Diffusion of Residual Monomer in Polymer Resins

by Warren T. Piver*

A simplified mathematical model which made use of Fick's laws of diffusion written in spherical coordinates was developed to describe the rate of diffusion of residual monomers from polymer resins. The properties of the monomer–polymer system which influenced the amount of monomer remaining in the polymer as a function of time were the diffusivity and solubility of the monomer in the polymer, and the particle size of the polymer resin. This model was used to analyze literature data on the diffusion of residual vinyl chloride monomer in polyvinyl chloride resins made by the suspension process.

It was concluded that particle size of the resin was a significant parameter which should be taken advantage of in process equipment designed to remove residual monomer from PVC resins. The diffusivity of the monomer in the polymer was a function of the solubility of the monomer in the polymer. Monomer solubility can be determined from Henry's law. It was suggested that this model could be adapted to describe diffusion of monomers from any monomer–polymer system, and would be a useful approach to modeling the transport of nonreactive chemical additives from plastics.

Introduction

The worldwide rate of growth of the synthetic polymer industry over the last three decades has been extraordinary. While other chemical industries have required 10 to 15 years to double their production output, the synthetic polymer industry has doubled its production capacity on the average of every five years since 1955.

To put the question of the size of the polymer industry into perspective, Table 1 presents U.S. production figures for 1974 for thermosetting and thermoplastic resins (1). Included with each resin type are the monomers from which these polymer resins are derived. In Table 1, the resins are ranked by production volume. It is interesting to note that most of the monomers and polymers in this table are derived from ethylene and propylene. Ethylene, ethylene glycol, vinyl chloride, vinylidene chloride, styrene, vinyl acetate, vinyl alcohol, and tetrafluorethylene all start from ethylene. Propylene, glycerol, epichlorohydrin, many polyglycols, acrylonitrile, acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, and methyl methacrylate all start from propylene. These

observations are significant from the standpoint that the growth of the polymer industry is very much a function of the availability of these two basic petrochemical feedstocks.

Several of the monomers used to make these synthetic polymer resins have been shown to have severe, acute, and chronic toxicity. Therefore, how much of the monomer remains within the polymer resin after polymerization is complete and how rapidly this residual monomer leaves the resin particle become important occupational and environmental exposure questions.

Diffusion Model Development

With this brief introductory identification of major resins and their monomers, a simple mathematical model which simulates the transport, or migration of unreacted, or residual monomer from the monomer-polymer system will be developed. The purposes of this simulation process are to identify the predominant modes of mass transfer and to identify those physical-chemical properties of this system which influence the rate of migration. The basic outline is to start from general considerations about diffusion in polymers and work toward a specific example which illustrates how these general considerations can be applied to real

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Resin/monomer (s)	Production volume, lb $\times 10^{-6}$
Polyethylene (low density)/ethylene	6030
PVC and copolymers/vinyl chloride, vinylidene chloride	4744
Polystyrene/styrene	4050
Polyethylene (high density)/ethylene	2799
Polypropylene/propylene	2249
Urethanes/toluene diisocyanate, polyethers, polyesters	1674
Phenolics/phenols, aldehydes	1598
Urea and melamine/urea-formaldehyde, melamine-formaldehyde	1236
Polyesters/terephthalic acid, ethylene glycol	944
ABS/acrylonitrile–butadiene–styrene	898
Acrylics/acrylonitrile, acrylic acid, methacrylic acid, esters of these acids	890
Alkyds/phthalic anhydride, ethylene glycol, glycerol, styrene	726
Poly(vinyl acetate)/vinyl acetate	543
Epoxies/epichlorohydrin, bisphenol A, glycerol, epoxidized polyolefins	312
Cellulosics/cellulose acetate, nitrocellulose, carboxymethylcellulose	224
Nylon type polyamides/hexamethylenediamine, adipic acids	173
Poly(vinyl alcohol)/vinyl alcohol	141
SAN/styrene–acrylonitrile	111
Polytetrafluoroethylene/tetrafluoroethylene	18

[a] Data from U.S. International Trade Commission Report, 1974 (1).

systems. It should be noted that the development of this model and the data to be used come from the work of Berens (2, 3). The rationale for presenting this work is to show how these considerations on diffusion in polymers can serve as a starting point for understanding diffusion of monomers in thermoplastic and thermosetting resins, and for diffusion of chemical additives in plastics. With this foundation, the occupational health problems associated with diffusion of residual monomers from polymers into the workplace atmosphere, and the migration of plastic additives from plastic products into contacting fluids, become more understandable.

The transport or diffusion of residual monomer from the monomer-polymer system can be described by Fick's laws of diffusion and an equilibrium relationship describing the concentration of the monomer in the polymer.

Two properties of this system which have an obvious influence on the diffusion rate are the diffusivity and solubility of the monomer in the polymer. In the monomer–polymer system, a third property, particle size of the resin, has a pronounced influence on how much residual monomer remains in the polymer as a function of time.

In vector notation, Fick's first law of diffusion is given as:

$$J_M = -\bar{D}_{M\text{-}P} \vec{\nabla} C_M \qquad (1)$$

where J_M is the mass flux of monomer (in g/cm²/sec) ; $\bar{D}_{M\text{-}P}$ is the average value of the diffusivity of the monomer in the polymer (in cm²/sec) ; and ∇C_M is the gradient of monomer concentration (in g/cm³/cm). Considering mass flow in a volumetric element of a polymer resin particle and assuming no chemical reaction is occurring, the time-dependent mass balance for this element gives Fick's second law of diffusion as:

$$\partial C_M / \partial t = -\underline{\vec{\nabla}} J_M \qquad (2)$$

$$\partial C_M / \partial t = \bar{D}_{M\text{-}P} \underline{\vec{\nabla}}^2 C_M \qquad (3)$$

In Figure 1, it is assumed that the shape of the polymer resin is spherical and that diffu-
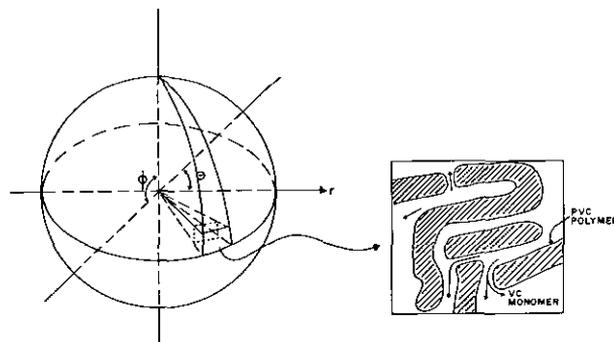
FIGURE 1. Spherical PVC resin particle showing volumetric element and microscopic view of cross section through element.

sion is mainly in a radial direction. For thermoplastic resins with a low glass content, this is a reasonable approximation to resin geometry and to the mode of monomer transport in the resin. The assumption of unidirectional flow is a good first approximation for these conditions. Making these assumptions, the rate of mass transfer of residual monomer in spherical coordinates is given by eq. (4)

$$\frac{\partial C_M}{\partial t} = \frac{\overline{D}_{M\text{-}P}}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial C_M}{\partial r}\right)\right] \qquad (4)$$

Crank (4) has solved this expression for the boundary conditions: the concentration of monomer at the outside surface of the resin particle is constant; and the initial distribution of monomer in the polymer resin is given as a function of radial position. Using these boundary conditions, the ratio of the monomer remaining in the resin at a time greater than zero, to the total amount of monomer in the resin at time equal to zero is given as eq. (5)

$$\frac{C_{MT}}{C_{Mo}} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{\frac{-4\overline{D}_{M\text{-}P}n^2\pi^2 t}{\overline{d}_R^{\,2}}\right\} \qquad (5)$$

where $\overline{d}_R$ is the average particle diameter. Since polymer resins can have a wide variation in particle size, this result can be extended to include the total amount of monomer diffusing from a polymer resin made up of a spectrum of different particle sizes as follows:

$$\frac{C_{Mt}}{C_{Mo}} = 1 - \frac{6}{\pi^2}\sum_{i=1}^{m}X_i\left[\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{\frac{-4\overline{D}_{M\text{-}P}n^2\pi^2 t}{\overline{d}_{Ri}^{\,2}}\right\}\right]$$

where $\qquad\qquad\qquad\qquad\qquad\qquad (6)$

$$\sum_{i=1}^{m}X_i = 1$$

and $\overline{d}_{Ri}$ is the average particle diameter of the resin particles which have size fraction X_i Figures 2 and 3 illustrate how the concentration of monomer remaining in the polymer resin changes with time for different individual
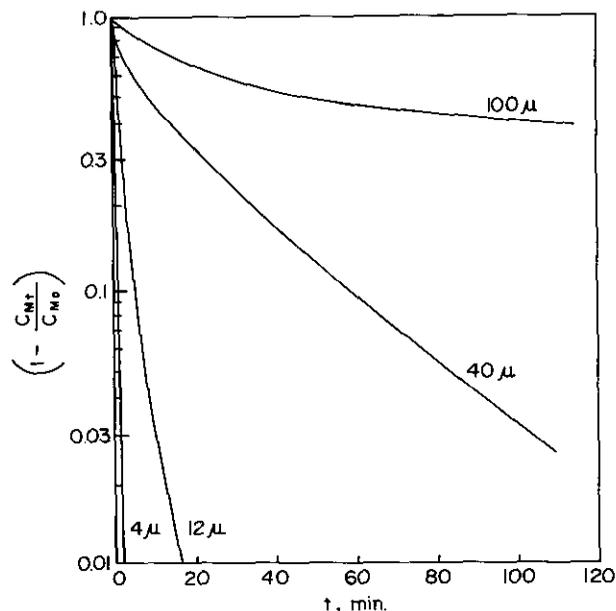

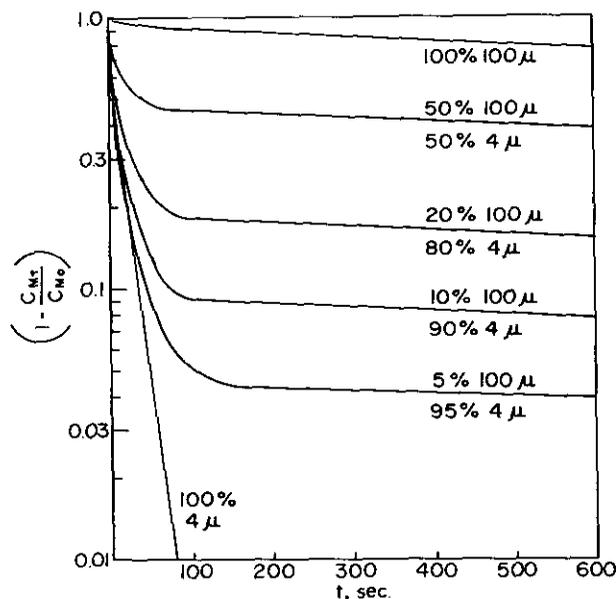FIGURE 2. Calculated $1 - (C_{M,t}/C_{M,o})$ vs. t curves for uniform particles, $D = 2 \times 10^{-10}$ cm²/sec.

FIGURE 3. Calculated $1 - (C_{M,t}/C_{M,o})$ vs. t curves for uniform particles and mixtures, $D = 2 \times 10^{-10}$ cm²/sec.

particle sizes and for mixtures of different particle sizes. In both plots, the diffusivity is held constant at 2×10^{-10} cm²/sec. For the

diffusion of gases in solids, this is a reasonable value for the diffusivity at moderate temperatures.

These two plots illustrate how particle size of the resin influences the kinetics of mass transfer of residual monomer from polymer resins when the diffusivity is held constant and the glass content of the polymer is very low. In Figure 2, for the 4 μm particles, within 2 min, 99.99% of the initial monomer concentration has migrated from the polymer resin. For the 100 μm particle, after 2 hr, the concentration has dropped to 40% of the original concentration. It is estimated that 20 hr will be required for the concentration to drop to 99.99% of the original concentration for the 100 μm particles. This demonstrates that the intrinsic rate of diffusion is the same regardless of particle diameter. However, the amount of monomer in the larger particle is greater than in the smaller particles. Therefore, it requires a greater time to remove a particular percentage of monomer from the larger particle sizes. This observation is of major significance and will be used in the subsequent discussion.

In Figure 3, the influence of particle size on the kinetics of diffusion is demonstrated for mixtures of particles. Again, it is significant to note how the larger 100 μm particles dominate the diffusion kinetics of monomer transport at a given temperature.

As was stated earlier, the transport of monomer from the monomer–polymer system is dependent on the solubility and diffusivity of the monomer in the polymer. Therefore, this portion of the model development will conclude with how these two quantities can be determined experimentally. Henry's law, which is derived from the more general Gibbs-Duhem equation describing multicomponent phase equilibria, defines the solubility of the monomer in the polymer as:

$$C_M = SP_v \qquad (7)$$

where P_v is the vapor pressure of the monomer (in atm), S is the solubility constant (in g/cm³ atm), and C_M is the concentration of the monomer dissolved in the polymer (in g/cm³).

A modified form of Fick's law has been used to study the diffusion of gases in polymeric films (5). This modified form of Fick's law relates the mass flux of the gas through the polymer structure to the solubility of the monomer in the polymer, the diffusivity of the monomer in the polymer, and the pressure drop across the polymer structure as:

$$J_M = \overline{D}_{M-P} S \left(\Delta P / L \right) \qquad (8)$$

where $\Delta P/L$ is the pressure drop (in atm/cm). Rearranging eg. (8) provides an experimental method of determining the diffusivity as follows:

$$\overline{D}_{M-P} = J_M / S \left(\Delta P / L \right)^{-1} \qquad (9)$$

Whereas the method developed by Barrer (5) is applicable for determining diffusivities in polymeric films, Berens (3) has developed a method for determining the diffusivities of monomers in polymer resins. The diffusivity is determined from the diffusion equation in spherical coordinates. In this method, the time at which $C_{M,t}/C_{M,o}$ is equal to 0.5 is measured experimentally for diffusion of monomer from a particular particle size resin. By using this information, the diffusivity is given by eq. (10):

$$\overline{D}_{M-P} = 7.6 \times 10^{-3} \overline{d}_R^2 / t_{1/2} \qquad (10)$$

where d_R is in centimeters and $t_{1/2}$ is the time in seconds at which $C_{M,t}/C_{M,o} = 0.5$. The two methods of determining diffusivity should yield similar results since a polymer film is composed of an array of resin particles.

Application of Model to Diffusion of Vinyl Chloride in Poly(vinyl Chloride)

At this point, it is important to ask, what is the utility of this analysis and does it have any practical applications? To answer these questions, a specific example of a monomer–polymer system will be used, namely, the vinyl chloride —PVC system. The reasons for the selection of this particular system are: there are considerable physio-chemical data on this system (2, 3); vinyl chloride has been linked with cancer of the liver (6, 7) and other clinical disorders in PVC workers (8–12); OSHA has set a work-

place concentration standard of 1 ppm for vinyl chloride (13); EPA has promulgated (14) an air emission level for vinyl chloride from PVC manufacturing plants; and a number of methods have been proposed to reduce air emissions from PVC manufacturing plants (14–16).

PVC resins are made commercially by two important processes, the suspension process and the dispersion or emulsion process. The suspension process accounts for about 80% of the total production and the dispersion process about 13%. Figure 4 shows a flowchart for the suspension process. Vinyl chloride alone or in combination with comonomers such as vinylidene chloride and vinyl bromide are fed into the weigh tanks. These measured streams are fed into a batch reactor alone with a polymerization initiator, suspending agent and surface active chemicals. Reaction proceeds until the desired average molecular weight of the poly-

mer resin is achieved. Normally, conversion of vinyl chloride to PVC is between 83 and 90%. The gas-phase vinyl chloride remaining after polymerization is recovered in the stripper and recycled, but the small amounts remaining in the slurry and in the polymer have not been removed in the past. From the stripper, the PVC slurry is pumped to a blend tank which holds three to five batches of resins, and then to a rotary drier. The dried product then is fed to holding bins where it is either bagged or sent to a storage silo for bulk shipping. The polymer resins produced by this process have a wide size distribution (5–300 μm). Table 2 was compiled by the EPA (14) and shows average air emission levels for each unit operation in this process. The capital letters refer to unit operations in the process as shown in Figure 4. It can be seen in Table 2 that the two highest contributors to air emissions of vinyl chloride are the holding bin–storage–bagging area and
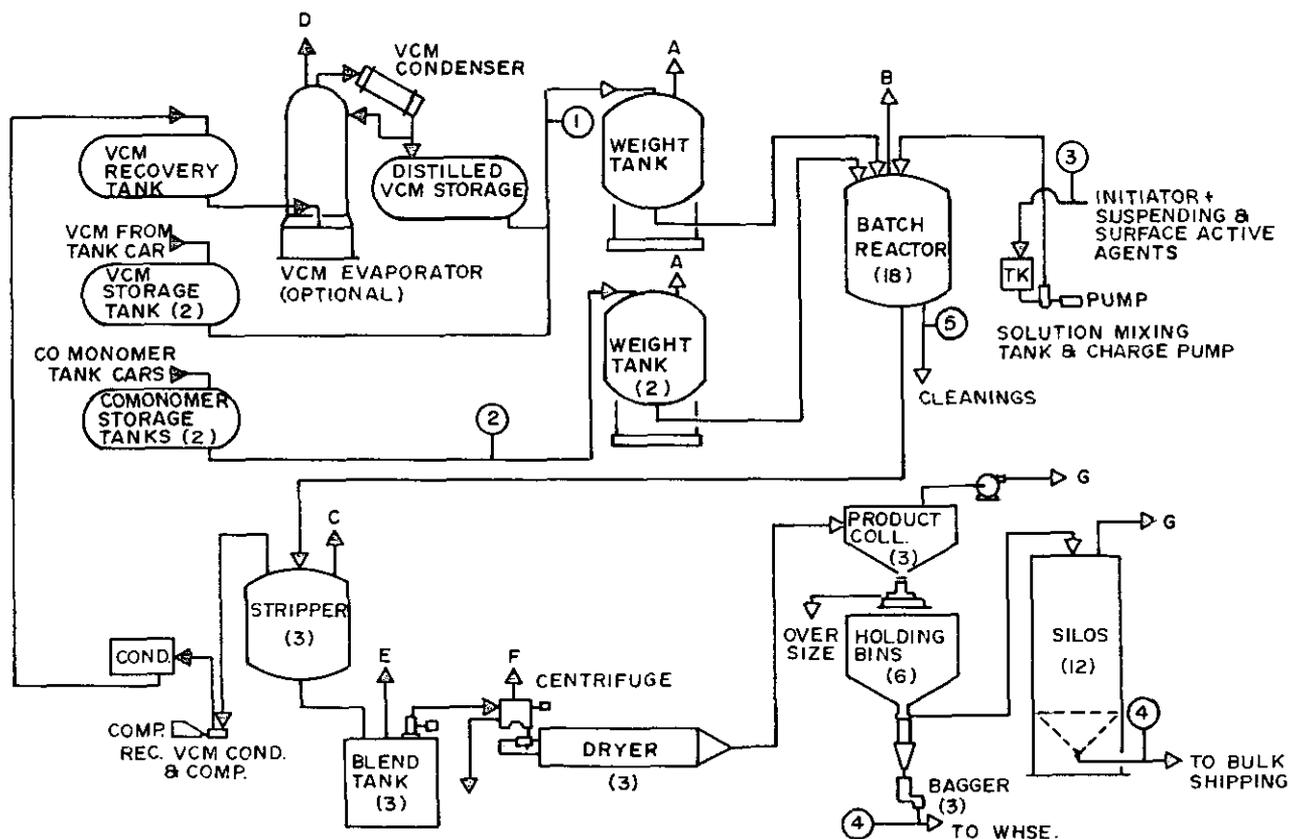

FIGURE 4. Poly(vinyl chloride) plant: suspension process.

the so-called fugitive emissions. The sources of fugitive emissions are shown in Figure 4 and can be classified as operating losses around seals, joints, and valves.

A similar process flowchart for the dispersion process is given in Figure 5. The polymer resin produced by this process has a very narrow size distribution (0.5–2 μm) and is used primarily to make paints and coatings. Instead of the rotary drier used in the suspension process, a spray drier is used. Aside from this equipment difference and the difference in reaction kinetic mechanisms, the two processes are very similar. Table 3 shows average air emissions for various unit operations in this process. Major losses occur in the holding bin–bagging–silo storage areas. In addition, fugitive emissions are high and there are significant losses from the stripper.

Table 2. Vinyl chloride emissions for suspension poly(vinyl chloride) process.[a]

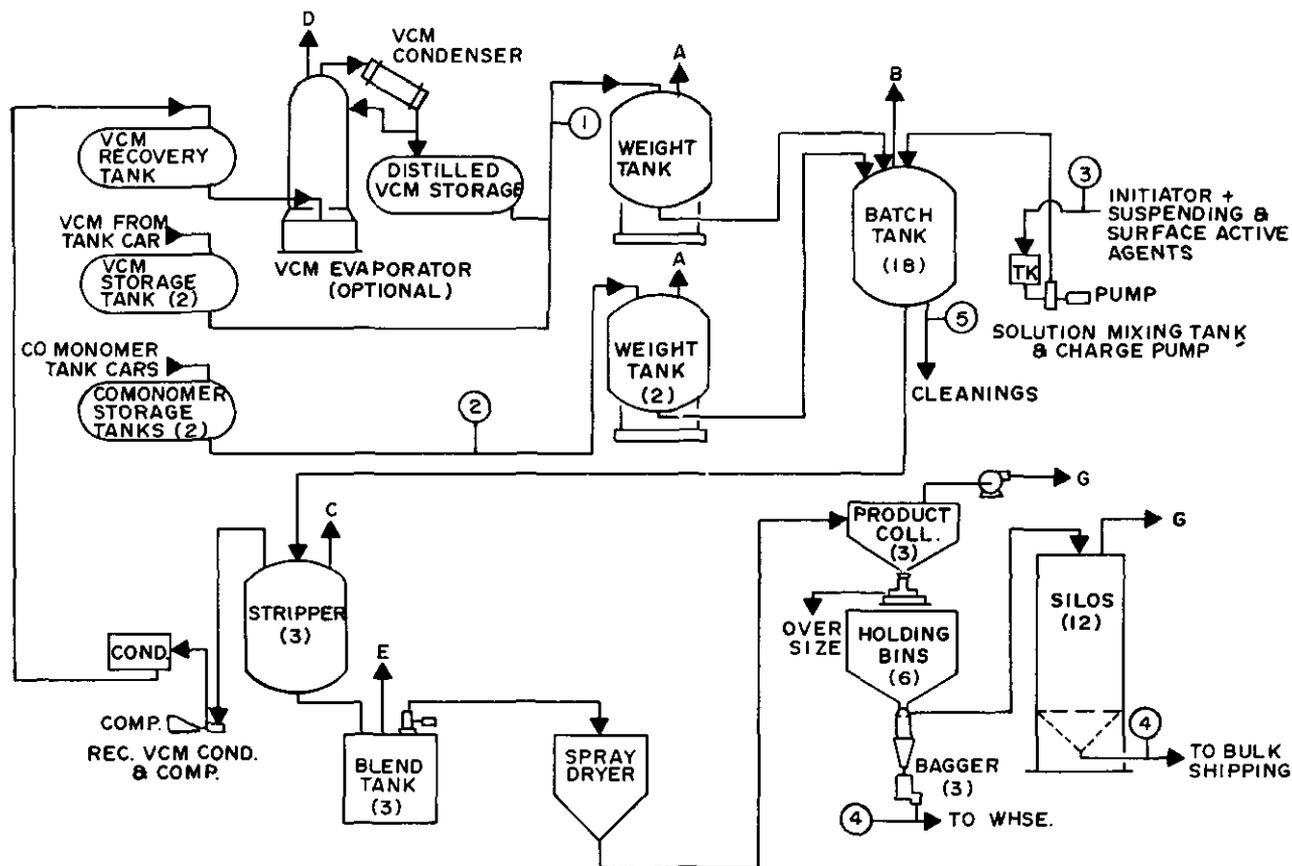| Source	Location on simplified flow chart (Fig. 4)	VCM emissions, kg/100 kg (lb VCM/100 lb) PVC
Fugitive emissions		1.50
Reactor opening loss	B	0.14
Stripper loss	C	0.32
Monomer recovery vent	D	0.48
Slurry blend tank	E	0.42
Centrifuge vent	F	0.13
Dryer exhaust	G	
Silo storage	G	
Bagger area	G	0.70
Bulk loading operations	G	
Reactor safety valve vents	B	0.20
Process water		0.025
Total		3.92

[a] EPA data (14).

FIGURE 5. Poly(vinyl chloride) plant: dispersion process.

Table 3. Vinyl chloride emissions for dispersion poly(vinyl chloride) process.[a]

Source	Location on sim- plified flow chart (Fig. 5)	VCM emissions, kg/100 kg (lb VCM/100 lb) PVC
Fugitive emissions		1.13
Reactor opening loss	B	0.15
Stripper loss	C	1.23
Monomer recovery vent	D	0.50
Slurry blend tank	E	0.34
Dryer exhaust	G	
Silo storage	G	
Bagger area	G	2.41
Bulk loading operations	G	
Reactor safety valve vents	B	0.22
Process water		0.025
Total		6.01

[a] EPA data (14).

Berens (2, 3) has studied the solubility and diffusivity of vinyl chloride in poly(vinyl chloride). In Table 4 the physicochemical properties of PVC resins from the suspension process are given. It should be remembered that both solubility and diffusivity are temperature-dependent properties. In addition, PVC resins made by the suspension process are amorphous polymers with a low glass content (5%) and a number-average molecular weight between 50,000 and 120,000. The particle diameter is determined from the surface area which is measured by N_2 gas adsorption, and the diffusivity is calculated from the particle diameter. As can be seen, the diffusivities are about the same for both particle diameters. Polymer resins with a high glassy content are very hard and brittle, and transport of gases in these polymers is characterized as non-Fickian" or anomalous diffusion, i.e., diffusivity becomes a strong function of position. Zones or regions in a polymer resin which are termed glassy have crystalline-like characteristics but do not possess the ordered geometry of idealized crystalline materials. More detail on the glassy content of polymers and its influence on adsorption and transport has been given by Park (17). The experiments reported by Berens (3) and given in Table 4 and Figure 6 were carried

Table 4. Physical characteristics of PVC resins from different manufacturing processes.[a]

| Sample	Type	Surface area, m^2/g [b]	Mean particle diam- eter, μm [c]	Calcu- lated diffu- sivity, cm^2/sec [d]	Glassy particle content
A	Suspension	2.3	1.86	6.6×10^{-11}	None
B	Suspension	0.21	20.43	1.1×10^{-10}	High

[a] Data of Berens (3).

[b] Surface area determined by BET technique.

[c] Diameter = 4.29/surface area.

[d] Diffusivity =
$$\frac{7.66 \times 10^{-3} \text{ (mean particle diameter, cm)}^2}{\text{(time for 50\% monomer loss from polymer, sec.)}}$$

A comparison of the diffusion data of Berens (3) with the proposed model presented earlier is given in Figure 6. As can be seen, there is a very good correlation between the observed conditions and the mathematical model at temperatures above the glass transition temperature.
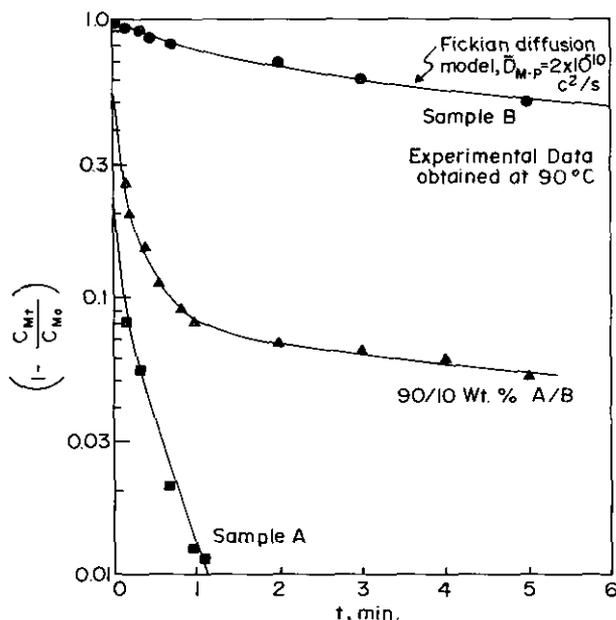
FIGURE 6. Comparison of experimental results (3) with Fickian diffusion models.

Table 5. Nonreactive additives for PVC.[a]

Type	Example	Concentrations and type of PVC product[b]
Antioxidants	Butylated hydroxytoluene 2,2'-Thiobis (4-methyl-6-*tert*-butylphenol)	0.1–0.5% by weight; F, R
Antistatic agents	Quaternary ammonium compounds	0.5–2.0% by weight; F, R
Colorants	Pigment scarlet Bis-azo red *Nickel-azo yellow* Carbon black TiO₂ Cd S	1.0–7.5% by weight; F, R
Fiberous reinforcement	Asbestos	5–60% by weight; R
Fillers	Silicas Ca(CO₃)₂ Carbon black Metal powders	Level depends on application; F, R
Flame retardants (additive type)	*Antimony trioxide* Phosphate esters PCBs Chlorinated paraffin	*Up to 50% by weight;* R
Lubricants	Low melting point waxes	1.0–3.0% by weight; R
Plasticizers	Dioctyl phthalate Adipic acid derivatives Azelaic acid derivatives Alkyl epoxy stearate	F 10–30% R 1–3%
Stabilizers	Ba-Cd stearate Lead carbonate Alkyl tin derivatives Calcium-Zn	*1.0–2.0% by weight;* F, R
Ultraviolet absorbers	4-Dodecycloxy-2-hydroxybenzophenone 2,4-Dihydroxybenzophenone Benzotriazole derivatives	1.0–5.0 pph; F, R

[a] Data of Schoengood (*26*).

[b] F = flexible PVC; R = rigid PVC.

Aside from the fact that it is possible to simulate the diffusion of residual monomers from PVC resins, this information can be used in equipment design to minimize exposure to vinyl chloride migrating from PVC resins. Quite obviously, at some stage after the resin leaves the drier, the particle size of the resin *should be reduced in size. Again, this is the* suggestion of Berens (*3*). After leaving the size-reduction operation, the resin must be screened, so that only the smaller size fraction particles enter the residual monomer removal equipment. Therefore by simply reducing the particle size of the entering resin, the residual vinyl chloride content can easily be reduced at temperatures above the glass transition temperature.

At room temperature, the rate of migration of residual VC monomer from PVC resins will be slower, since the diffusivity will be lower. At 20°C, Berens (*3*) determined the diffusivity of vinyl chloride in PVC as 10^{-12}cm²/sec, as opposed to 10^{-10}cm²/sec at 90°C. This simply re-emphasizes the need to remove the residual monomer at the higher temperatures before it is fabricated into end-products. The temperature dependence of the diffusivity has been determined experimentally (*3*) to conform to eq. (11):

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$$\overline{D}_{M\text{-}P} = 0.6 \exp\left\{-8150/T\right\}$$

(11)

where T is absolute temperature.

Conclusions

The major conclusions of this analysis of transport of residual monomers in polymers are:

(1) The diffusion model written in spherical coordinates simulates the diffusional process of residual vinyl chloride in PVC resins made by the suspension process.

(2) The particle size of PVC resisn and the temperature, are important properties of the resin when specifying technology for reducing residual monomer levels in polymer resins.

(3) The methods of transport modeling and of determining solubility and diffusivity of vinyl chloride in PVC can be applied to the analysis of transport of residual monomers from other monomer-polymer systems.

One of the stated purposes of the development of diffusion models for polymers was to provide a conceptual framework to examine the transport of non-reactive chemical additives from plastics. A plastic is defined as the polymer plus those chemicals which are blended with it either to make processing easier, or to change the physical, chemical, or electrical properties of the polymer. Conceptually, it is not difficult to consider the additive–polymer system as a multicomponent mass transfer situation. The mathematical basis for this type of analysis has been given previously (18–20). There are many literature references which refer to the migration of nonreactive chemical additives from plastics (21–25). However, attempts to present this information quantitatively in a manner which would be useful in understanding what parameters of this system influence the rate of migration of nonreactive chemical additives from plastics have not been reported.

In Table 5 are listed the types of additives used in PVC resins, representative examples of these chemicals, and representative ranges of concentration (26). PVC was chosen to illustrate the use of additives because by far most additives are made for and used in PVC, the reason being that PVC is fabricated into a large variety of flexible and rigid plastics

and that additives are necessary for fabrication. In considering diffusion of nonreactive chemical additives from plastics, it is important to determine the solubility and diffusivity of the additives in the polymer, in other additives, and in the fluid which contacts the plastic. By remembering this, it is possible to understand how plasticizers are transported into edible oil stored in PVC bottles (22, 23).

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