

# Kinetics of Vinylchloride Removal from Polyvinylchloride by Thermal Treatment in a Flow of Inert Gas

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## Synopsis

The kinetics of free monomer removal from powdered suspension polyvinylchloride at elevated temperatures in a nitrogen flow is studied. It is found that in fluidized bed the monomer concentration decreases linearly with time. This behavior cannot be explained by a model of molecular diffusion in single spheres because of particle degradation during the treatment. Conditions for complete vinylchloride removal from the polymer are proposed.

## INTRODUCTION

Vinylchloride (VC) is related to the primary group of toxic chemical carcinogens<sup>1,2</sup> and its absence in polyvinylchloride (PVC) is of great importance for polymer use and processing. Polyvinylchloride packagings were tested for vinylchloride migration in a model media and it was established that only those containing monomer below 1 ppm<sup>3-5</sup> can be allowed by the health authorities. Therefore, the raw material must not contain monomer in excess to 10 ppm.<sup>6</sup> This can be achieved by several methods which are well described in the patent literature. They can be divided into two basic groups: (a) methods of decreasing the free monomer content in polyvinylchloride during its production<sup>7-11</sup> and (b) methods of decreasing the free monomer content by treating the powdered polymer before its processing.<sup>12-16</sup>

The patents from the latter group, to which our experiments are related, suggest technological conditions favoring monomer diffusion from the inside to the outside surface of the PVC particles and monomer desorption. For this purpose thermal treatment in the temperature range of 60–160°C with varying duration (from 10 minutes to several hours) in inert gas flow (nitrogen or overheated steam) and vigorous stirring (mechanical or pneumatic) are used.<sup>12-15</sup> Heating in closed mixers in vacuum is also recommended.<sup>16</sup> Some authors<sup>12,13</sup> suggest addition of different compounds (water, phenol, diglycol, etc.) to the powdered polymer prior to thermal treatment. The content of free vinylchloride in the resulting polymers varies over a broad range (from 21 to 0.3 ppm) depending on the methods and conditions of treatment and on the type of the raw polymer.

The available patent information shows that the methods of the second group can satisfy the criteria of minimum polyvinylchloride content. However,

the lack of a model concept and kinetic data in the patents limits their applicability.

Some fundamental aspects of monomer desorption are discussed in refs. 17–19. Berens<sup>17</sup> has established that emulsion polyvinylchloride can be considered as being comprised of spherical particles of diameter 0.1–1  $\mu\text{m}$ , in which the monomer diffusion above the glass transition temperature is described by the equation:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4Dn^2\pi^2t/d^2) \quad (1)$$

This equation is a solution of the differential equation for unsteady-state molecular diffusion if the sphere is initially at a uniform concentration of the diffusing species, the surface concentration is maintained constant, and the diffusion coefficient is constant.<sup>20</sup>

Treating his own data for vinylchloride sorption and desorption, Berens has derived the following equation for vinylchloride diffusion coefficient in the polymer:

$$D = 3.7 \exp(-17000/RT) \quad (2)$$

valid in the temperature range 25–110°C.

Powdered suspension polyvinylchloride, however, consists of large irregular agglomerates of little spherical particles.<sup>17,18</sup> In this case, the kinetics of monomer desorption would be hardly predicted by Eq. (1) or its modifications, assuming some particle size distribution.<sup>18</sup>

Under these circumstances our aim was to study the kinetics of monomer removal from suspension polyvinylchloride, treating it at elevated temperatures in a flow of inert gas.

## EXPERIMENTAL

The test subject was powdered suspension polyvinylchloride of density 1310  $\text{kg}/\text{m}^3$ , prepared for experimental purposes. An initial monomer content of 203 ppm was obtained by additional contact with vinylchloride vapors.<sup>19</sup> Four fractions of different particle sizes were tested: I, 0.08–0.1 mm; II, 0.1–0.125 mm; III, 0.125–0.160 mm; IV, 0.160–0.180 mm.

Vinylchloride desorption was carried out in a flow of pure nitrogen (99.99%). The apparatus used consisted of a fritted glass filter of diameter 36 mm, fitted to the end of a glass tube with regulated external electric heating. The flow rate of the nitrogen entering the tube was measured by a rotameter. The gas temperature was controlled at the entrance and at the exit of the fluidized bed. The quantity of each test sample was chosen so as to form a layer of thickness equal to the diameter of the fritted glass filter. The nitrogen temperature was varied in the range 60–120°C. The gas flow rate and the treating time were also varied. Experiments were carried out predominantly at fluidization coefficient near 2. At this value, for powdered materials consisting of particles of indicated size, a homogeneous fluidization and intensive mass-transfer from the particle surface to the fluidizing agent take place.<sup>21</sup>

Vinylchloride content in the polymer was determined by gas chromatography. A Perkin-Elmer apparatus Sigma-3, equipped with a computer device Sigma-10 was used for this purpose. Samples were introduced by a Headspace method. The chromatography parameters were as follows: column temperatures: initial  $-60^{\circ}\text{C}$ , end  $-180^{\circ}\text{C}$ ; injector temperature:  $110^{\circ}\text{C}$ ; detector temperature:  $250^{\circ}\text{C}$ , headspace adaptor temperature:  $60^{\circ}\text{C}$ ; test sample conditioning time: 15 min.

The column used was 2 m long and had an inside diameter of 2 mm. The column was packed by 30% Apiezon L on Chromosorb P. The analysis sensitivity was 0.5 ppm and the reproductivity  $\pm 7\%$ .

The form and structure of the polymer particles were determined by an optical microscope MIN-8 with magnification  $\times 200$ .

### RESULTS AND DISCUSSION

Figure 1 demonstrates the effect of nitrogen velocity on the monomer end concentration (as a part of the initial vinyl concentration in the polymer) at  $90^{\circ}\text{C}$  and 15 min treating time. The results are related to the fraction of 0.125–0.160 mm particle sizes, which is the most representative for the suspension polyvinylchloride.<sup>17,18</sup> Figure 1 shows that the influence of the hydrodynamic conditions on the monomer removal rate is significant. At low gas velocities the mass-transfer resistance from the particle surface to the nitrogen cannot be neglected, and the quantity of the released monomer, resp., the diffusion coefficient, should be determined by the equation:

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{6Bi^2 \exp(-4\beta_n^2 Dt/d^2)}{\beta_n^2(\beta_n^2 + Bi^2 - Bi)} \quad (3)$$

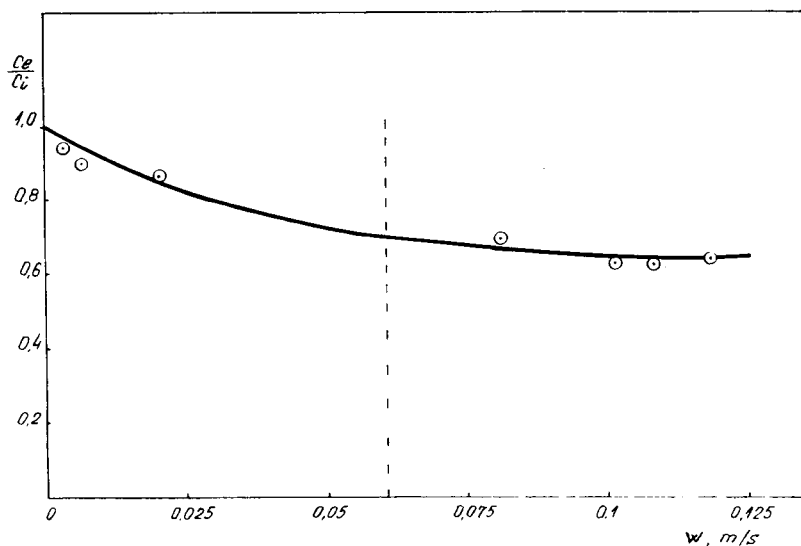


Fig. 1. Effect of nitrogen velocity on the end monomer concentration for fraction of the particle sizes 0.125–0.16 mm for treating time 15 min and temperature  $90^{\circ}\text{C}$ .

Herein,  $\beta_n$  are the roots of the transcendental equation:

$$\beta_n \cotg \beta_n = 1 - Bi \quad (4)$$

After the bed fluidization (which is marked on the figure by a dotted line) takes place, the diffusion resistance is located in the solid phase (i.e., Bio number  $Bi \rightarrow \infty$ ). Under these conditions Eq. (3) transforms into Eq. (1). It is not impossible that part of the observed effect results from the sample heating after the polymer introduction onto the filter, since this heating will be faster at higher gas flow rates. However, the effect of the gas dynamics on the monomer removal is certain, because of the considerable duration of the treatment.

All subsequent results were obtained in a fluidized bed, which provides material homogenization and opportunities to realize a multistep continuous process.<sup>21</sup>

Figure 2a-d shows the decrease of the free monomer concentration in the fractions investigated, depending on the treating time at temperature 90°C and the rate of fluidizing agent 0.12 m/s. The observed linear dependence suggests a relaxation characteristic of the diffusion process. However, it is most unlikely for the monomer desorption to have such a characteristic above the glass transition temperature of the polymer. We assume that the linear dependence is due to the structural change in the material during thermal treatment. Initially, there are visible particle agglomerates in the fluidized bed which degradate subsequently as due to interparticle impacts. This degradation creates new contact surfaces with the gas phase.

Figure 3(a) and (b) (microscope pictures of the particles before treating) and the results given in Table I confirm our assumption. The agglomerative structure of suspension PVC, shown in Figure 3(a) and (b), has been estimated by other authors<sup>17,18</sup> as well. Table I details the data from the sieve analysis on the samples prior to and after treating for 30 min, and indicates a considerable increase in the quantity of smaller sized particles after treatment.

The precise description of the monomer desorption process is very difficult, because of the complicated mechanism and the irregular form of the polymer particles. As a first approximation it can be considered like a diffusion in single solid spheres (whose diameter is equal to the mean diameter of the related fraction) at uniform initial monomer distribution and constant concentration on the sphere surface. In the fluidized bed this concentration can be assumed equal to zero. Under these conditions Eq. (1) can be used and the molecular diffusion coefficient can be determined by the method of least squares. The values obtained at 90°C are as follows:

$$\bar{d} = 0.09 \text{ mm}, D = 0.5 \cdot 10^{-8} \text{ cm}^2/\text{s};$$

$$\bar{d} = 0.112 \text{ mm}, D = 0.6 \cdot 10^{-8} \text{ cm}^2/\text{s};$$

$$\bar{d} = 0.142 \text{ mm}, D = 0.9 \cdot 10^{-8} \text{ cm}^2/\text{s},$$

and

$$\bar{d} = 0.17 \text{ mm}, D = 1.15 \cdot 10^{-8} \text{ cm}^2/\text{s}.$$

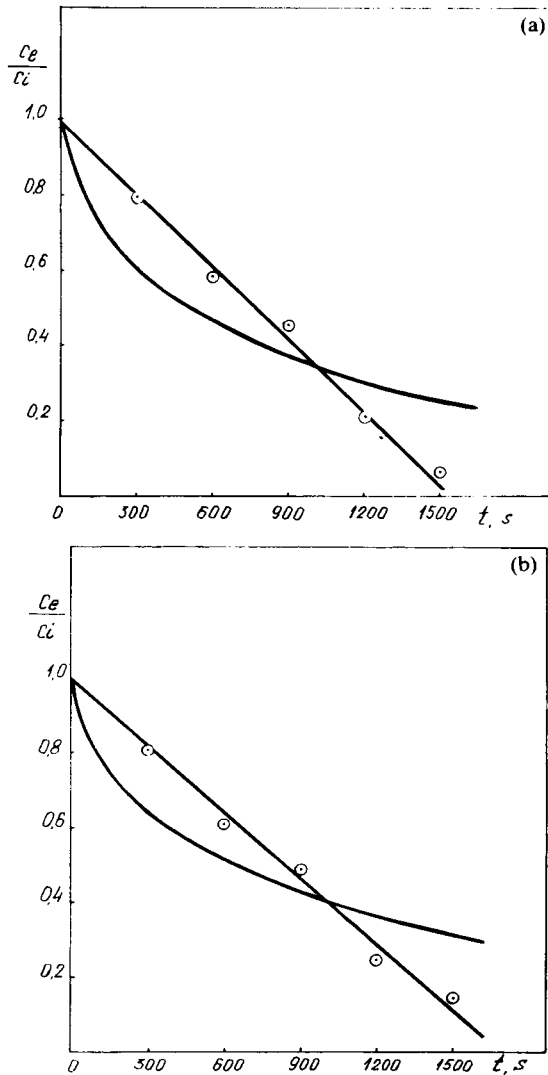


Fig. 2. Effect of the treating time on the residual monomer concentration at temperature 90°C and nitrogen velocity 0.12 m/s for the fractions of average sizes (a) 0.09 mm, (b) 0.112 mm (c) 0.142 mm, and (d) 0.170 mm.

Using these values, the theoretical curves of monomer desorption were calculated and plotted on Figure 2a–d. It can be seen that they deviate considerably from the experimental results. The negative deviation for the first time intervals can be explained by the particle agglomeration resulting in a limited gas contact. Some patents<sup>12,13</sup> claim a prewetting of the powdered material by suitable liquids, aiming to decrease the agglomeration. The lower initial temperature of the sample at the beginning of the treatment could also cause a negative deviation. The positive difference at the end of the process can be explained by the particles' degradation (Table I). The resulting values for the diffusion coefficient are only apparent ones. They differ considerably from

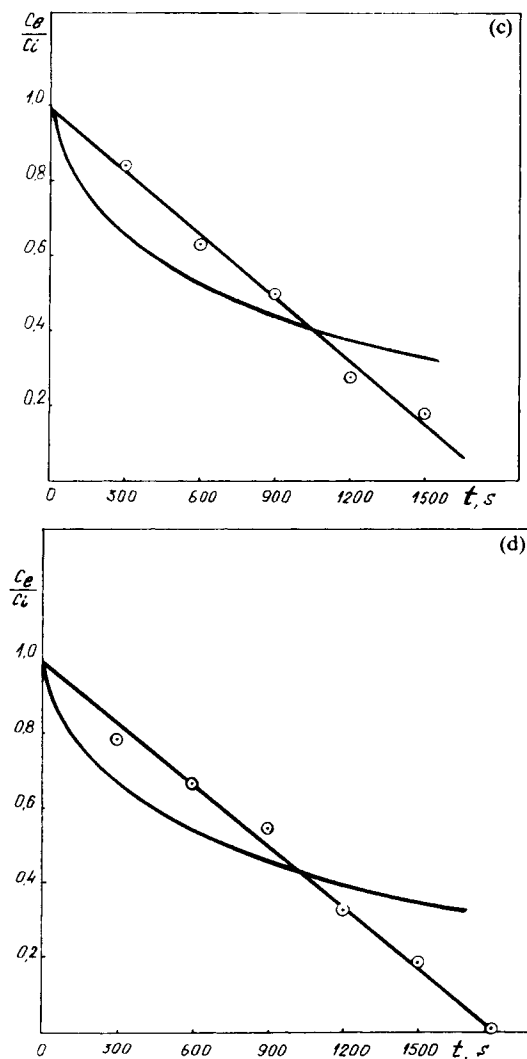
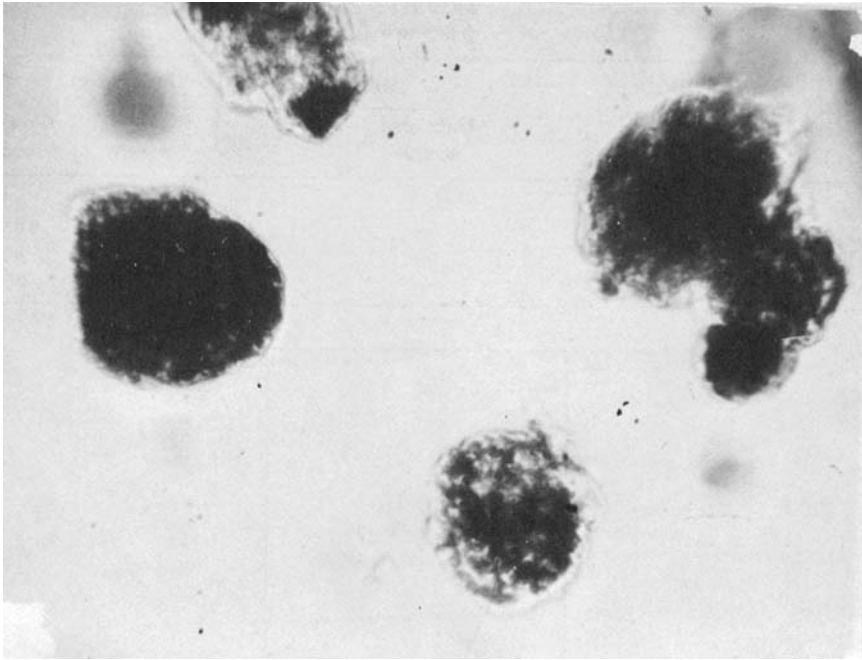


Fig. 2. (Continued from the previous page.)

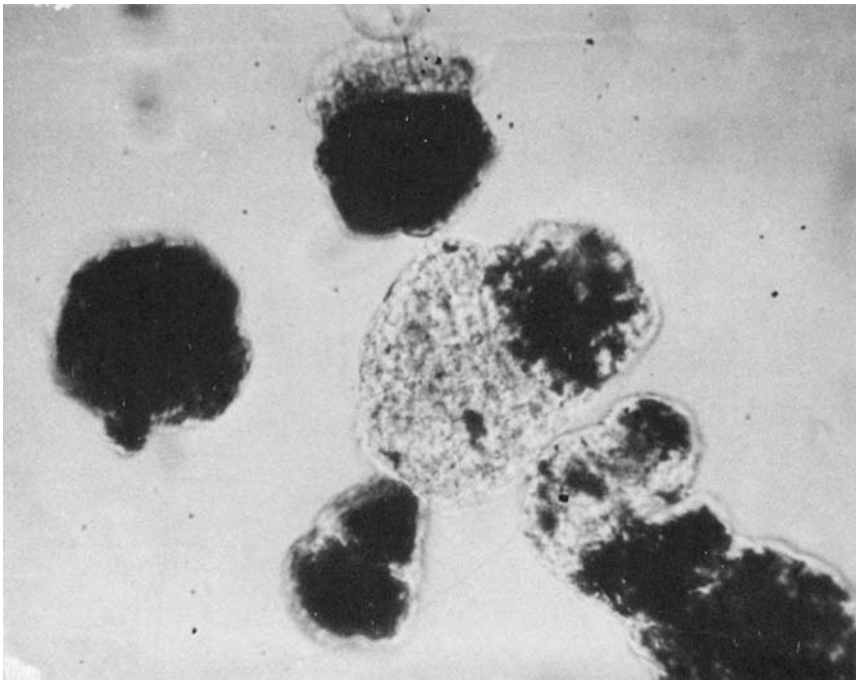
those calculated by Eq. (2). If these values were used for calculating the required time of treatment by Eqs. (1) or (3) for particles, whose sizes are estimated on the base of the sieve analysis, this will result in oversizing the equipment.

Figure 2 shows that the time for obtaining free monomer concentration below 10 ppm in PVC for different fractions at 90°C is in the range of 25–30 min. If the initial vinylchloride content is 138 ppm, at the same temperature and fraction 0.063–0.2 mm, this time is about 20 min (Fig. 4). As one can expect, taking into account the information from Figure 2, the linearity of the  $C_e/C_i = f(t)$  dependence is retained for this wider fraction, as well.

Treating time for reaching the required low content of free monomer can be decreased by increasing the temperature (Fig. 5). The optimum combination



(a)



(b)

Fig. 3. Microscope pictures of polyvinylchloride particles prior to treating ( $\times 200$ ).

TABLE I  
Decrease of Particle Size in Treated PVC

Sieve size (mm)	Material retained on the sieve (g)	
	Untreated sample	Treated sample
0.16	29.9	4.17
0.125	—	16.99
0.1	—	6.29
0.063	—	2.00

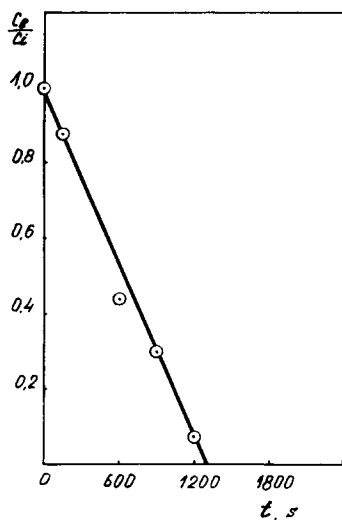


Fig. 4. Effect of treating time on the residual monomer content at 90°C for the fraction of particle sizes 0.063–0.2 mm and initial concentration 138 ppm.

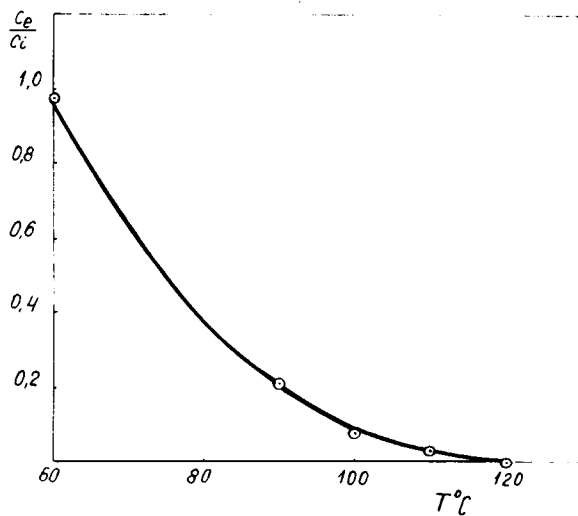


Fig. 5. Effect of temperature on the residual monomer concentration in the fraction 0.063–0.2 mm for treating time 15 min and nitrogen velocity 0.12 m/s.



TABLE II  
Fickentscher Constants of the Treated and Untreated PVC

Sample no.	Treating conditions		K values
	Temperature (°C)	Duration (min)	
1		Untreated	57.1
2	100	15	57.1
3	110	15	57.1
4	90	40	57.1
5	90	20	57.1

of temperature and time of treating must be determined for every particular case by technical-economic evaluations.

Another very important problem in PVC thermal treatment in inert gas flow is the polymer quality preservation. For this reason the Fickentscher constant of the original PVC and for some of the treated samples was estimated. The samples were tested under the most severe conditions (long duration, high temperature treatment). The obtained results are shown in Table II.

Visual observations on the samples did not show any changes in their color. All results show that thermal treatment in nitrogen flow at temperatures up to 110°C does not lead to polymer degradation.

### CONCLUSIONS

The present investigation shows that by thermal treating of suspension PVC at 90–120°C in a fluidized bed, created by nitrogen flow, the free monomer content can be decreased from 203 ppm to the limits established by the health authorities. The monomer concentration decreases linearly with time, which cannot be predicted by a model of molecular diffusion in single spheres of uniform sizes. This pattern is probably due to the degradation of agglomerates resulting in formation of new contact surfaces with the gas phase. Treatment under the conditions described above up to the point of complete vinylchloride removal does not cause a detectable polymer destruction.

### NOMENCLATURE

- $C_e$  vinylchloride concentration at the end of the treatment (ppm)  
 $C_i$  initial monomer concentration in the polymer (ppm)  
 $d$  diameter of the particle (m)  
 $D$  effective molecular diffusion coefficient of the vinylchloride in the polymer (m<sup>2</sup>/s)  
 $M_\infty$  initial monomer quantity in the particle (kg)  
 $M_t$  quantity of the removed vinylchloride from the particle after a given time of thermal treatment (kg)  
 $R$  universal gas constant

$t$	duration of the thermal treatment of the particle (s)
$T$	temperature (K)
$\alpha$	coefficient of mass-transfer from the particle to the gas phase (m/s)
$Bi = \frac{d\alpha}{2D}$	Bio number, dimensionless number for evaluating the ratio of external diffusion rate to the internal one

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