

Structural Heterogeneities of Suspension Poly(vinyl Chloride). II. Formation of Compact Glassy Particles and the Cause of Their Difficult Processing

RUDOLF LUKÁŠ, JAROSLAVA MICHALCOVÁ, and VĚRA TYRÁČ KOVÁ, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

Synopsis

By modifying the polymerization process of suspension polymerization of vinyl chloride, poly(vinyl chloride) (PVC) samples were prepared containing various amounts of compact glassy particles. It was found that these particles probably arise by a different polymerization mechanism than usual suspension particles, namely, as a result of the nonhomogeneous distribution of initiator in vinyl chloride drops of the polymerization system. It was proved experimentally that the lower heat stability of difficultly processible particles is due to a side reaction between the initiator radical and the PVC polymer chain which causes dehydrochlorination of PVC already under polymerization conditions. This reaction may also explain the yet unknown mechanism of formation of internal double bonds in PVC produced by the radical polymerization of vinyl chloride. In conclusion, the difficult processibility of compact glassy particles is discussed as a consequence of the insufficient drying of these particles in the usual drying process.

INTRODUCTION

The presence of particles ranging from difficultly processible to unprocessable in PVC powders has a negative effect on the quality, appearance, and transparency of products from plasticized PVC. The only method which allows us to determine the amount of these particles in PVC powders is to prepare foils filled with soot in which these particles appear as colorless translucent points known in the literature as "fish eyes" (FE particles). These particles are the originally difficultly processible particles in PVC powders altered by processing; unlike FE particles which appear in the foils, they are referred to below as precursors of FE particles (PFE particles).

In our preceding paper¹ PFE particles were defined as particles which, if treated with a plasticizer during polymer processing, do not pass into the gel-like state at all or pass only with difficulty. Such particles must differ from the common particles of suspension PVC either in the structure on the molecular level (particles containing crosslinked or strongly branched macromolecules) or in morphology, i.e. in the supermolecular structure, or in both structures simultaneously. To decide which of these structures accounts for the difficult processibility of PFE particles or which of them predominates, we prepared laboratory samples of suspension PVC with a high content of difficultly processible PFE particles. The particles were

isolated and subjected to a morphological investigation which revealed that the PFE particles under study are nonporous compact glassy particles. Their structure was also examined viscometrically, by the light scattering method, GPC, IR spectroscopy, and X-ray diffraction; their specific surface area and heat stability were also measured. The results showed¹ that the difficult processibility of PFE particles compared with the usual particles of suspension PVC is not due to differences on the level of molecular structure, but is a consequence of their different morphology. This study is concentrated on the elucidation of causes of formation of compact glassy particles and on the solution to the question why processibility of these particles is so much affected by their morphology.

EXPERIMENTAL

Materials

The formation of difficultly processible particles was investigated using the modified suspension polymerizations of vinyl chloride^{1,2}: 0.28 g dilauroyl peroxide, 0.09 g dicetylperoxydicarbonate, 12 mL of a 3.8 wt % aqueous solution of hydroxypropylmethylcellulose, 10 mL of a 1 wt % aqueous solution of sodium hydroxide, and 350 mL of distilled water were gradually introduced into a 1 L glass reactor (Ingenierbureau, SFS, Zurich, Switzerland) provided with built-in stops and a propeller stirrer. The mixture was stirred 15 min (500 rpm) at room temperature, and after that 200 mL of vinyl chloride was added without stirring. The polymerization mixture was stirred at 500 rpm, and the polymerization temperature of 54°C was reached within 15 min. The polymerization times were 2.5, 4.5, and 6 h (the respective polymerizations being I, II, and III). Polymerizations IV and V were carried out under the same polymerization conditions (amount of polymerization components, time, temperature, stirring) as in the case of polymerization III, but the polymerization mixtures were prepared as described below: The aqueous phase containing hydroxypropylmethylcellulose and sodium hydroxide was homogenized by stirring 15 min at 500 rpm. After that, vinyl chloride was added without stirring and, into the layer thus formed, the initiators dissolved either in 10 mL of pentane (polymerization IV) or in 7 mL of vinyl chloride (polymerization V) were added with a pressure burette. To homogenize the initiators uniformly in the whole volume of the vinyl chloride layer, the polymerization mixture was cautiously stirred for 5 min, in such a way that the mixing of water and monomer phases was prevented. The revolutions of the stirrer were then increased to 500 rpm and the thermostating of the polymerization mixture was started. The results are summarized in Table I.

Reactions of dilauroyl peroxide and dicetylperoxy dicarbonate with PVC (Neralit S-682, Spolana Neratovice, Czechoslovakia) were produced by heating PVC foils containing these peroxides and by heating THF solutions of PVC with peroxides to 54°C for 8 h (Table II). Solutions of PVC and peroxides in THF were prepared in argon atmosphere in which also the reactions described above were carried out. On completion of the reaction (a) the PVC

TABLE I
Formation of Difficultly Processible Particles in the Course of the Suspension
Polymerization of Vinyl Chloride

Polymerization	Polymerization temperature (°C)	Polymerization time (h)	Conversion (%)	Number of FE particles ^a per 1 g of polymer
I	54	2.5	31.7	430
II	54	4.5	54.4	710
III	54	6.0	76.2	1100
IV ^b	54	6.0	77.9	3
V ^c	54	6.0	78.5	1

^a For the meaning of FE particles, cf. text.

^b Initiation system dosed dissolved in pentane.

^c Initiation system dosed dissolved in vinyl chloride.

foils were extracted with diethyl ether for 8 h and dried at 40°C in the vacuum of a water and oil pump, or (b) PVC was precipitated from THF solutions with methanol, isolated PVC samples were precipitated three times in the system deperoxidized THF-methanol and dried by the same procedure as that used in the case of PVC foils.

Methods

Electron Microscopy. Vacuum gold sputtering was used to deposit a gold layer c.10 nm thick on PVC samples. A Balzers sputtering apparatus was used at a pressure of 13.3 Pa at 15 mA for 3 min. Micrographs were

TABLE II
Reaction of PVC with Dilauroyl Peroxide (DLP) and Dicylperoxy Dicarboxylate (DCPDC) at 54°C, Reaction Time 8 h

Sample ^a	Type and concentration of initiator ^b (mol %)	Concentration of double bonds [(mol/g) × 10 ⁴]	Number of structural PVC units per one double bond
1	—, —	0.20	790
2	DLP, 1.9	0.46	354
3	DLP, 3.8	0.55	294
4	DLP, 7.6	0.67	240
5	DCPDC, 1.4	0.42	380
6	DCPDC, 2.8	0.50	322
7	DCPDC, 5.6	0.62	261
8	—, —	0.20	790
9	DLP, 0.3	0.27	597
10	DLP, 0.6	0.32	505
11	DLP, 1.2	0.38	431
12	DCPDC, 0.2	0.26	613
13	DCPDC, 0.4	0.29	560
14	DCPDC, 0.8	0.32	505

^a Samples 1–7 represent the reaction between initiator and PVC in foils; samples 8–14 represent the reaction between initiator and PVC in THF solutions.

^b Related to moles of PVC.

obtained by means of a scanning electron microscope (JSM-35, JEOL) at 25 kV, magnifications $200\times$, $2000\times$.

Infrared Spectroscopy. Infrared spectra were measured with a Perkin-Elmer 580 B Spectrometer by the KBr pellet technique using the same weight concentration for all PVC samples (10 mg per pellet).

Dehydrochlorination Tests. The dehydrochlorination apparatus has been described previously.³ The samples were degraded at 180°C in a stream of nitrogen and their conversion ξ and dehydrochlorination rate time dependence, $\Delta\xi/\Delta t = f(t)$, were calculated from the amount of released hydrogen chloride determined potentiometrically.³⁻⁵

Determination of Double Bonds. The total numbers of double bonds in samples were determined ozonometrically, using quantitative addition of ozone on multiple bonds. Measurements were performed with an ADS-3-VD (USSR) ozonometer, flow rate of O_2 10 L/min, voltage 5500 V. Under such conditions a constant amount of ozone corresponding to $6 \times 10^{-6} \text{ mol} \cdot \text{min}^{-1}$ was generated in oxygen. A change in ozone concentration due to addition to the double bonds was recorded with a UV detector. The number of double bonds, D ($\text{mol} \cdot \text{g}^{-1}$ of the sample), was calculated from

$$D = \frac{C}{a}(I - I_r) \quad (1)$$

where I is the number of pulses corresponding to a change in ozone concentration in the injected sample, I_r is correction of the number of pulses for absorption by the solvent corresponding to the injected volume, a is the sample weight (g), C is the proportionality constant defined by

$$C = \frac{a_s V_r N}{M_s V_0 (I_s - I_r)} \quad (2)$$

where a_s is the weighed standard added to the solvent volume V_0 , V_r is the injected volume of standard solution, M_s is molecular weight of the standard (stilben), I_s is the number of pulses corresponding to a change in ozone concentration after injection of the standard, I_r is correction in the number of pulses for the volume of injected solvent, and N is the number of multiple bonds in the molecule of the standard.

Determination of "Fish Eyes" Particles. A standard method as given by the Czechoslovak Office for Normalization and Measurement (ČSN 643,200) was used for the determination of FE particles⁶: A mixture of 140 g PVC, 60 g dioctyl phthalate, 2 g lead (II) stearate, and 1 g carbon black (Urx Works, Ostrava, Czech.) was calandered on a laboratory two-roll mill Schwabenthan Polymix U 200, friction 1:1.3, 24 rpm, $152 \pm 2^\circ\text{C}$, thickness of calandered foil 1.0 ± 0.1 mm. A sample (3 g) was taken from the centre of the foil thus obtained and molded on a laboratory press Schwabenthan Polystat S 300 at $165 \pm 5^\circ\text{C}$. The foil, 0.10 ± 0.02 mm thick, was used for the determination of unprocessed FE particles by means of a slide projector.

RESULTS AND DISCUSSION

The basic finding which ensued from experimental measurements carried out in the preceding study¹ was that in the course of polymer processing, compact glassy particles form FE particles in standard foils, and are therefore typical PFE particles. Standard foils prepared according to the standard of the Czech. Office for Normalization and Measurement are of defined thickness, and it is obvious, therefore, that only compact glassy particles having a diameter larger than the thickness of these foils are detected as FE particles in the determination of the amount of FE particles. Compact glassy particles with a diameter smaller than the thickness of standard foils are not detected as FE particles; hence, although they are also difficultly processible, formally they are not PFE particles. This drawback of the standard method, i.e., the dependence of the amount of FE particles to be determined on the thickness of the standard foil often is the cause of a different evaluation of PVC powders in various laboratories, e.g., when the suitability of PVC powder for the preparation of transparent foils is to be determined. With respect to the difficult separation of small compact glassy particles, this study, similarly to the preceding one,¹ is concerned only with compact glassy particles having a diameter larger than the thickness of standard foils, i.e. in our case with particles with a diameter larger than c. 100 μ m.

Formation of Compact Glassy Particles

In our preceding article¹ we investigated the physicochemical properties of samples of PFE particles and of common particles of suspension PVC isolated in the same suspension polymerization of vinyl chloride. We found that compared with the usual particles of suspension PVC, PFE particles possess a lower heat stability, because they contain a higher concentration of double bonds, and thus also a higher concentration of allyl-activated chlorine atoms which are sites of initiation of the thermal dehydrochlorination of PVC.^{4,5} A question must therefore be solved why PFE particles contain a higher concentration of double bonds.

In view of compactness of the glassy PFE particles under investigation, one could assume overheating of these particles due to the relatively insufficient removal of the reaction heat from polymer particles into the aqueous phase. Since, however, molecular parameters of macromolecules in PFE particles are the same as those of macromolecules contained in the usual particles of suspension PVC and since in the samples of PFE particles no traces of branching or crosslinking of macromolecules could be detected,¹ it may be assumed that no overheating of PFE particles takes place during the polymerization. In connection with the investigation of the mechanism of thermal degradation of PVC, it was found that the thermal degradation of PVC foils proceeds in presence of dilauroyl peroxide at a temporarily increased rate of dehydrochlorination.⁵ Similarly, with respect to the observed acceleration of dehydrochlorination of PVC with dilauroyl peroxide, we formulated a working hypothesis, according to which the dehydrochlorination of PVC may be produced by radicals arising by the decomposition of the initiator already under the polymerization conditions. Since

the higher concentration of double bonds was present in PFE particles and not in common particles of suspension PVC, we assumed, furthermore, that PFE particles arise from vinyl chloride drops containing a major amount of initiator; in other words, we assumed a nonhomogeneous distribution of initiator in vinyl chloride drops of the dispersion system of suspension polymerization of vinyl chloride.

Vinyl chloride in an aqueous suspension is polymerized in the presence of protective colloids, in our case, hydroxypropylmethyl cellulose, which at the beginning of polymerization stabilizes the organic phase against coalescence and prevents the later aggregation of polymer particles formed in the process. Already at an early stage of polymerization a skin of pericellular membrane consisting of the graft copolymer of vinyl chloride and protective colloid is formed on the surface of monomer vinyl chloride drops⁷; this skin prevents coalescence of the dispersed organic phase. It is obvious, therefore, that the thermodynamically controlled coalescence of vinyl chloride and initiator drops must proceed quickly, before the skin of pericellular membrane is formed on the drops. Distribution homogeneity of the initiator should be achieved more readily by dosing the initiator as a solution in the monomer or in a suitable solvent.

Nonhomogeneous distribution of the initiator may also be explained by the diffusion degradation of the suspension of initiator and monomer. From the thermodynamical point of view the molecular diffusion of initiator and monomer depends on the size of drops in which these components are dispersed; the solubility of initiator and monomer increases with decreasing drop size.⁸ In the initial stage of formation of the aqueous vinyl chloride suspension the small drops of initiator disappear quickly; its molecules diffuse into large monomer drops which represent the main fraction in the size distribution of monomer drops. In the initial stage the ratio of the fraction of initiator drops which participate in the fast diffusion to that of large monomer drops determines the number of monomer drops in which the polymerization will start. An analogous mechanism may also be considered for the molecular diffusion of small vinyl chloride drops into large initiator drops. The ratio of the amount of small monomer drops to that of large initiator drops will determine the polymerization in the initiator drops, and thus the formation of PFE particles. In connection with this mechanism one should consider that in those drops into which the monomer has penetrated by diffusion the polymerization will set in, and the polymer thus formed will stabilize the forming particle against diffusion degradation, because macromolecules are not capable of molecular diffusion through the aqueous phase. This mechanism explains not only the formation of PFE particles in the initial stage of polymerization, but also its further formation in the course of polymerization. The mechanism just described makes the polymerization set in only in a certain fraction of initiator drops; small monomer particles disappear quickly due to molecular diffusion, both into large initiator and monomer drops in which the polymerization has already set in. As a result, only a certain fraction of large initiator drops contains the monomer. In the following stage the diffusion processes are slowed down, because the finest initiator and monomer drops have disappeared, and, consequently, large initiator drops in which the polymerization has not yet begun are present in the system.

It may be deduced from these views that if PFE particles arise due to the nonhomogeneous distribution of initiator in monomer drops, the PFE particles must be present in PVC already at low conversions of polymerization. For this reason, vinyl chloride was polymerized first to various degrees of conversion (polymerizations I,II,III). The results summarized in Table I suggest that with increasing conversion of vinyl chloride the number of FE particles in the standard foils under investigation increases; a large amount of PFE particles already contains PVC obtained in polymerization I (conversion of vinyl chloride 31.7%). Dosage of the initiator in pentane (polymerization IV) or in vinyl chloride (polymerization V) leads virtually to the disappearance of FE particles (Table I).

Further information was provided by scanning electron microscopy. Figure 1 shows scanning electronmicrographic sections of the developing PFE particles of various conversion stages of polymerization (polymerizations I, II, III, Table I). While due to the existence of internal pores a PFE particle from polymerization I (conversion of vinyl chloride 31.7%) still appears as a white particle, a PFE particle from polymerization II (conversion of vinyl chloride 54.4%) already contains much fewer internal pores and therefore seems to be grey; and a PFE particle from polymerization III (conversion of vinyl chloride 76.2%) is already virtually a monolithic compact glassy particle. An interesting finding is that which concerns the inner structure of a PFE particle from polymerization I, well visible at the magnification 2000x in Figure 1(f). In the inner structure of this soft spongy particle one can see large pores usual for common particles of suspension PVC. It seems surprising, however, that the observed inner structure does not contain microglobular domains typical of suspension particles^{1,9} and arising by the aggregation of microglobules of primarily precipitated polymer particles.⁷ It follows from the character of the inner structure that the polymerization of vinyl chloride does not proceed in PFE particles via the typical precipitation mechanism. We imagine the probable mechanism of polymerization of vinyl chloride in PFE particles to be like this: The source of PFE particles is represented by dispersed large drops of initiator which did not manage to undergo coalescence with drops of vinyl chloride. Vinyl chloride is intensively diffused through the water phase into drops of initiator where it is immediately polymerized on the decomposing initiator. At the polymerization temperature used (54°C) the initiators, both dilauroyl peroxide (DLP) and dicetylperoxy dicarbonate (DCPDC), are in the liquid state and, judging by their solubility in 2,4-dichloropentane, are also capable of solvating the forming polymer PVC chains, at least to a limited extent. In the polymerization of vinyl chloride proceeding as described, the primary polymer particles do not precipitate, microglobular aggregates are not formed, and the polymerization proceeds quickly from the surface to the center of the arising PFE particle until the latter is completely polymerized. Such a concept of the formation of a PFE particle is an extreme, assuming that no coalescence of the initiator drop with the vinyl chloride drop takes place. A similar polymerization process may, however, also be assumed for vinyl chloride drops with a high concentration of initiator, arising by the coalescence of the monomer and of the initiator drop, when vinyl chloride is quickly consumed in the monomer drop and the further polymerization proceeds already by the mechanism described above.

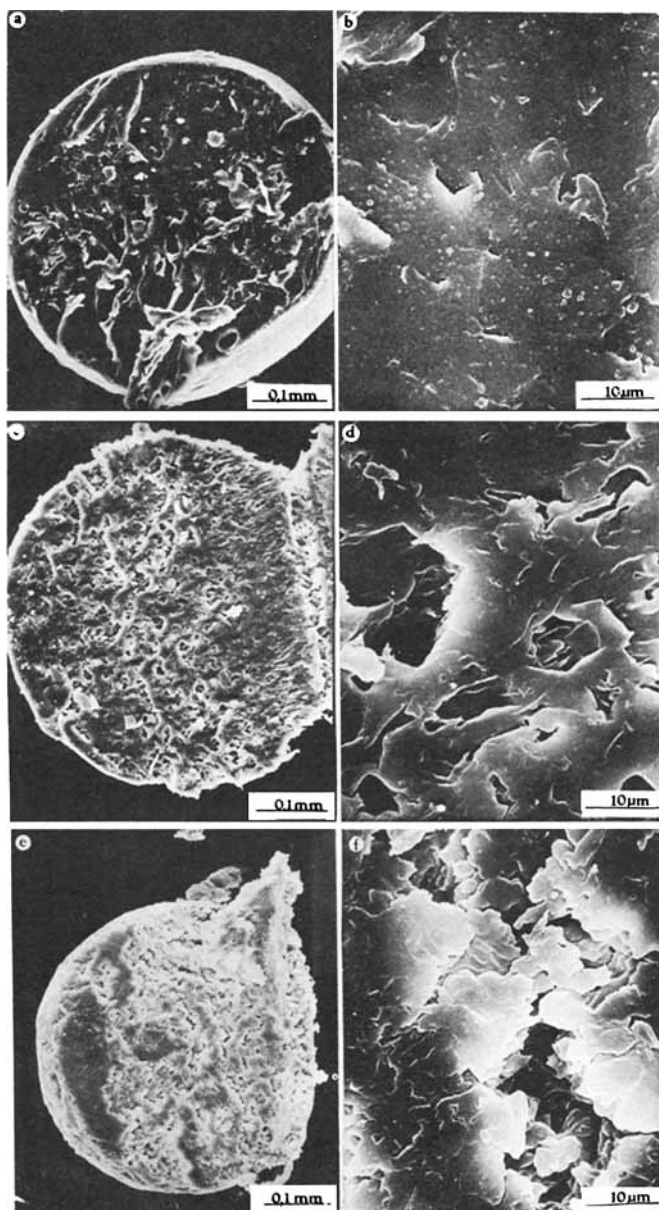


Fig. 1. Scanning electronmicrographs of PFE particles from various stages of the suspension polymerization of vinyl chloride: (a,b) section and a detail of section of a PFE particle from polymerization III (conversion 76.2%); (c,d) section and a detail of section of a PFE particle from polymerization II (conversion 54.4%); (e,f) PFE particle and a detail of its section, sample from polymerization I (conversion 31.7%).

The suggested mechanism of formation of PFE particles assumes solvation of PVC chains by molecules of the initiator. Since the polymerization in these particles proceeds probably with a relative deficiency in free vinyl chloride, it may be assumed that radicals arising by the decomposition of the initiator vigorously attack the polymer PVC chains in their vicinity,

which might lead to the dehydrochlorination of structural PVC units and to an elucidation of the observed higher concentration of double bonds in PFE particles. We therefore attempted a model investigation of the reaction between DLP and DCPDC, on the one hand, and PVC, on the other, both in PVC foils and in THF solutions of PVC. The reaction time and temperature were chosen similarly to the polymerization conditions. The results given in Table II and Figure 2 demonstrate that both in the case of DLP and in that of DCPDC, in foils and in THF solutions of PVC the number of double bonds in polymer PVC chains increases; hence, initiator radicals cause the dehydrochlorination of PVC already under the polymerization conditions. It can be seen in Figure 2 that PVC samples with a higher content of double bonds obtained by reacting DLP and DCPDC with PVC foils are dehydrochlorinated more quickly than a PVC sample treated in the same way, without addition of the initiator. All these experiments also allow us to assume that the so-far unknown formation of internal double bonds⁷ in PVC prepared generally by the radical polymerization of vinyl chloride is a consequence of the side reaction between the initiator radical and the polymer PVC chain.

It may be concluded, therefore, that the results obtained confirm the assumed influence of the nonhomogeneous distribution of initiator in vinyl chloride drops on the formation of FE particles. In a recently published paper¹⁰ the firm Akzo Chemie also considers the nonhomogeneous distribution of initiator in vinyl chloride drops as the cause of formation of FE particles; these findings are thus in agreement with our conclusions.

Difficult Processibility of Compact Glassy Particles

The study of physicochemical properties of compact glassy particles has revealed that macromolecules of these PFE particles do not differ in their

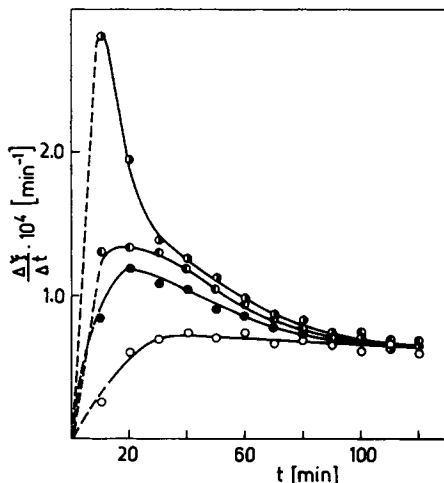


Fig. 2. Dehydrochlorination rate time dependence of PVC after the reaction with radical initiators: (○) PVC from blank test, $A = 790$; (●) PVC from the reaction with various concentration of DLP, $A = 294$; (◐) $A = 240$; (◑) PVC from the reaction with DCPDC, $A = 261$; DLP, DCPDC = dilauroyl peroxide and dicetylperoxy dicarbonate respectively, A = amount of structural PVC units per one double bond (Table II).

molecular structure from macromolecules of common particles of suspension PVC to any important degree. Within the limits of experimental error their distribution curves of molecular weights are the same; they are neither branched nor crosslinked.¹ It seems evident, therefore, that the different morphology of these particles is the cause of their difficult processibility. It can be seen in a scanning electronmicrograph section through a typical PFE particle with a diameter of c. 450 μm [Figs. 1(a),(b)] that the inner structure of these particles consists of compact hard material, with an insignificant number of inner pores. When describing the morphology of a similar PFE particle in the preceding paper¹, we reported that the inner structure of these particles was passing into the particle surface proper in a continuous manner, without the surface shell being discernible, and, also, that the surface of these particles is smooth, finely granular at larger magnifications, resembling orange peel and having traces of closed large pores. These particles have a small specific surface area (0.03 m^2/g), approaching the theoretical value of the specific surface area of model smooth glass spheres (0.005–0.03 m^2/g). Since in the processing of the polymer the transition of polymer particles into the gel-like state is controlled by diffusion of the plasticizer into polymer particles, it may be assumed that it is just the slow diffusion of the plasticizer into nonporous compact glassy PFE particles that is the cause of their difficult processibility. This conclusion does not explain, however, why a section of a PFE particle or a section of a FE particle obtained by microtone from a standard foil swells only reluctantly and slowly after being treated with a plasticizer.¹¹

In our preceding paper¹ we compared the IR spectra of samples of PFE particles and of common polymer particles of suspension PVC. The only difference found in the IR spectrum of PFE particles was an absorption band of conjugated double bonds at 1610 cm^{-1} . In addition, in repeated measurements of IR spectra of PFE particles we found that the IR spectra of similarly dried samples of PFE particles and of the common polymer PVC particles differ also in the intensity of the absorption band with a maximum at c. 3450 cm^{-1} , which means that the samples taken for comparison contain different amounts of hydroxyl groups, probably water (Fig. 3). With respect to the character of PFE particles, this finding is not so surprising, because it may be assumed that the morphology of these particles renders their drying difficult. Since the moisture present in polymer

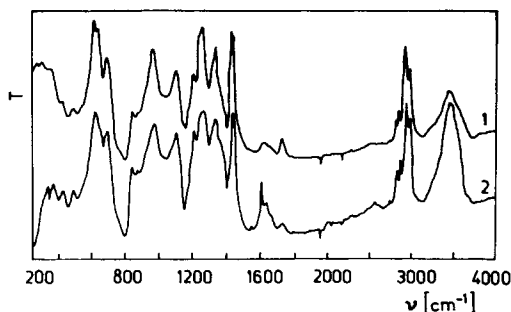


Fig. 3. Infrared spectra of PVC samples: (1) of common particles of suspension PVC; (2) of PFE particles; samples isolated from polymerization III and dried at 40°C for 60 h (Table III).

TABLE III
Effect of Drying on the Amount of Difficultly Processible Particles

Sample, type of drying	Temperature of drying (°C)	Time of drying (h)	Number of FE particles per 1 g of polymer
From polymerization III, dried in the usual laboratory drying box	40	24	2300
	40	60	1100
From polymerization III, predried 60 h at 40°C, dried over P ₂ O ₅ in the vacuum of an oil pump	25	24	60

particles might repel the plasticizer or impede its diffusion into the particles, we examined for PVC samples obtained by polymerization III (Table I) the effect of intensive drying on the formation of FE particles. The results summarized in Table III show that the drying of the PVC sample leads to a considerable decrease in the number of FE particles. Thus, the observed dependence of the amount of FE particles on the time of blending of the little dried PVC sample used in the processing (Table IV, Fig. 4) may be explained by a mechanical processing of PFE particles connected with their additional drying. The observed effect of the intensity of drying on the formation of FE particles is so important as to bring us to a conclusion that the difficult processibility of compact glassy particles is predominantly due to the presence of moisture in micropores of these particles.

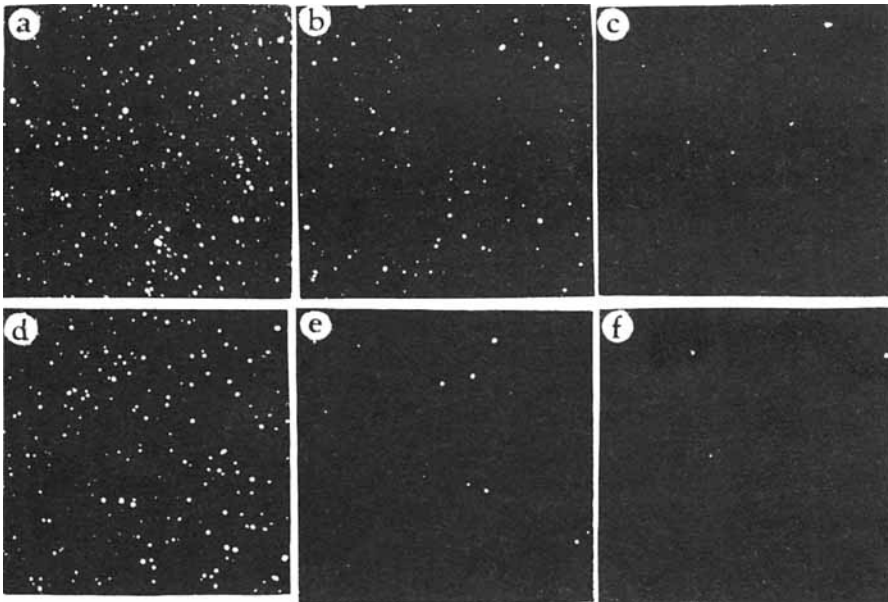


Fig. 4. Dependence of the number of FE particles on the intensity of drying and time of blending. PVC sample from polymerization III dried (a) 24 h at 40°C; (b) 60 h at 40°C; (c) 60 h at 40°C, and then in vacuum over P₂O₅ for 24 h at 25°C; PVC sample from polymerization III dried at 40°C for 24 h blended: (a) 10 min; (d) 20 min; (e) 40 min; (f) 60 min. (Micrographs of parts of standard foils demonstrate the loss of FE particles only qualitatively. Numbers of FE particles are given in Tables III and IV.)

TABLE IV
Effect of the Time of Blending on the Number of Difficultly Processible Particles^a

Time of blending (min)	10	20	30	40	50	60
Number of FE particles per 1 g of polymer	2300	1300	570	95	50	30

^a A PVC sample from polymerization III dried in the usual laboratory drying box at 40°C, for 24 h was processed by extending the blending time in the standard procedure of determination of the number of FE particles; cf. Methods.

CONCLUSIONS

1. Nonhomogeneous distribution of the initiator in vinyl chloride and especially large drops of the initiator cause the formation of difficultly processible compact glassy particles, the so-called PFE particles.

2. The polymerization of vinyl chloride in forming PFE particles probably proceeds via a different mechanism than that involving the common particles of suspension PVC.

3. The lower heat stability of PFE particles is a result of the side reaction between the initiator radical and the polymer PVC chain. This reaction leads to the dehydrochlorination of PVC already under polymerization conditions.

4. The difficult processibility of PFE particles may be explained by a higher moisture content due to the poor drying of the particles in the common drying process.

5. The still unexplained formation of internal double bonds in PVC prepared by the general radical polymerization of vinyl chloride may be explained by a side reaction of the initiator radical.

The authors thank Dr. K. Bouchal for valuable comments on the formulation of the mechanism of formation of PFE particles.

References

1. R. Lukáš, V. Tyráčková, and M. Kolínský, *J. Appl. Polym. Sci.*, **29**, 901 (1984).
2. Czechoslovak Appl., PV-5253/83 (July, 1983).
3. J. Michalcová, R. Lukáš, and M. Kolínský, Proceedings of the Vth National Conference MAKROTEST, Pardubice, Czech, Preprint 231, 1978.
4. J. Světlý, R. Lukáš, J. Michalcová, and M. Kolínský, *Makromol. Chem., Rapid Commun.*, **1**, 247 (1980).
5. J. Světlý, R. Lukáš, J. Michalcová, and M. Kolínský, *Makromol. Chem.*, **185**, 2183 (1984).
6. A. Šarman, J. Kopal, and J. Kobes, Proceedings of the XIVth Days of New Technique, Bojnice, Czech, Preprint 107, 1979.
7. J. A. Davidson and D. E. Witenhafer, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 51 (1980).
8. W. I. Higuchi and J. Misra, *J. Pharm. Sci.*, **51**, 459 (1962).
9. L. M. Barclay, *Angew. Makromol. Chem.*, **52**, 1 (1976).
10. Technical Bulletin, Akzo Chemie, Noury Initiators, in *From Vinyl Chloride to PVC: By Which Initiator*, p. 8, 1983.
11. Z. Pelzbauer and F. Lednický, unpublished results.

Received May 15, 1984

Accepted June 19, 1984