

Desorption of Residual Monomer from PVC Resins in a Fluidized Bed Drier

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SYNOPSIS

The present study deals with the investigation of the desorption of vinyl chloride from various commercial and experimental suspension PVC resins in a laboratory fluidized bed drier simulating an industrial drier. The results show that PVC resins may differ widely in the rate at which the monomer is desorbed. The rate of diffusion of the monomer is a function of the drying time, the fluidization air temperature, the porosity, and the amount of glassy particles in the PVC. The residual monomer content decreases with increasing air temperature, drying time, and resin porosity. After 105 min of drying with hot air at 80°C, the residual monomer content in the grade with the highest porosity is reduced from 3400 to 2 ppm, whereas for the grade with the lowest porosity, it is reduced from 4300 to 172 ppm on a dry basis. It appears that the resins of the high molecular weight grades are more porous and the low molecular weight grades contain a high proportion of nonporous or glassy particles and, hence, the desorption rate is smaller in these grades. The proportion of glassy particles and the size of glassy domains are estimated in this study by applying the experimental desorption data at long times to a desorption model. The model is useful in differentiating the interior structure of various PVC grades. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

PVC is a highly versatile thermoplastic material in terms of processing and applications. This is due to the existence of suitable stabilizers and other additives that enable the production of useful PVC compounds. PVC is currently widely used for food packaging and medicinal applications. However, the residual vinyl chloride monomer in PVC presents a major health hazard. Vinyl chloride is a toxic and carcinogenic gas and it may be released to the environment during processing or storage and may migrate into the liquids in contact with PVC products.¹⁻⁹ The accepted threshold values of residual monomer in PVC resins are as follows:

K57, low molecular weight bottle grades < 0.1 ppm

K70, high molecular weight film grades < 0.1 ppm
K64-68, medium to high molecular weight grades for rigid PVC applications 1 ppm

The present study deals with the desorption of residual vinyl chloride monomer from commercial and experimental suspension PVC resins in a laboratory fluidized bed drier simulating an industrial drier. The PVC grades studied were in cake form and initially contained 26% water and between 2500 to 3200 ppm of residual monomer on a wet basis. The quantity of the monomer in the PVC resins was determined by gas chromatography. The removal of residual monomer as a function of the fluidizing air temperature and residence time was investigated. The PVC grain interior structure was evaluated by scanning electron microscopy and surface area measurements using the N₂ adsorption, Brunauer-Emmett-Teller (BET) method. The PVC grades were also characterized in terms of their key commercial properties. Correlations between the inherent viscosity, plasticizer absorption time, grain

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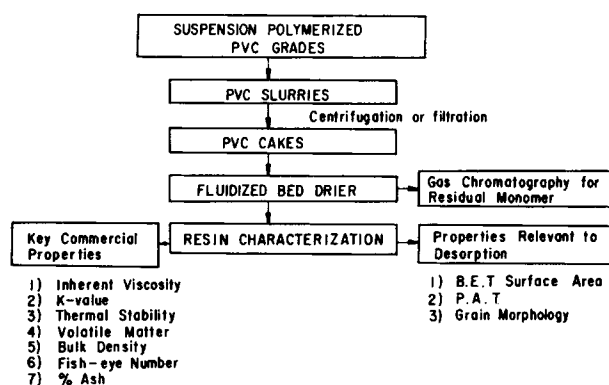


Figure 1 Flowchart of the experimental work.

morphology, and amount of residual monomer were established. Finally, this study presents a modification of the Berens model¹ to describe the desorption of residual monomer from PVC cakes.

EXPERIMENTAL

The experimental work carried out during the course of this study is summarized in the flowchart given in Figure 1. The grades of suspension PVC resins produced for this study offer a range of morphological properties that are known to affect the rate of desorption of the residual vinyl chloride monomer. Table I lists the reaction temperatures, agitation speeds, initial and final pressures, total pressure drops, and reaction times employed for the production of the PVC resins. The polymerization recipes and conditions result in products with different molecular weights. PVC grades 3000 H and 4000 M are of high and medium molecular weights and were produced in the plant reactor. The PVC grade 4000 MM is produced by incorporating SPAN 20 (sorbitan monolaurate) as a secondary suspending agent into the basic recipe for 4000 M, whereas 4000 L

and 4000 LL are PVC grades of low and very low molecular weights and were produced in a laboratory autoclave reactor of 7.5 L. The total pressure drop given in Table I is a relative measure of the conversion of monomer, and the conversion is lower for 3000 H, 4000 M, and 4000 MM compared to 4000 L and 4000 LL. At the end of the reaction, most of the unreacted monomer is flashed when the reactor is decompressed. After the PVC slurry is decanted and filtered, the amount of monomer in water becomes negligible. However, considerable dissolved monomer remains in the resin after filtration.

A laboratory fluidized bed drier shown in Figure 2 was used to compare the efficiency of removing the residual vinyl chloride monomer from the PVC cakes. The cakes of 3000 H and 4000 M were obtained directly from the centrifugal decanter in the production plant. The other grades were removed as slurries from the laboratory reactor and were filtered to obtain the cakes. The drier consists of a line for air, an air-control valve, a flowmeter, and a silica gel column to remove the humidity of the air. The air flow rate to the drier is kept at 144 L/min, which corresponds to the Reynolds number, N_{Re} , used in the plant drier. The desired air temperature is achieved in a glass-bead-filled column that is heated from the outside by an electrical resistance. The air temperature used to fluidize the PVC cakes varied from 60 to 85°C and the drying times varied from 0 to 105 min. The quantity of PVC cakes put into the drier depends on the grade and corresponds to the mass-to-volume ratio employed in the plant drier. For example, the quantity of cake employed in the drier was 199 g for 3000 H and 321 g for all other grades.

The residual vinyl chloride in the PVC resins that have been dried for various times was determined in a gas chromatograph fitted with a flame ionization detector. To prepare the calibration curve for the monomer, a flask with a silicon rubber stopper was weighed (w_1) and 95 mL of tetrahydrofuran (THF)

Table I Polymerization Conditions for the Suspension PVC Grades

Grade	3000 H	4000 M	4000 MM	4000 L	4000 LL
Reaction temp (°C)	52.4	58.2	58.2	64.5	64.5
Agitation speed (rpm)	240	240	850	850	850
Initial pressure (kg/cm ²)	7.4	8.8	8.8	10.4	10.4
Final pressure (kg/cm ²)	5.0	6.5	6.5	5.0	5.0
Total pressure drop (kg/cm ²)	2.4	2.3	2.3	5.4	5.4
Reaction time (h : min)	11 : 30	9 : 20	8 : 50	9 : 55	13 : 20

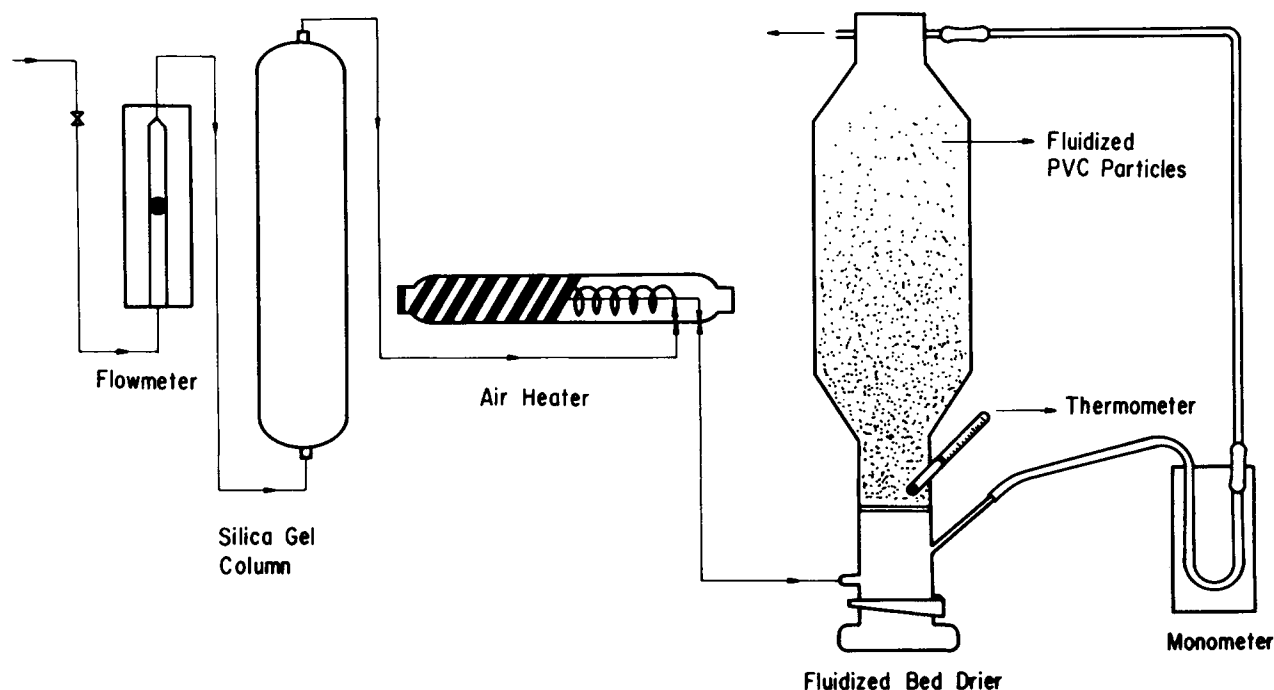


Figure 2 Laboratory fluidized bed drier.

was introduced. The flask was weighed again (w_2) and immediately chilled to about -20°C . Then, 2 mL of monomer at -14°C was injected into the flask and the weight of the flask was recorded (w_3). This stock solution was stored at -80°C . The concentration of monomer in parts per million (ppm) is given by

$$C_m = [(w_3 - w_2)/(w_3 - w_1)] \times 10^6 \quad (1)$$

Standard solutions of known concentration were prepared by diluting the stock solution in THF. Five milliliters of each standard solution was injected into the gas chromatograph and the column was maintained at 45°C . The known monomer concentrations were plotted against the peak areas, A_p , and the calibration factor, F , was obtained.

To determine the concentration of residual monomer in the PVC resins, the PVC was carefully weighed (w_{PVC}) and dissolved in a known weight of THF (w_{THF}). Five microliters of this solution was injected into the chromatograph and the amount of monomer in ppm was calculated from

$$C = FA_p w_{\text{THF}} / w_{\text{PVC}} \quad (2)$$

Each PVC grade was also characterized in terms of

key commercial properties, such as inherent viscosity, K value, thermal stability, volatile matter, bulk density, fish-eye number, and percent ash.

The desorption of residual monomer and the rate of absorption of plasticizers in PVC resins are controlled by the nature of the interior structure of the grains. The physical adsorption of N_2 , i.e., the BET method, was used to determine the specific surface area of 3000 H, 4000 M, and 4000 MM.

The plasticizer absorption time (PAT) was measured according to the plant method. In this method, the temperature of a special mixer is kept at 100°C by immersing it in an oil-heated bath. Fifty grams of PVC powder is introduced into the mixer and agitated for 3 min at 450 rpm. Twenty-five milliliters of dioctyl phthalate (DOP) at 35°C is added, and the time to obtain a dry blend is taken as the PAT value of the resin. The PAT value provides a practical indication of the porosity of the PVC particles. A low PAT value indicates that the PVC grains have a porous internal structure, whereas a high PAT value implies a glassy internal structure.

Scanning electron microscopy (SEM) was used to examine the grain interior morphology of 3000 H, 4000 MM, and 4000 LL at several magnifications. The PVC grains were well mixed with a fast-curing epoxy resin. After curing, the samples were chilled

Table II Key Commercial Properties of the PVC Grades

Grade	3000 H	4000 M	4000 MM	4000 L	4000 LL
Inherent viscosity (mL/g)	1.141	0.964	0.972	0.820	0.710
<i>K</i> value	72	66	66	61	57
Thermal stability (min)	> 60	> 60	> 60	> 60	> 60
Volatile matter (% w/w)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Bulk density (g/mL)	0.45	0.52	—	0.53	0.55
Fish-eye number	< 20	< 20	< 20	< 20	< 20
Ash (%)	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03

in dry ice and were broken to obtain sharp fracture surfaces suitable for viewing in the scanning electron microscope.

RESULTS AND DISCUSSION

Table II lists the key commercial properties of the PVC grades. All grades passed the standard specifications for thermal stability, % volatile matter, fish-eye number, and % ash. The inherent viscosities and the *K* values are proportional to the molecular weight of the resins: 3000 H has the highest molecular weight, whereas 4000 LL has the lowest molecular weight among the grades studied. Besides differences in the recipes, the higher polymerization temperature employed for 4000 LL increases the rate of polymerization, and this results in lower molecular weight. Using the same test procedure, 3000 H yields the lowest bulk density, implying a highly porous grain interior. The polymerization temperature for this grade is the lowest, and the reaction is stopped at a low conversion.

Figure 3 shows the PAT for the PVC resins that have been dried in the laboratory fluidized bed drier at 80°C for various residence times. It is observed that, initially, the moisture in the pores of the grains compete with the absorption of the plasticizer. As the drying time of the cakes increases, the PAT values decrease and plateau values are reached in relation to the porosity of the grains. Among the grades studied, 3000 H has the lowest PAT value, suggesting that this high molecular weight resin is more porous, and the removal of residual vinyl chloride monomer from this resin will be much easier. Figure 4 shows that there is a strong correlation between the PAT plateau value and the inherent viscosity of the resins. The PAT value decreases as the inherent viscosity of the resin increases.

Table III gives the specific surface areas of 3000 H, 4000 M, and 4000 MM as measured by the BET

method. It is observed that the high molecular weight resin 3000 H has the highest specific surface area.

The average diameter, d_p (in μm), of an absorbing solid particle within the PVC grains is given by (2)

$$d_p = 4.29/S_g \quad (3)$$

where S_g is the specific surface area in m^2/g and ρ_s is the density of the solid particle and is taken as 1.4 g/cm^3 . The particle diameters for 3000 H, 4000 M, and 4000 MM calculated according to Eq. (3) are given in Table III. The high molecular weight resin is made up of smaller particles that did not have chance to grow since the monomer conversion was low. Table III also shows the measured pore volume, V_g , the calculated pore diameter, α , the grain porosity, ϵ , and the grain density, ρ_g .

Regardless of the complexity of the pore structure

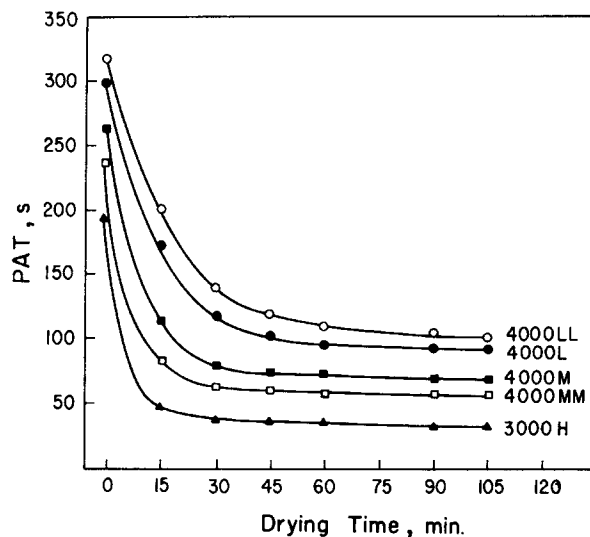


Figure 3 Plasticizer absorption time vs. residence time in the drier.

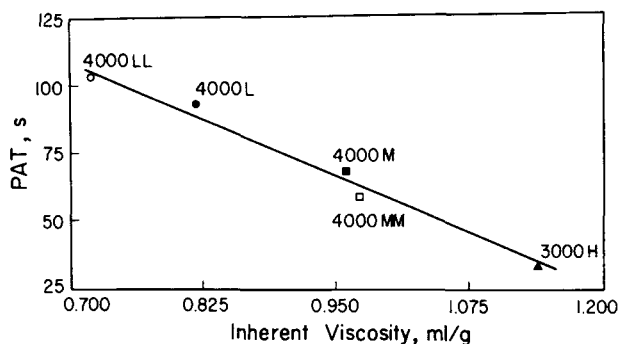


Figure 4 Plasticizer absorption time vs. inherent viscosities.

of the PVC grains, it is assumed that the voids may be taken as cylindrical pores. The average pore diameter, a (in μm), is calculated from the pore volume, V_g , and the specific (pore) surface area, S_g , as (3)

$$a = 4V_g/S_g \quad (4)$$

where V_g is in cm^3/g and S_g is in m^2/g . It is seen from Table III that the calculated pore diameters are close to the particle diameters.

The grain porosity ε is calculated from

$$\varepsilon = \frac{V_g \rho_s}{V_g \rho_s + 1} \quad (5)$$

and the grain density from

$$\rho_g = \rho_s(1 - \varepsilon) \quad (6)$$

The PVC grades have porosities greater than 50%, and 3000 H has the highest porosity. The addition of 0.06 phr (parts per hundred) of SPAN 20, i.e., sorbitan monolaurate, as a secondary suspending agent to the basic recipe for 4000 M improves the porosity of 4000 MM and it results in an increase

in the pore diameter. However, SPAN 20 does not practically affect the size of the particles in the grains.

A suspension PVC grain measures 100–150 microns in diameter. The interior of the PVC grains were examined in the scanning electron microscope. The sample preparation explained in the Experimental section does not always preserve the original structure since some details may be lost and some artifacts may also be created. The internal grain structures of 3000 H, 4000 MM, and 4000 LL at 1000 magnification are given in Figure 5(a)–(c). It is observed that the grains have complex and porous internal structures. The clustering of solid particles and the presence of larger particles are evident in the micrograph of Figure 5(b). In Figure 5(c), it appears that the particles of 4000 LL have been fused to a large extent. The knitting of spherical solid particles in 4000 LL is clearly evident at 5000 magnification in Figure 6. Although the micrographs are helpful to elucidate the internal structure of PVC grains, by experience, it appears that the differences among the grades can be best inferred from the BET measurements or simply from the PAT values.

Table IV gives % volatile matter and residual monomer in the PVC resins for different drying times. The effect of the drying time on the residual vinyl chloride monomer in the PVC resins is shown in Figure 7. The cakes were dried at 80°C in the fluidized bed drier and samples were taken at regular intervals to measure the residual monomer. The cakes initially contain about 26% of water and the amount of dissolved monomer in water under atmospheric conditions is negligible compared to the monomer in the resin. Practically, most of the water evaporates during the first 15 min of drying. The concentrations given in Figure 7 are based on dry resin, i.e., resins containing less than 1% of moisture. It is noticed that the residual monomer concentration decreases as the drying time increases. Among the grades studied, 3000 H exhibits the lowest amounts of residual monomer at comparable drying

Table III BET Results for 3000 H, 4000 M, and 4000 MM

Grade	3000 H	4000 M	4000 MM
Specific surface area (m^2/g)	1.310	0.849	0.873
Pore volume (cm^3/g)	1.3580	0.9477	1.1549
Particle diameter (μm)	3.2	5.0	4.8
Pore diameter (μm)	4.1	4.5	5.3
Grain porosity (%)	65.5	57.1	62.0
Grain density (g/cm^3)	0.49	0.60	0.53

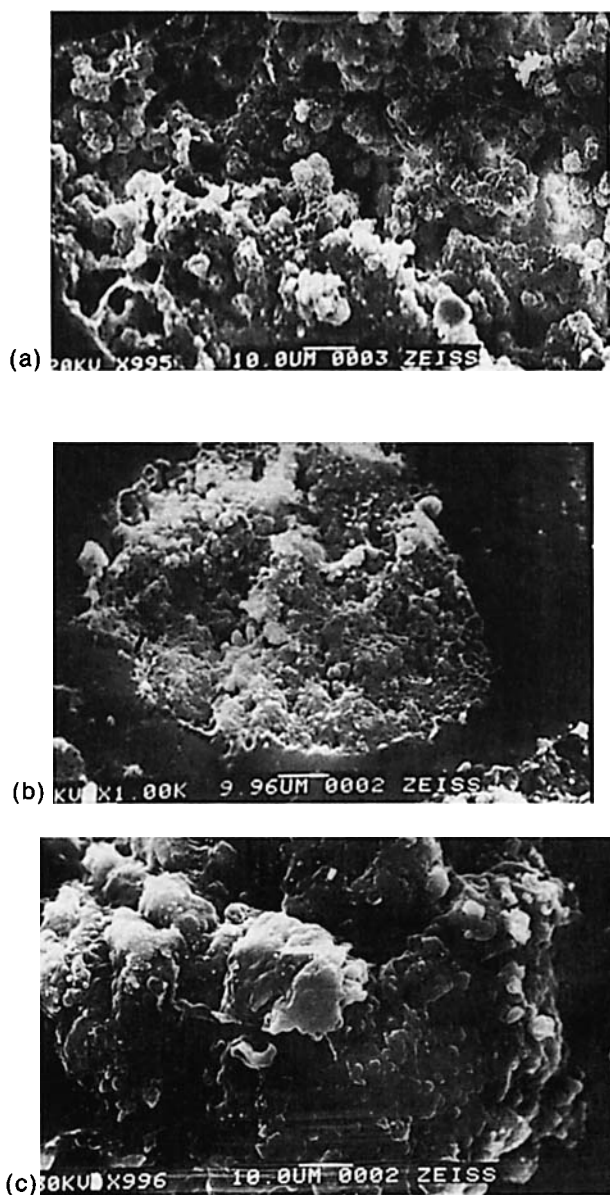


Figure 5 (a) Grain structure of 3000 H at 1000 \times . (b) Grain structure of 4000 MM at 1000 \times . (c) Grain structure of 4000 LL at 1000 \times .

times. After 105 min of drying, 3000 H contains 2 ppm of monomer, whereas 4000 LL contains 172 ppm. The grades 4000 M and 4000 MM contain 9 ppm of residual monomer and show also a relatively rapid loss of monomer. These results illustrate that suspension-polymerized PVC resins may differ widely in the rate at which the residual monomer is desorbed, and as expected, the VCM in the porous grades 3000 H, 4000 M, and 4000 MM desorb faster compared to the less porous grades 4000 L and 4000 LL.

Figure 8 shows the drying of 3000 H at different temperatures ranging from 60 to 85°C. It appears that the desorption of residual monomer is quite fast at temperatures close to the T_g of the resin, i.e., 85°C. However, there exists the risk of thermal degradation of the resins if drying is done at or above the T_g since the resins are not stabilized prior to the drying step. Therefore, in this work, the drying of the resins at 80°C was considered to be optimum.

The diffusion model due to Berens¹ was modified to describe the drying of PVC cakes in the fluidized bed drier and is given by the following expression:

$$C/C_0 = 6(1-f) \sum_{n=1}^{\infty} (1/n^2\pi^2) \times \exp(-4n^2\pi^2 D_w t/d_p^2) + 6f \sum_{n=1}^{\infty} (1/n^2\pi^2) \times \exp(-4n^2\pi^2 D t/d_g^2) \quad (7)$$

In eq. (7), f is the weight fraction of glassy (large) particles and $(1-f)$ is the weight fraction of porous (small) particles; t , the duration of drying; C_0 , the initial concentration of residual monomer in the PVC cakes on a dry basis; and C , the remaining monomer in the PVC grain. Equation (7) with $f=1$ or $f=0$ is actually the solution for the unsteady-state Fick's equation of diffusion in a solid sphere initially having a solute uniformly distributed. Equation (7) employs two diffusion coefficients, D and D_w , rather than one in contrast to the work of Berens,^{1,2} Daniels and Longeway,⁴ Patel et al.,⁵ and Quy,⁶ where only the desorption of the monomer from dry PVC resins were investigated.

During the initial stages of drying, the monomer diffuses from the particles into the surrounding pores that initially contain capillary-held water. Water in



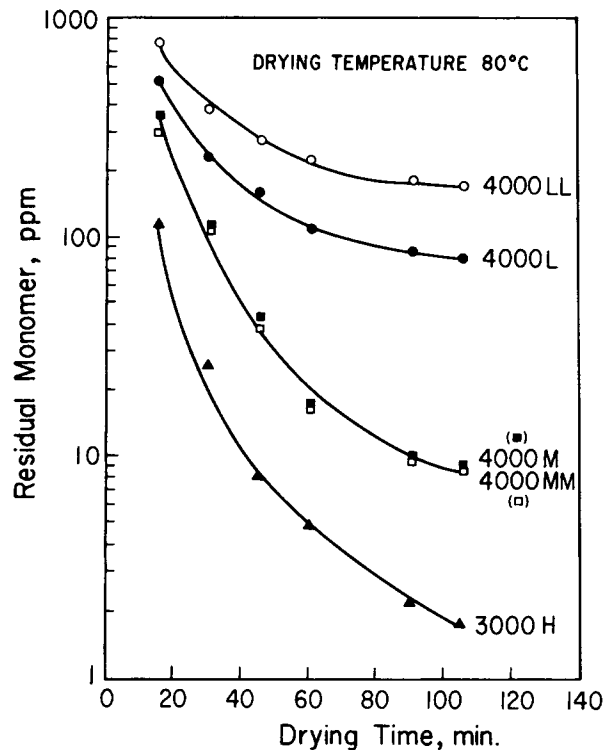
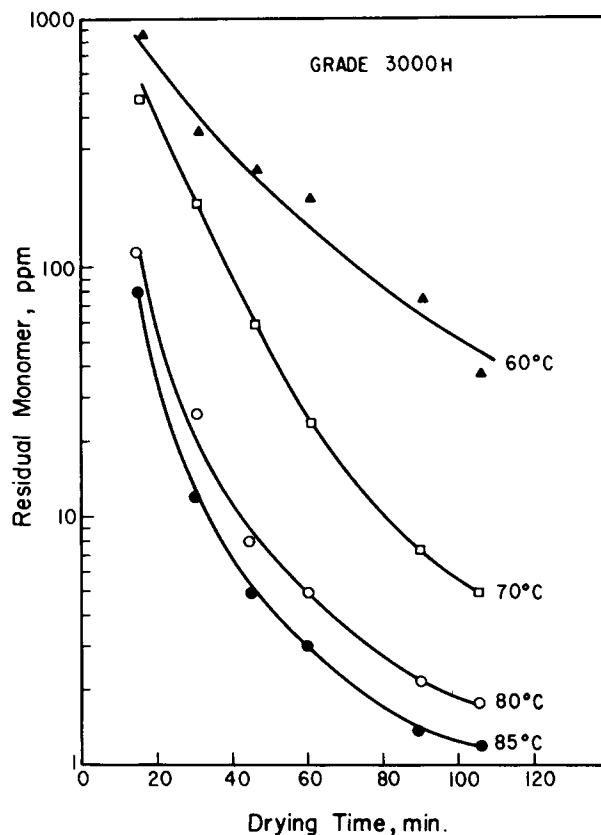
Figure 6 Grain structure of 4000 LL at 5000 \times .

Table IV % Volatile Matter (First Row) and Residual Monomer in ppm (Second Row) vs. Drying Time in Minutes at 80°C

Resin	Drying Time (Min)						
	0	15	30	45	60	90	105
3000 H	26.0	0.96	0.68	0.28	0.22	0.20	—
	3342	114	27	8	5	2.2	1.8
4000 M	26.1	1.10	0.69	0.40	0.27	0.21	—
	4270	360	111	44	17	10.1	9.2
4000 MM	26.0	1.07	0.65	0.49	0.26	0.26	—
	3342	308	108	39	17	9.2	8.8
4000 L	26.0	2.1	0.77	0.72	0.36	0.24	—
	3837	506	232	157	111	86	81
4000 LL	26.0	2.2	0.87	0.59	0.42	0.28	—
	3890	772	394	282	228	183	172

the grains hinders the desorption of monomer and, hence, the “effective” diffusion coefficient given by D_w is dominant in eq. (7) in the early stages of drying. When the water in the pores is evaporated, the resistance to diffusion becomes less and the diffusion coefficient given by D now becomes dominant

in eq. (7). The desorption of the monomer at small times is controlled by small particles that desorb fast and, hence, are termed “porous.” The desorption


Figure 7 Residual vinyl chloride monomer vs. drying time at 80°C.

Figure 8 Residual vinyl chloride monomer vs. drying time at various temperatures for the grade 3000 H.

at long times is controlled by large particles that desorb slowly and, hence, are termed "glassy." Equation (7) is therefore a diffusion model taking into account the additive contribution of both fast- and slow-desorbing particles and that the diffusion coefficient is not constant during desorption. Equation (7) is therefore a superposition of two Fickian behaviors.

The diffusion coefficient of vinyl chloride from dry PVC grains has been determined by Berens^{1,2} and is given by

$$D = 0.8574 \exp(-16060/RT) \text{ in cm}^2/\text{s} \quad (8)$$

In the above expression, R is the gas constant, 1.987 cal/g mol K, and T is the absolute temperature in K. At 80°C, D is calculated to be 1×10^{-10} cm²/s using eq. (8).

D_w is estimated from the desorption data of porous resins 3000 H, 4000 M, and 4000 MM at short times. Therefore, only the first term in eq. (7) needs to be considered. Furthermore, taking $f = 0$ and neglecting the terms with $n > 1$, D_w is then given by

$$D_w = -\frac{d_p^2}{4\pi^2 t} \ln\left(\frac{C}{C_0} \frac{\pi^2}{6}\right) \quad (9)$$

D_w is calculated from the BET value of d_p and the experimental value of C/C_0 at the first 15 min of drying. In Figure 9, the plot of $\ln D_w$ vs. $1/T$ is given

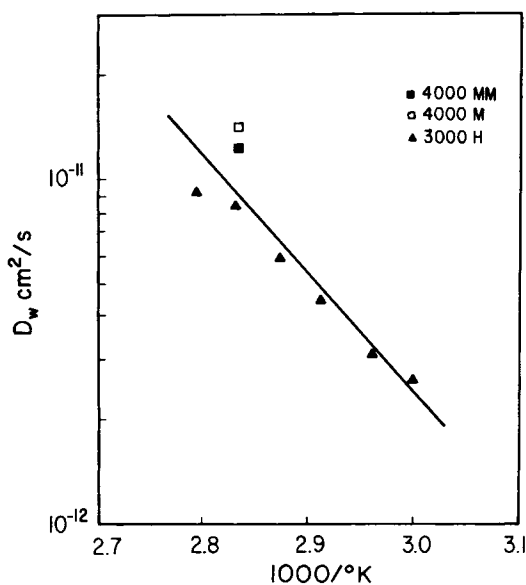


Figure 9 Arrhenius plot of D_w vs. $1/T$ (1/K).

Table V Grain Structural Parameters from Eq. (7)

PVC Grades	f (%)	d_p (μm)	d_g (μm)
3000 H	0.40	3.2 ^a	40.3
4000 M	0.70	5.0 ^a	58.0
4000 MM	0.62	4.8 ^a	76.0
4000 L	5.0	4.7 ^b	76.0
4000 LL	11.0	4.7 ^b	72.0

^a From BET data.

^b From eq. (7).

and the following expression for D_w is obtained from a least-square regression:

$$D_w = 0.082 \exp(-16060/RT) \text{ in cm}^2/\text{s} \quad (10)$$

At 80°C, D_w is calculated to be 9.3×10^{-12} cm²/s using eq. (10).

The diffusion coefficient of monomer from wet grains is about 10 times smaller compared to that of dry grains given by eq. (8). The activation energy for the diffusion of vinyl chloride is about 16,000 cal/mol and it is not affected by the considerable moisture present in the PVC cakes.

Initial estimates for the structural parameters of the PVC grain such as f and d_g can be made by fitting the second term in eq. (7) to the experimental data of residual monomer concentration, especially at long times for $n = 1$. The diameters of the "porous" particles, d_p , for grades 3000 H, 4000 M, and 4000 MM are available from BET measurements, and d_p was estimated for 4000 L and 4000 LL from their desorption data at short times. The initial estimates of f and d_g were tuned such that the best fit between the model in eq. (7) and the entire experimental data for a given grade was obtained. The results for the structural parameters are given in Table V and they indicate that the grains of 3000 H, 4000 M, and 4000 MM consist of practically of "porous" particles, whereas the grains of 4000 L and 4000 LL consist of a mixture of "porous" and "glassy" particles. The glassy particles are believed to arise from the excessive knitting of primary particles during polymerization.⁶ It should be emphasized that the values of f , d_g , and d_p are average results for a multitude of grains, and as such, they may not correlate with the morphological observations made on a few grains. The structural parameters are useful to discern subtle or gross structural differences among various PVC resins.

CONCLUSIONS

The results show that PVC resins may differ widely in the rate at which the residual monomer is desorbed. The rate of desorption of monomer is a function of the drying time, fluidization air temperature, porosity, and amount of glassy particles in the PVC resins. The residual monomer content decreases with increasing air temperature, drying time, and resin porosity. It appears that the high molecular weight resins 3000 H, 4000 M, and 4000 MM are more porous and the low molecular weight resins 4000 L and 4000 LL contain a high proportion of glassy particles and the desorbing rate of the monomer is smaller in these grades. The diffusion coefficient of vinyl chloride from wet PVC resins is about 10 times smaller than the value observed in dry resins, and this ratio is independent of temperature. After 105 min of drying with hot air at 80°C, the residual monomer in 3000 H is reduced from 3400 to 2 ppm, whereas for 4000 LL, it is reduced from 4500 to 172 ppm.

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NOMENCLATURE

a	pore diameter (mm)
A_p	peak area (mm ²)
C	concentration of residual monomer (ppm)
C_m	concentration of stock solution (ppm)
C_0	initial concentration of residual monomer in the cakes (ppm)
d_g	size of glassy particles in PVC grains (μm)
d_p	solid particle diameter in PVC grains (μm)

D	diffusion coefficient of monomer in glassy particles (cm ² /s)
D_w	effective diffusion coefficient of monomer (cm ² /s)
f	fraction of glassy domains in PVC grains
F	gas chromatograph calibration factor (ppm/mm ²)
N_{Re}	Reynolds number
n	counting index
S_g	BET surface area of PVC grains (m ² /g)
t	drying time in the laboratory drier (min)
T	drying temperature (K)
V_g	pore volume of the PVC grains (cm ³ /g)
w	weight (g)
ϵ	porosity
ρ_g	PVC grain density (g/cm ³)
ρ_s	density of solid particles in PVC grains (g/cm ³)

REFERENCES

1. A. R. Berens, *Polymer*, **18**, 697 (1977).
2. A. R. Berens, *Polym. Prepr.*, **15**, 203 (1974).
3. A. Wheeler, in *Catalysis*, P. H. Emmett, Ed., Reinhold, New York, 1955, Vol. II, Chap. 2.
4. C. A. Daniels and G. D. Longeway, *Polym. Eng. Sci.*, **19**(2), 181 (1979).
5. C. B. Patel, R. Houck, R. Gupta, and R. K. S. Chan, *J. Polym. Sci. Polym. Chem.*, **17**, 3775 (1979).
6. B. R. Quay, *J. Macromol. Sci.-Phys. B*, **20**, 235 (1981).
7. R. K. S. Chan, C. B. Patel, R. Gupta, C. H. Worman, and R. E. Grandin, *J. Macromol.-Sci. Chem.*, **A**, **17**, 1045 (1982).
8. E. Benfenati, M. Natengelo, E. Davoli, and R. Fanelli, *Fd. Chem. Toxicol.*, **29**, 131 (1991).
9. A. Y. Lazaris, S. M. Schumujlovic, and T. A. Kalmikova, *J. Chromatogr.*, **198**, 337 (1986).

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