform although its volumetric contraction is not necessarily equal to that of the primary particles network. Therefore cracks may form.

**Figure 4. Suspension PVC particle formation mechanism.**

effect on porosity of the suspending agents and should be a function of variables such as polymerization temperature and chemical structure and concentration of the suspending agent. Equation 17 is valid only for conversions in the range $X_m$ to $X_f$, which are both a function of temperature. However, Eq. 17 can be extended to conversions greater than $X_f$.

According to the mechanism proposed above, at conversions higher than $X_f$, the volume fraction porosity of the primary particles network remains constant. Therefore $V_{pp}$ can be expressed as

$$V_{pp} = \frac{mX}{\rho_{\mathrm{PVC}}(1 - \varepsilon_{Xf})} \qquad X > X_f \tag{18}$$

where $\varepsilon_{Xf}$ is the value of $\varepsilon$ at conversion $X_f$. Substituting $\varepsilon$ by its value according to Eq. 11 results in the following expression

$$V_{pp} = \frac{mXX_m}{\rho_{\mathrm{PVC}}(1 - \varepsilon_0)X_f} \qquad X > X_f \tag{19}$$

Because $V_s$ remains constant at any conversion, $\phi$ can be expressed for conversions higher than $X_f$ as

$$\phi = \frac{V_s - \lambda(V_s - V_{pp}) - \dfrac{mX}{\rho_{\mathrm{PVC}}}}{mX} \qquad X > X_f \tag{20}$$

If Eqs. 18 and 19 are substituted in Eq. 20 the following expression is obtained

$$\phi = \frac{X_m(1 - \lambda)}{XX_f\rho_{f\mathrm{PVC}}(1 - \varepsilon_0)} + \frac{\lambda XX_m}{XX_f\rho_{\mathrm{PVC}}(1 - \varepsilon_0)} - \frac{1}{\rho_{\mathrm{PVC}}} \qquad X > X_f \tag{21}$$

Equations 17 and 21 provide a mathematical function that relates the porosity of S-PVC to conversion and temperature of polymerization. These equations contain three unknown parameters: $\lambda$, the contraction factor of the pericellular membrane; $\psi$, the sphericity of the primary particles; and $\alpha$, the initial packing condition. Previous experimental data provide information that allows the supposition that the sphericity of primary particles is close to 1, whereas the initial packing condition is a value between 0.36 and 0.4. With respect to $\lambda$, there is no way to calculate it theoretically and therefore the value should be estimated from experimental data.

## Parameter Estimation

The equations obtained above that relate the porosity per unit mass of PVC to polymerization temperature and conversion can be summarized as

$$\phi(T, X) = \begin{cases} \phi = \left[\dfrac{X_m}{X(1 - \varepsilon_0)}\left(\dfrac{1 - \lambda}{X_f\rho_{f\mathrm{PVC}}} + \dfrac{\lambda}{\rho_{\mathrm{PVC}}}\right) - \dfrac{1}{\rho_{\mathrm{PVC}}}\right]1000 & X < X_{f(t)} \\ \phi = \left[\dfrac{X_m(1 - \lambda)}{XX_f\rho_{f\mathrm{PVC}}(1 - \varepsilon_0)} + \dfrac{\lambda XX_m}{XX_f\rho_{\mathrm{PVC}}(1 - \varepsilon_0)} - \dfrac{1}{\rho_{\mathrm{PVC}}}\right]1000 & X > X_{f(T)} \end{cases} \tag{22}$$

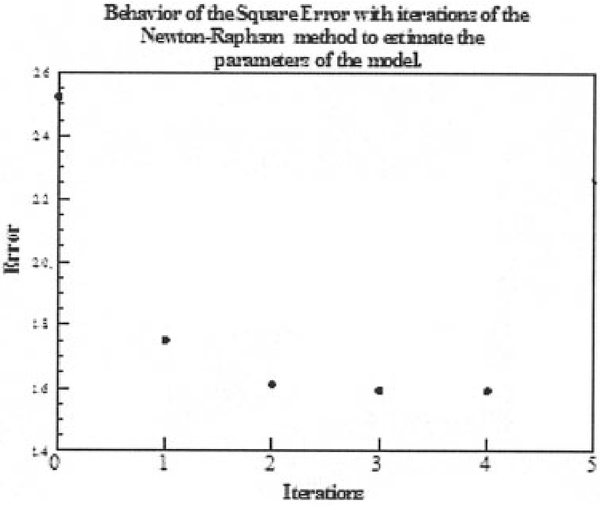


**Figure 5. Variation of square error with number of iterations of the Newton–Raphson method to adjust the model parameters.**

where $\psi$ and $\alpha$ are unknown parameters and $\lambda$ is a function of temperature, suspension agent chemical composition, and concentration. To estimate these parameters the following approach was followed. Data containing S-PVC porosity results and polymerization conditions, from several researchers, were collected and used together to estimate the values of the model parameters. $\lambda$ was assumed to be a linear function of temperature

$$\lambda = aT + b \tag{23}$$

because many suspending agents and interfacial properties are known to depend on temperature. However, the parameters $a$ and $b$ may be a complex function of the properties and concentration of the suspending agent and other variables of the system such as agitation speed.

Because $\alpha$ belongs to a narrow range (0.36–0.4), it was assigned a value of 0.38. The square error function, with a penalty factor to avoid negative values of porosity, was set as

$$E(\vec{p}) = \sum_{i=1}^{n} \{\phi(\vec{p}) - x_i + K \exp[\phi(\vec{p})]\}^2 \tag{24}$$

where $\vec{p}$ is a column vector defined as $(\vec{p})^T = (\psi, a, b)$, $K$ is a weight factor, $n$ is the number of experimental data taken from the literature, and $x_i$ are the experimental values. $E(\vec{p})$ was minimized with the Newton–Raphson method. Initial estimates were obtained visually and set to the following values : $\psi = 1$, $a = 0.028$, $b = -0.9$. Figure 5 shows how the square error decreased as the number of iterations increased until it reached a steady value. The final parameter values obtained were $\psi = 0.97$, $a = 0.015$, $b = -0.11$. The sphericity value reached is very close to 1, which agrees with the spherical shape of primary particles experimentally observed. There are two general features of the porosity of S-PVC widely observed in practice: that it decreases with conversion and that it decreases (at equivalent conversions) as polymerization temperature increases. The model, tested for these two phenomena by comparing its behavior against the data collected previously, was found to be satisfactory, as shown in Figure 6. The curves in Figure 6 represent the evolution of porosity according to the model proposed in this work at different temperatures, which agree with the behavior seen in practice (Allsopp, 1981). The change in slope of the curves occurs as a result of the change in polymerization rate that takes place when the monomer phase depletes.

Figures 7 and 8 compare the results of the model against experimental data reported by Cebollada et al. (1989). In Figure 7 the model follows closely the behavior of the experimental data, including the change in slope at high conversion when the monomer phase depletion occurs. In Figure 8 the theoretical curve obtained goes through the cluster of data taken at the same conversion with different suspension systems, which reflects the fact that the porosity can be significantly modified by the suspension agents and its concentrations, whose effect is not included totally in the model proposed.

Figures 9 and 10 compare the model with data obtained by Sarkar and Archer (1991) at polymerization temperatures of 65 and 55°C, respectively. All the data were taken at a fractional conversion of 0.7 (Sarkar and Archer, 1991). The model adequately follows the experimental data, which again shows dispersion attributed to the differences in suspension systems used in the polymerization experiments.

Smallwood (1986) reported S-PVC porosity values obtained at different temperatures and a conversion of 0.85 with different suspension systems and agitation speeds. Figure 11 depicts a curve of S-PVC porosity vs. temperature according to the model and the experimental data of Smallwood. The model closely follows the trend of the data with temperature, despite the dispersion that is caused by the different conditions under which they were obtained.

Data of Cheng (1981), obtained at 60°C with different suspension conditions, were also contrasted against the model in Figure 12 with similar results to those previously obtained. The model agrees closely with most of the data, which show considerable dispersion as a consequence of the different suspension conditions used in the experiments.

Finally, in Figure 13 data reported by Zerfa and Brooks

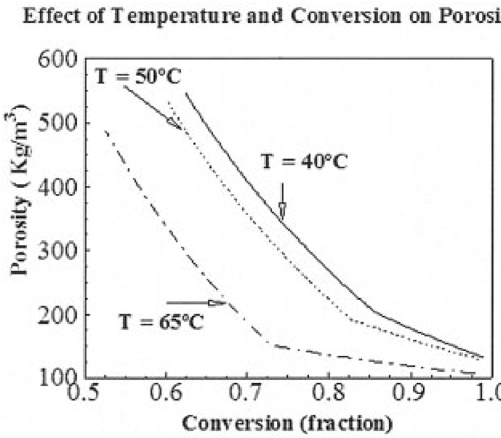


**Figure 6. Effect of conversion and polymerization temperature of suspension PVC on porosity.**

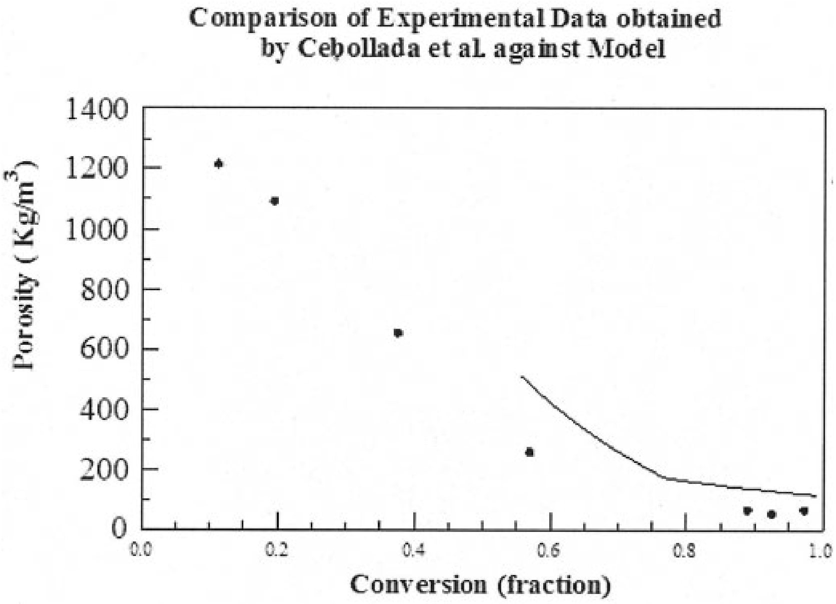


**Figure 7.** **Comparison of model (—) against experimental data (●) reported by Cebollada et al. (1989), expressed as kg/m$^3$ and obtained at a polymerization temperature of 60°C under similar reaction conditions at different conversions.**

(1996) are used to assess the model against experimental information. These results allow us to visualize the effect of conversion on the porosity of S-PVC at 55°C under similar suspension conditions. Again, the model closely follows the experimental results within its range of validity, although there is high dispersion of experimental results that is seen, particularly among the low polymerization temperature data, which may be a consequence of the effect of the suspension agents used or of the dispersion of porosity, which normally is very wide.

Although the effect of suspension agents on the porosity of PVC is a well-established fact (Allsopp, 1981; Smallwood, 1986) the model presented does not account for it at its present stage. However, by fitting the model to experimental data obtained with identical suspension systems, as is usually the case in industrial operation for the production of specific grades, a good prediction of porosity, as is shown in Figures 14 and 15, can be obtained as a function of conversion and temperature. In practice the latter variables can show variability because of different operation conditions and the model presented can be readily used to estimate and understand the expected amount of variation in porosity.

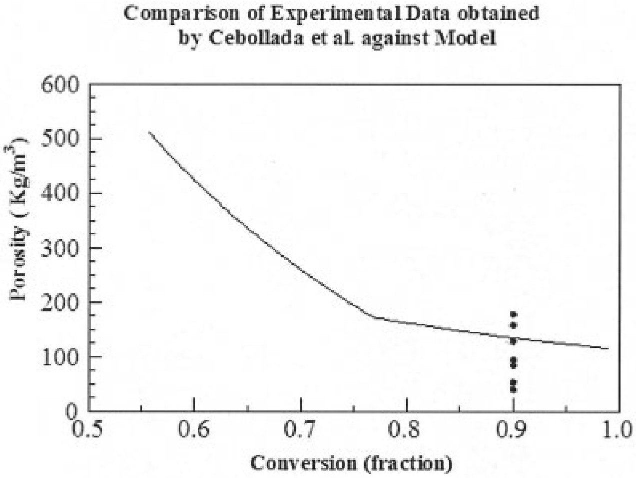


**Figure 8.** **Comparison of model (—) against experimental data (●) reported by Cebollada et al. (1989), expressed as kg/m$^3$ and obtained at a polymerization temperature of 60°C and a conversion of 90% with different suspension systems.**

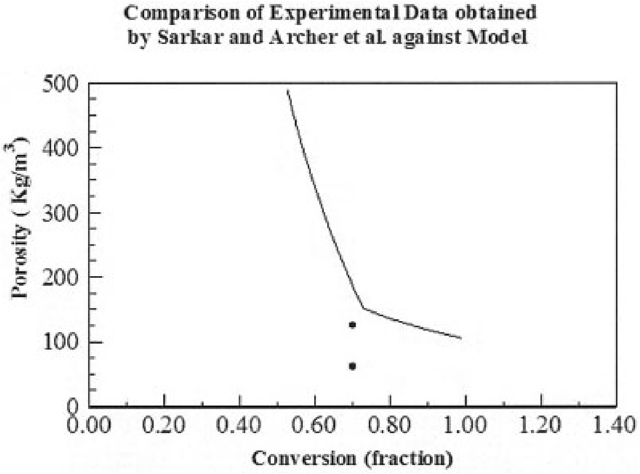


**Figure 9.** **Comparison of model (—) against experimental data (●) reported by Sarkar and Archer (1991), expressed as kg/m$^3$ and obtained at a polymerization temperature of 65°C and a conversion of 70% with different suspension systems.**

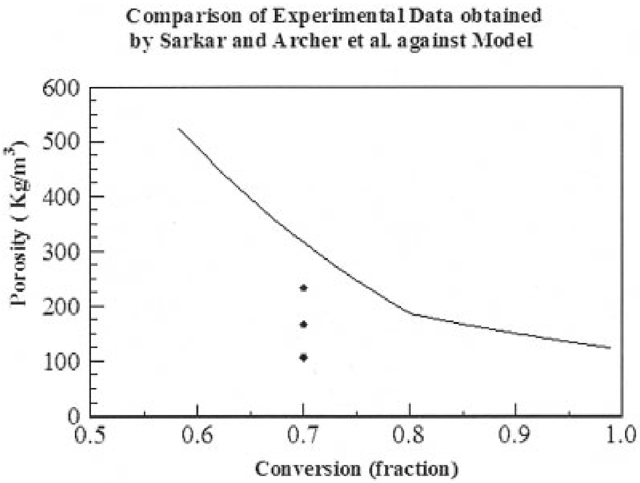


**Figure 10. Comparison of model (—) against experimental data (●) reported by Sarkar and Archer (1991), expressed as kg/m$^3$ and obtained at a polymerization temperature of 55°C and a conversion of 70% with different suspension systems.**

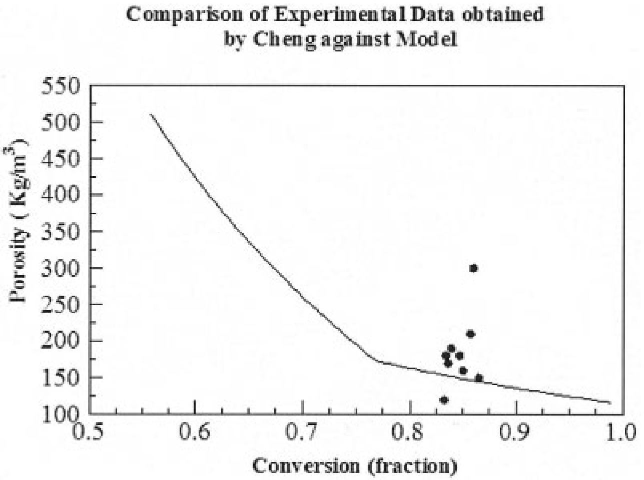


**Figure 12. Comparison of model (—) against experimental data (●) reported by Cheng (1981), expressed as kg/m$^3$ and obtained at a polymerization temperatures of 60°C at conversions close to 85% with different suspension systems and agitation speeds.**

## Conclusions

The effect of polymerization temperature and conversion on the porosity of S-PVC was modeled with an equation obtained from the morphological features of the primary particles and the pericellular membrane. The model does not account for either the uneven distribution of initiator among the monomer drops or differences in thermal history of the latter. Therefore, after its parameters are adjusted, it accounts for the mean porosity achieved by the population of particles. The model was built on the concept of motionless point or conversion at which the primary particles stop moving inside the polymerizing droplet. Furthermore, this point can be calculated from the porosity of groups of particles with known sphericity. The model considers the difference in contraction between the pericellular membrane and the network of particles attributed to polymerization and residual VCM desorption. According to the model, this difference can have a significant influence in the final porosity of the resin. The model contains three parameters, two of which are related to the capacity of contraction and deformation of the pericellular membrane and depend on the temperature, the physicochemical properties of the suspending agents, its concentration, and the hydrodynamics of the reactor. The third parameter is related to the initial packing condition of the primary particles at the motionless point. Average, typical

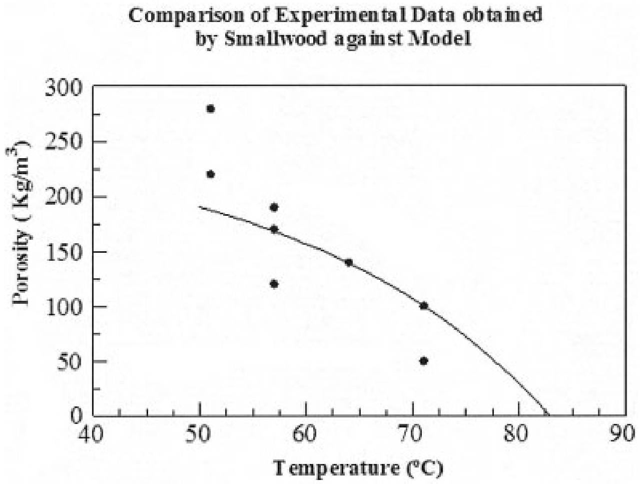


**Figure 11. Comparison of model (—) against experimental data (●) reported by Smallwood (1986), expressed as kg/m$^3$ and obtained at various polymerization temperatures at a conversion of 85% with different suspension systems and agitation speeds.**

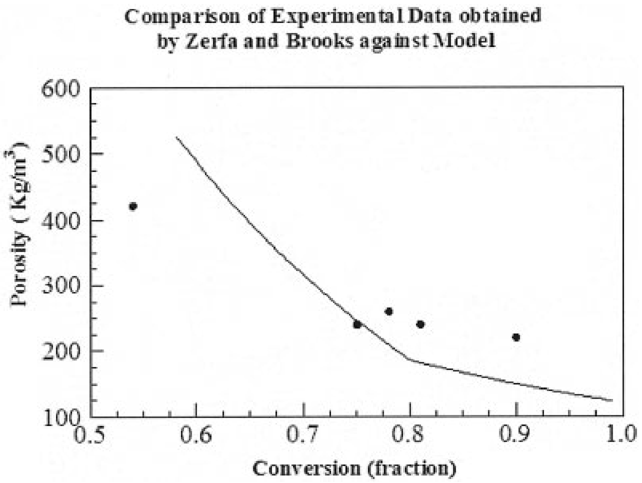


**Figure 13. Comparison of model (—) against experimental data (●) reported by Zerfa and Brooks (1996), expressed as kg/m$^3$ and obtained at a polymerization temperature of 55°C with similar suspension conditions.**

values for all the parameters were estimated from different experimental data from the open literature.

With these parameters the effect of conversion and polymerization temperature predicted by the model was compared to the trends of the experimental data. The agreement was satisfactory, considering the diversity of suspension systems and experimental conditions used by the different researchers that were considered. Furthermore, a better fit would have been obtained if the parameters had been adjusted for individual sets of experimental data because the number of experimental points is usually small. However, this would not have been representative of the general trend of the effect of conversion and polymerization on porosity and how the model accounts for it.

## Acknowledgments

This work is dedicated to the memory of our colleague and friend Neil González.

## Notation

$a$, $b$ = empirical parameters used to relate $\lambda$ to temperature
$m$ = total mass of a subgrain
$m_p$ = mass of the subgrain after residual VCM is desorbed
$T$ = temperature
$V_{emp}$ = empty volume of particles per unit mass of PVC
$V_p$ = volume of particles in a subgrain
$V_{po}$ = volume of polymer phase at the motionless point
$V_{pp}$ = volume of primary particles network
$V_{pt}$ = overall volume of polymer phase in a particle
$VPVC_m$ = volume of PVC phase
$V_s$ = inner volume of subgrains if no contraction at all is experienced by the pericellular membrane
$V_{\phi}$ = volume of pores among primary particles
$V_{\phi}$ = volume of pores at motionless point
$VVCM_m$ = volume of VCM phase
$X$ = conversion
$X_f$ = weight fraction of polymer in the polymer phase in thermodynamic equilibrium with the VCM phase
$X_m$ = conversion at which primary particles in a subgrain become motionless

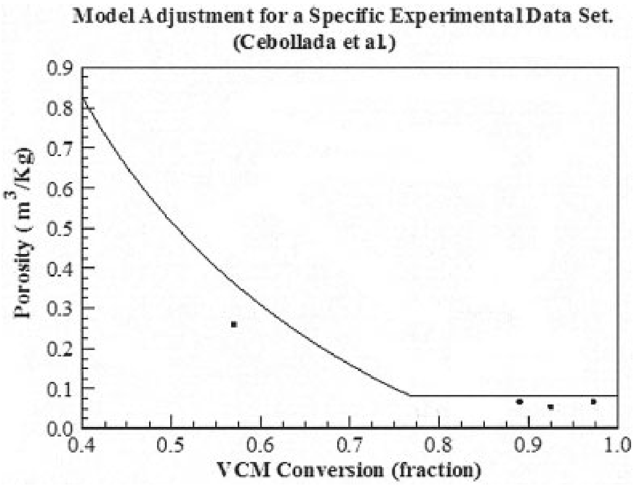


**Figure 14. Comparison of model (—) against experimental data (●) reported by Cebollada et al. (1989), expressed as kg/m$^3$ and obtained at a polymerization temperature of 60°C.**

The parameters were adjusted for this specific data set.

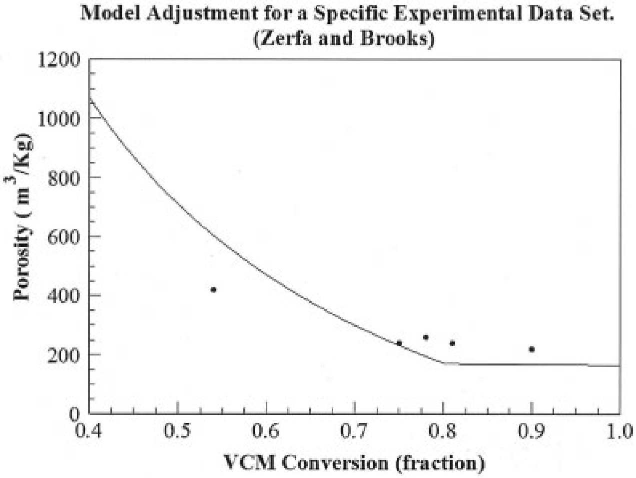


**Figure 15. Comparison of model (—) against experimental data (●) reported by Zerfa and Brooks (1996), expressed as kg/m$^3$ and obtained at a polymerization temperature of 55°C.**

The parameters were adjusted for this specific data set.

### *Greek letters*

$\alpha$ = porosity of spherical particles at a given initial packing condition
$\varepsilon$ = porosity expressed as volume fraction
$\varepsilon_o$ = porosity of subgrain expressed as volume fraction at motionless point
$\varepsilon_{Xf}$ = value of $\varepsilon$ at conversion $X_f$
$\rho_{fPVC}$ = density of the PVC phase
$\rho_{PVC}$ = density of the PVC phase
$\rho_{VCM}$ = density of the monomer phase
$\lambda$ = fraction of maximal possible contraction actually experienced by the pericellular membrane
$\phi$ = porosity of subgrains expressed as volume per unit mass
$\psi$ = sphericity

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