

Structural Heterogeneities of Suspension Poly(vinyl Chloride). I. Compact Glassy Particles

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Synopsis

By using the modified suspension polymerization of vinyl chloride, samples of poly(vinyl chloride) (PVC) were prepared with a high content of unprocessable particles which were isolated and subjected to a morphological investigation. Their structure was examined viscometrically, by the light-scattering method, GPC, IR spectroscopy, and X-ray analysis; the specific surface area of the particles was measured, and their heat stability was determined. The results lead to a conclusion that the unprocessibility of the particles compared with the usual particles of suspension PVC is not caused by differences on the level of molecular structure, but ensues from the difference in their morphology.

INTRODUCTION

The polymerizations of vinyl chloride in aqueous dispersions known as suspension, microsuspension, and emulsion polymerizations are the polymerization processes most in use for the production of PVC. Of these, the suspension polymerization of vinyl chloride is the most important: by employing this procedure, the physicochemical properties of PVC may be widely influenced on varying the polymerization conditions. An unwelcome effect which accompanies the formation of polymeric particles of suspension PVC is the formation of particles whose processibility ranges from difficult to virtually unfeasible. Their existence in the processed polymer particularly deteriorates its mechanical properties, the surface quality, appearance, and transparency of finished products. The problem of the existence of such particles was encountered by us in the course of evaluation of the processing properties of internally plasticized PVC prepared by the suspension polymerization of vinyl chloride in the presence of polymer plasticizers.¹ As generally the formation of these particles has not been explained unambiguously, and their structure has not been demonstrated, we tried to elucidate their character in some detail.

The only method which allows us to ascertain the number of unprocessable particles in PVC powders is based on the preparation of a foil filled with carbon black in which these particles appear as colorless translucent points known in the literature as "fish eyes" (FE particles). These particles are in fact the original unprocessable particles in PVC powders, altered mechanically, which unlike the FE particles occurring in the prepared foils are from here onwards called precursors of FE particles (PFE particles).

By summarizing the reported data,²⁻¹¹ it can be said that PFE particles, defined as particles which, during the polymer processing, change into the gel-like

state either with difficulty or not at all, must differ from the usual suspension PVC particles either in the structure on molecular level (particles containing crosslinked or strongly branched macromolecules) or in morphology, i.e., in the supermolecular structure, or in both structures at the same time. To decide on which level the structure of the PFE particles leads to the unprocessibility of these particles, or which of the structures predominates, is a difficult task, as in the polymer powder there usually is one PFE particle per some 10^5 ordinary particles of suspension PVC. Hence, to detect and separate PFE particles in order to examine their structure and properties is not easy.

Since up to now the investigation of PVC samples obtained by the usual polymerization procedure has not provided an unambiguous answer to the question regarding the nature of the PFE and FE particles, we attempted to prepare such PVC samples which would contain a large number of unprocessable particles. In these samples, our attention was focussed on the detection, separation and structural investigation of PFE particles, with the aim to deciding whether the unprocessibility of these particles was due to a different molecular or supermolecular structure.

EXPERIMENTAL

Sample Preparation. By using a modified procedure of the suspension polymerization of vinyl chloride¹² (initiation system dilauroyl peroxide and dicytetylperoxydicarbonate; stabilization of the suspension with hydroxypropylmethylcellulose, polymerization temperature 51°C , polymerization time 6 h, conversion 70%, polymerization denoted as I), PVC samples were prepared which, after being processed to foils, contained a large number of FE particles of different size. The PVC powders were therefore examined morphologically under an optical and an electron microscope, which revealed the presence of heterogeneous particles possessing the character of variously large nonporous compact glassy particles. The larger of these particles were trapped by sifting the samples on sieves with mesh size $250\ \mu\text{m}$. One part of the sample trapped in the sieve and containing mainly glassy particles was added to commercial PVC (Neralit, Spolana Neratovice, ČSSR) not containing any unprocessable particles. A foil prepared from such PVC mixture contained a large amount of FE particles, the number of which corresponded by its order of magnitude to the added amount of glassy particles. Also, differences in the size of FE particles approximately corresponded to those in the size of the observed glassy particles (Fig. 1). Thus, the added glassy particles behaved in the processing as PFE particles. Another

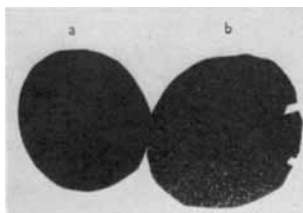


Fig. 1. PVC foils filled with carbon black prepared by the standard procedure for testing FE particles; (a) PVC Neralit; (b) PVC Neralit with the addition of sieve residue from polymerization I (photographed using diffusion counter-lighting, reduction 1:2.6).

modification of the polymerization process by changing the hydrodynamic conditions (polymerization II) gave a PVC sample containing only major glassy particles which could be trapped in sieves with mesh size 250 μm . The sifted polymer contained no glassy particles, and the foil prepared therefrom did not contain any FE particles. The sample thus prepared was therefore taken as a standard (PVC standard) for the investigation of the properties of glassy particles. Glassy particles (PVC-PFE) were isolated from the residue on the sieve by selecting them under an optical microscope (Carl Zeiss Jena, GDR, magnification 40 \times). Their addition to commercial PVC again induced the formation of FE particles in the process of foil production. In the course of determination of the molecular parameters of PVC samples, the unsorted residue of PVC trapped in the sieve (mesh size 250 μm ; PVC-SR) was also examined.

METHODS

Gel Permeation Chromatography. GPC measurements were carried out with an apparatus built at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, provided with a differential refractometer R 403 (Waters Associates, Milford, Mass.). The columns were thermostated to 25°C. Tetrahydrofuran (THF), distilled from cuprous chloride and potassium hydroxide in nitrogen, was used as the mobile phase at a flow rate of 0.375 mL/min. The elution volume was measured by means of a calibrated siphon (1.704 mL at a flow rate of 0.375 mL/min). The solutions were injected from a calibrated loop (1.636 mL).

Concentration of the injected solutions was 0.25% (w/v). The columns were packed with silica Sphérosil (Produits Chimiques, Péchiney-Saint-Gobain, France), types B,D,E, and arranged in a series containing two columns of each type in the order 2 \times E, 2 \times D, 2 \times B.

The universal calibration curve¹³ of the separation system was constructed by using polystyrene standards (Waters), for which (THF, 25°C) the Mark-Houwink equation is valid¹⁴:

$$[\eta] = 1.17 \times 10^{-4} M^{0.717} \quad (1)$$

The differential distribution curves, molecular weight averages, and intrinsic viscosities of the samples were calculated from the chromatograms by using the Mark-Houwink equation¹⁵:

$$[\eta] = 1.50 \times 10^{-4} M^{0.77} \quad (2)$$

which holds for linear PVC in THF at 25°C. No correction for axial dispersion was applied.

Light Scattering. Light scattering measurements were performed with a FICA 50 apparatus (ARL, France) with unpolarized light ($\lambda = 546 \text{ nm}$) and in the angular range of 30–150°. Benzene (Rayleigh ratio at 90°, $16.3 \times 10^{-6} \text{ cm}^{-1}$) was used as standard. Optically pure solutions were prepared by filtration through a Jena G5 sintered-glass filter under overpressure of nitrogen. The refractive index increment in THF determined with a Brice Phoenix differential refractometer (25°C, 546 nm) was $dn/dc = 0.107 \text{ cm}^3 \cdot \text{g}^{-1}$. Experimental data were treated by the Zimm method, i.e., by extrapolating Kc/R_θ values to zero angle and zero polymer concentration.

Viscometry. A standard Ubbelohde viscometer was used at $25 \pm 0.005^\circ\text{C}$. Solutions in THF were prepared by shaking at 40°C for about 2 h. \overline{M}_n values were calculated from eq. (2).

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/pellet).

Specific Surface Area. The specific surface area was measured by dynamic nitrogen desorption, using a Quantasorb apparatus (Quantachrome Corporation). The BET equation was applied in the calculations.¹⁶

Dehydrochlorination Tests. The dehydrochlorination apparatus has been described previously.¹⁷ 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.^{17,18}

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 obtained by means of a scanning electron microscope (JSM-35, JEOL) at 25 kV, magnifications 60 \times , 200 \times , 800 \times , and 3000 \times .

X-Ray Diffraction. X-ray measurements were made on a powder diffractometer (Hilger and Watts). $\text{CuK}\alpha$ radiation was recorded with a scintillation counter.

Determination of "Fish Eye" Particles. A standard method for the determination of FE particles as given by the Czechoslovak Office for normalization and measurements (ČSN 64 3200) was used in order to decide if the isolated compact glassy PVC particles are PFE particles.¹⁹ A mixture of 140 g PVC, 60 g dioctyl phthalate, 2 g lead (II) stearate, and 1 g carbon black (Urx Works, Ostrava, ČSSR) was calandered on a laboratory tworoll 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 center of the foil thus obtained and molded on a laboratory press (Schwabenthan Polystat S 300) at $156 \pm 5^\circ\text{C}$. The foil, 0.10 ± 0.02 mm thick, was used for the determination of unprocessed FE particles, e.g., by means of a slide projector. The number of FE particles thus determined usually relates to a standard area of the molded foil or to the unit weight of the polymer.

RESULTS AND DISCUSSION

As has been said above, the only method by which the amount of unprocessable or difficultly processible particles in powders can be determined consists in the preparation of carbon-black-filled foils by the standard procedure in which the particles appear as colorless translucent points—FE particles. Since the thickness of foils prepared in the standard way¹⁷ varies about 100 μm (in our case, 80–120 μm), it is obvious that only those unprocessable or difficultly processible particles whose diameter exceeds c. 100 μm appear as FE particles, and thus may be the sought PFE particles. Particles with a diameter below the foil thickness (c. 100 μm) cannot appear as FE particles, and hence are not the PFE particles. This shortcoming of the standard method of evaluation of PVC may distort the relative comparison between the usual PVC, on the one hand, and the unprocessable or difficultly processible particles, on the other. A typical example is PVC

prepared by polymerization I which contained a major amount of compact glassy particles, ca. 40–500 μm in diameter. When sifted on a sieve with mesh size 250 μm , the polymer yielded a residue on the sieve containing glassy particles, 250–500 μm in diameter. Their addition to the polymer without FE particles [Fig. 1(a)] showed that the observed glassy particles were PFE particles [Fig. 1(b)]. The sifted polymer containing glassy particles 40–250 μm in diameter again contained FE particles in the standard foil owing to the content of glassy particles, ca. 100–250 μm in diameter. In contrast with the polymer obtained by polymerization I, polymerization II gave a polymer containing only glassy particles with a diameter of ca. 300–500 μm , which were again trapped on sieves with mesh size 250 μm . Neither the optical nor the scanning electron microscope could reveal glassy particles in the sifted polymer, and no FE particles could be traced in the standard foil prepared from the polymer. The result leads to a conclusion that the sifted polymer does not contain glassy particles ca. 100–250 μm in diameter. Hence, it is likely that it also does not contain glassy particles with a diameter below ca. 100 μm . The sifted polymer was therefore taken as a standard sample when comparing the properties of the usual suspension PVC particles and PFE particles.

Morphology. Figures 2(a) and 2(b) shows scanning electromicrograph sections of the usual suspension and a PFE PVC particle isolated from the same

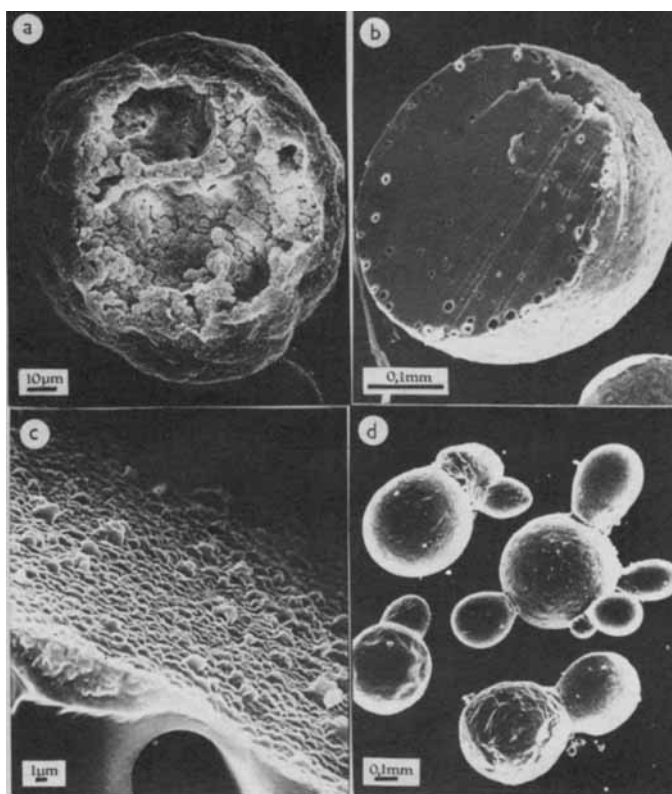


Fig. 2. Scanning electron micrographs: (a) section of the usual particle of suspension PVC, sample PVC standard; (b) section of a compact glassy particle, sample PVC-PFE; (c) boundary between surface and interior on the section of a compact glassy particle, sample PVC-PFE; (d) agglomerates of compact glassy particles, samples from the sieve residue of polymerization I.

suspension polymerization of vinyl chloride (polymerization II). In the section of the usual suspension particle, 115 μm in diameter, chosen from the PVC-standard sample, one can clearly see the skin of pericellular membrane surrounding a PVC particle and the internal structure of the particle consisting of agglomerates of microglobules and of internal pores of two types,⁷ viz., pores between the individual microglobules or agglomerates of the latter and pores formed by major voids which predominantly hem the surface shell of the particle. The thickness of the surface shell whose folds and depressions correspond to the contraction of a polymer drop during polymerization²⁰ is c. 0.7 μm ; the diameter of microglobules which form agglomerates is ca. 1 μm . Both the size of this particle, thickness of the surface shell, and the internal structure and size of microglobules correspond to the character and values reported for the usual type of a suspension PVC particle.^{8,20} The specific surface area of these particles amounted to 0.18 m^2/g (Table I).

Figure 2(b) shows the section of a typical PFE particle, ca. 400 μm in diameter, chosen from a PVC-PFE sample. These particles have a compact glassy character, relatively high density, and are mostly spherical in shape. However, various bizarre shapes arising by the addition of minor glassy particles to one large glassy particle [Fig. 2(d), samples from polymerization I] may also be encountered. On major magnification, the surface of such particles is finely granular and resembles orange peel [Fig. 2(c)], with contracted large pores visible on it [Fig. 2(b)]. The internal structure which can be seen in full in Figure 2(b) and in detail with major magnification in Figure 2(c) is also quite different from the usual suspension PVC particles. The internal part of these particles consists of a compact hard mass in which large pores appear only sporadically, mostly near the particle surface. The smaller glassy particles have a minor number of internal pores or none at all. Figure 2(c) shows that the inner part of internal pores is smooth, with no traces of microglobules. In some pores, however, a more divided structure of sintered microglobules was detected, resembling the finely granular structure of the particle surface. Also, no shell differing in structure can be observed, because the compact and structurally homogeneous interior of the particle passes without change into the particle surface [Fig. 2(c)]. The structural irregularities at the margin of the section are due to deformation of the surface caused by cutting the particle. The specific surface area of these particles compared with the PVC-standard sample is lower, being 0.03 m^2/g (Table I), which indicates that the surface of PFE particles is smooth and non-porous. For the sake of comparison, it should be pointed out that the theoretical specific surface area of model smooth glass spherical particles varies between 0.005 and 0.03 m^2/g , depending on their diameter.

TABLE I
Characteristics of the Samples of Suspension PVC

Sample	Intrinsic viscosity $[\eta] \times 10^{-2}$ (cm^3/g)	Molecular weight				Specific surface area (m^2/g)	
		Viscometry $\bar{M}_\eta \times 10^{-3}$	Light scattering $\bar{M}_w \times 10^{-3}$	Gel permeation chromatography			
				$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$		\bar{M}_w/\bar{M}_n
PVC standard	1.050	98.5	143	170	48	3.5	0.18
PVC-PFE	1.055	99	197	210	60	3.5	0.03
PVC-SR	1.050	98.5	150	190	54	3.5	—

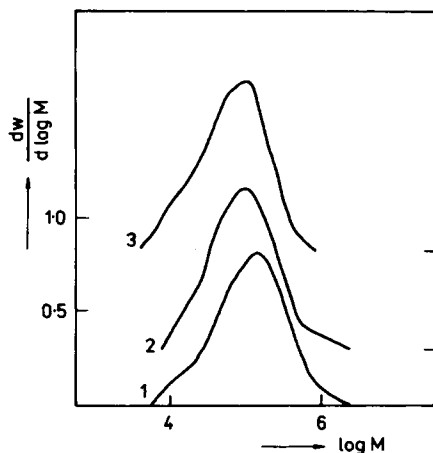


Fig. 3. Differential distribution curves of molecular weights: (1) PVC standard; (2) PVC-PFE; (3) PVC-SR. Scale ($dw/d \log M$) plotted for the first curve; only zero lines are given for the other curves.

Molecular Structure. Molecular parameters of the PVC samples PVC standard, PVC-PFE, and PVC-SR were investigated by GPC, light scattering, and viscometrically. Results summarized in Figures 3 and 4 and in Table I show that, within the limits of experimental error, all three samples have the same average molecular weights and differential distribution curves of molecular weights. Using light scattering measurements, it was possible to decide if the PFE particles were composed of crosslinked or partly crosslinked macromolecules, the presence of which has up to now been regarded as the cause of the difficult processing of PFE particles, leading to the formation of FE particles.¹¹ The character of the Zimm plot of the PVC-PFE sample (Fig. 4) allows an unambiguous conclusion to be drawn that this sample does not contain particles of microgel character, and, consequently, that the PFE particles do not contain strongly branched or crosslinked macromolecules. (The Zimm plots of PVC-SR and PVC-standard samples were of the same character). Also, the same values of viscometric average molecular weight prove that the PFE particles do not contain branched macromolecules. It may be concluded, therefore, that the PVC samples investigated here appear as identical with respect to molecular structure,

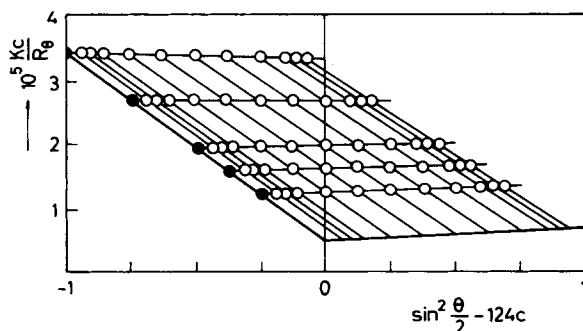


Fig. 4. Zimm plot of the PVC-PFE sample in tetrahydrofuran.

and the PFE particles contain neither branched nor crosslinked macromolecules. This conclusion is in agreement with the results reported on solubility of the usual and difficultly processible particles.⁴

In the course of heterogeneous chlorination of suspension PVC controlled by the diffusion of chlorine into polymer particles, it was found that the chlorination of syndiotactic sequences of structural PVC units proceeded more slowly than in the case of isotactic sequences, probably due to their higher degree of ordering to crystallites.²¹ Similarly, the ability of PVC particles to pass into the gelatin state is controlled by diffusion of the plasticizer into polymer particles. In order to find out if PFE particles contain domains of macromolecules of higher ordering (crystallites), the PVC-standard and PVC-PFE samples were examined by X-ray diffraction. The observed diffraction patterns of both samples were virtually identical and corresponded to the amorphous structure of the polymer without crystallites.

Figure 5 shows IR spectra of the samples PVC standard and PVC-PFE. A comparison between both IR spectra has revealed that compared with the standard sample, the PFE particles have a new absorption band at 1610 cm^{-1} , indicating the presence of conjugated double bonds. The existence of conjugated double bonds should have a negative effect, reflected in the lower heat stability of PFE particles. For this reason, both samples were subjected to the dehydrochlorination test, and the experimental data obtained confirmed that the PFE particles dehydrochlorinate more quickly than usual particles of the standard sample (Fig. 6). Of course, the occurrence of conjugated double bonds is not the cause underlying the unprocessibility of these particles, but it is probably closely related to the still unknown mechanism of formation of electrically charged species which probably affect the formation of the internal structure of suspension PVC particles.^{20,22} These electrically charged species cause that the primarily precipitated polymer particles in monomer drops carry a negative charge and are directed to the positive electrode in an external direct electric field.²⁰ Electrically charged species are probably represented by chlorine anions,²⁰ and it may therefore be assumed that polymer particles contain a certain concentration of hydrogen chloride which is known to catalyze the dehydrochlorination of PVC. In the forming PFE particles, the catalytic effect of hydrogen chloride may be enhanced by a somewhat higher temperature caused by the relatively poorer removal of the polymerization heat. Overheating of the PFE particles should, however, lead to a change in the molecular weight distri-

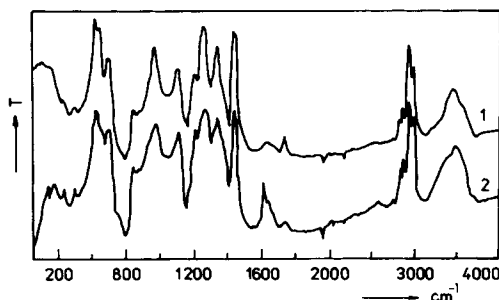


Fig. 5. Infrared spectra of PVC samples: (1) PVC standard; (2) PVC-PFE.

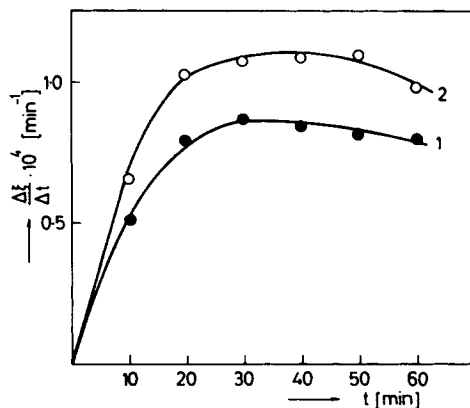


Fig. 6. Time dependence of the rate of dehydrochlorination: (1) PVC standard; (2) PVC-PFE.

bution, or to the formation of branched or crosslinked macromolecules, which has not been observed. It is probable, therefore, that hydrogen chloride or chlorine anions catalyze the further dehydrochlorination of primarily formed chloroallyl structures already at the polymerization temperature. The PFE particles may contain a relatively higher concentration of hydrogen chloride or chlorine anions owing to their impaired diffusion to the particle surface.

Summarily, it can be said that the observed compact glassy particles are difficulty processible PVC particles. These particles, with a diameter above ca. 100 μm , have been proved to be the PFE particles which in processibility tests give rise to the FE particles. The different behavior of the PFE particles compared with the usual particles of suspension PVC is not caused by differences on the level of molecular structure, but results from their different morphology. Further study of the PFE particles and of the FE particles formed from them will be dealt with in a forthcoming paper.

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