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Paper

Compressibility and compactibility of powdered polymers: poly(vinyl chloride) powders

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Abstract

The present investigation is concerned with the possible effects of material-related properties (molecular mass, glass transition and melting temperatures, crystallinity, tacticity) and particle-related properties (shape, size, specific surface area) on the compression characteristics of the chosen model polymer powder: poly(vinyl chloride) (PVC). Four grades were selected known in literature for providing compacts of varied mechanical strength. The compression characteristics were determined using an instrumented single-punch tableting machine. The differences in tableting characteristics could not be ascribed to any of the material-related properties, but a direct relationship was observed between the compact strength and the specific surface area of the particles, as measured by nitrogen adsorption. The compact hardness was thus only dependent on the inter- and the intraparticulate contact area, which in turn is dictated by the very peculiar morphology of the grains of the PVC powders, whether prepared by emulsion or suspension polymerization. © 1997 Elsevier Science B.V.

Keywords: Polymer; Poly(vinyl chloride); Molecular mass; Crystallinity; Tacticity; Morphology; Specific surface area; Compression characteristics; Tableting

1. Introduction

Pharmaceutically acceptable polymer powders are nowadays widely used in prolonged release compressed tablets as matrix systems, but surprisingly the basic compression characteristics of these materials have not been investigated extensively. Few studies have been published, summarized by Rime and Doelker [1].

Several properties related either to the material or to the particle, may influence the compressibility and the compactibility of a given polymer in powder form:

- molecular mass
- crystallinity
- tacticity
- particle size
- particle shape
- particle rugosity/surface area

Poly(vinyl chloride) was the first polymer to be used for the so-called 'inert' compressed matrices [2] and very significant differences in tableting properties were reported in the literature depending on the grade used [3–7]. Using PVC as a model polymer, four grades were selected which were synthesized using different methods (suspension or emulsion polymerization) and resulted in polymers with different molecular mass and particle size. The present work was undertaken with the aim of detecting which factor(s) among the ones listed above that can explain the observed differences in tableting properties.

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Table 1
PVC grades and relevant data obtained from the manufacturer

PVC sample	Abbreviation used	Manufacturer	Polymerization method	K_v^a	Particle size (μm)
Pevikon PE 737 P	Pevikon	Kemanord	Emulsion	73	10–25
PVC high molecular mass	F-HMW	Fluka	Suspension	70	100–200
PVC low molecular mass	F-LMW	Fluka	Suspension	58	100–200
Sicron 2302[b]	Sicron	Montedison	Suspension	57	63–250

[a] The Fikentscher's K_v-value is an indication of the molecular weight (ISO 1628-2).
[b] Evipol SH5730 (European Vinyls Corporation) is the new product name of this grade.

2. Materials and methods

2.1. Materials

The four commercial grades of PVC selected are listed in Table 1, together with relevant data obtained from the manufacturers. The products were confirmed to be pure homopolymers by elemental analysis.

2.2. Polymer characterisation

2.2.1. Molecular mass

The molecular mass determination was done by viscosimetry in cyclohexanone at 25°C. The automatic dilution viscosimeter Shott AVS 310 (Hofheim, Germany) was used, equipped with a capillary viscosimeter according to Ubbelohde (type I). In dilute solutions, the intrinsic viscosity $[\eta]$ and viscosity molecular mass $\bar{M}_v$ are related by the Mark–Houwink equation:

$$[\eta] = K.\bar{M}_v^a \quad (1)$$

where $K = 13.8 \cdot 10^{-3}$ and $a = 0.78$ [8].

2.2.2. True density

The true density of the products was measured using the air comparison pycnometer Beckman 930 (Fullerton, CA, USA).

2.2.3. Thermal properties

The glass transition temperature T_g, the melting point T_m and the enthalpy of fusion ΔH_f of the samples were measured by differential scanning calorimetry (DSC) using the Perkin-Elmer power compensation calorimeter DSC-4 (Nowalk, CT, USA). The scanning conditions were those used by Juijn et al. [9], i.e. the thermograms were recorded at a heating rate of 30°C/min, under nitrogen flow. Two successive scans were recorded (cooling rate: 30°C/min) and the difference in the enthalpy of fusion between them was calculated, in an attempt to deduce the degree of crystallinity.

2.2.4. Crystallinity and tacticity

Because of various technical difficulties, the degree of crystallinity of the polymer samples was evaluated using three different methods.

Initially, it was inferred from the enthalpy of fusion. However, the direct calculation from a comparison with the enthalpy of a 100% crystalline PVC sample was not possible due to the overlapping between the decomposition and melting range of PVC [10]. Instead, the indirect method of Juijn et al. [9] was used (see above). In this method, the crystallinity is removed step by step using heat treatment and the difference in the enthalpy of fusion between two successive runs reflects the melting of the crystalline region.

The degree of crystallinity was also estimated by Raman spectroscopy using the method reported by Robinson et al. [11]. The spectra were obtained using an argon laser tuned at 488 nm (Spectra-Physics, Darmstadt, Germany). The C–Cl stretching region (600–720 cm) provides an estimate of the tacticity and syndiotactic content of the samples.

Finally, the crystallinity was qualitatively assessed by X-ray powder diffractometry using the model FR 552 Nonius camera with Guinier geometry and $C_oK_{\alpha_1}$ radiation (Delft, The Netherlands). Silicium was used as reference.

2.3. Particle characterization

2.3.1. Particle size and shape

The particle size distribution and shape of the powder samples were determined by measurement of 200–300 particles with a light microscope (Nikon Optiphot-2, Tokyo, Japan) coupled to a Sony CCD video camera (Baar, Switzerland) and an image analyser (Microscale TC, Digithurst, Royston, UK). Three parameters were calculated:

- the mean projected area diameter d_p,
- the elongation ratio n, defined as the quotient of the maximum diameter to the minimum diameter [12],
- the circularity K defined as [13]:

$$K = \frac{4\pi \text{area}}{(\text{perimeter})^2} \quad (2)$$

The aspect of the particles and cross-section of the compacts (after diametral crushing test) was also examined by taking scanning electron micrographs of the powders coated with gold at a magnification of 100 or 2000 times with the Jeol JSM-6400 apparatus (Tokyo, Japan) while using an accelerating voltage of 15 kV.

2.3.2. Specific surface area

The specific surface area of the powders S_w was determined by the BET method using the Gemini 2375 instrument (Micromeretics, Norcross). Samples were first dried at 90°C and nitrogen was the adsorbate.

2.4. Compression characteristics

The compression properties were studied on an instrumented eccentric machine (Korsch EK-O, Berlin, Germany) equipped with force and displacement transducers for both punches as described in a previous publication [14]. An accurately weighed powder sample sufficient to produce a compact 2 mm thick at zero theoretical porosity was manually introduced into a 12 mm diameter die and was compressed using flat faced punches. Two sets of runs were performed:

- at fixed upper punch pressure (135 MPa)
- at the pressure necessary to produce compacts with a nominal porosity of 20% after ejection.

In contrast to the first procedure (generally followed in industrial production), the second procedure allows a comparison of products densified at identical packing fraction. Double compression on the same compact was performed in order to evaluate the elastic component of the densification stage [15,16]. Thus, after ejection, the compact was systematically pushed back into the die and a second compression was carried out. Using the data acquisition and processing system described in a previous paper [14], the work balance and the Heckel parameters were determined (see [17] for more details). In particular, a plasticity index was calculated as the ratio of the net work to the lower punch work of compression. The lower punch data were used because they make it possible to eliminate the differences in friction that might be observed during the first and the second compression cycles.

Additionally, the porosity at maximum pressure and after ejection was calculated from the dimensions of the compacts, as well as the elastic recovery ER, defined as [18]:

$$\mathrm{ER} = \frac{H - H_c}{H_c} \cdot 100 \qquad (3)$$

where H and H_c are respectively the height of the compact after ejection and at maximum pressure.

In the Heckel treatment, both the compression and the decompression parts of the cycle were considered, as suggested by Paronen [19]. Thus, in addition to the usual yield pressure P_y (reciprocal of the slope of the upward part of the Heckel plot), a yield pressure was calculated from the downward part of the Heckel plot. Paronen [19] calculated the slope of the downward part at the lowest first derivative value, i.e. at the maximum value of $\ln(1/1 - D)$ value (D = relative density), generally appearing on the Heckel plot, which corresponds to the minimum height of the compact. According to the author, the yield pressure so calculated reflects the fast elastic deformation (elastic recovery) of the material. However, we are of the opinion that the viscoelasticity of the material is responsible for the occurrence of the maximum which appears on the plot after the maximum pressure has been applied. This would explain why Paronen [19] obtained a very low value of 'yield pressure of elastic deformation' for modified starch, well known to deform plastically. We thus propose to calculate the yield pressure from the slope of the low pressure range beyond the maximum observed on the downward part of the Heckel plot. This value, called yield pressure at decompression P_{yd}, is indicative of the plastic deformation of the material during strain recovery. Plastic deformation at low pressure range during decompression has been postulated by both Long [20] and Hiestand [21,22].

2.5. Mechanical strength of the compacts

The crushing force necessary to diametrally break the compacts was measured 48 h after ejection with the Schenk-Trebel RM 50 mechanical testing machine (Ratingen, Germany) at a crosshead rate of 3 mm/min. A sensitive load cell (HBM Z3H2, Hattinger Baldwin Messtechnick, Darmstadt, Germany) was used.

3. Results and discussion

3.1. Polymer characteristics

The properties related to the material itself are listed in Table 2. The polymers can be ranked according to their molecular mass values, which parallel the Fikentscher K values given by the manufacturers and reported in Table 1. The polymers vary with respect of their true density but the method used (air displacement) is not accurate enough to assign these differences to differences in crystallinity.

Both the glass transition and melting temperatures are in the range reported in the literature for commercial PVCs, and are very close. This shows that all products were produced under approximately the same polymerization temperature conditions (usually around 50°C), as this factor is known to affect both T_g and T_m [23]. It can be stated that temperature is thus not the processing factor responsible for the differences observed here in molecular mass.

The indices of crystallinity, as measured by Raman spectroscopy, are typical for PVCs produced at the above mentioned temperature [24] and correspond to values obtained by Robinson et al. for commercial samples [11]. However, slightly higher values were found here for the lower molecular mass products

Table 2
Molecular mass, true density, thermal properties, crystallinity and tacticity of the four PVC powders

PVC sample	$\bar{M}_v$[a]	ρ_v^b (g/cm^3)	T_g^c (°C)	T_m^d (°C)	ΔH_f^e (J/g)	$\Delta H_{f_1} - \Delta H_{f_2}$[f] (J/g)	X_c^g (%)	S.C.[h] (%)
Pevikon	104 000	1.450	85.0	176.0	4.0	1.2	13.4	60.1
F-HMW	100 600	1.497	85.0	174.0	5.7	2.3	12.5	57.3
F-LMW	65 000	1.451	85.0	174.4	4.9	1.4	19.8	60.4
Sicron	46 000	1.406	84.0	176.0	4.5	1.6	17.7	65.7

[a] Average viscosity molecular mass.
[b] True density.
[c] Glass transition point.
[d] Melting point.
[e] Heat of fusion during the first scan.
[f] Difference between the heats of fusion recorded during the first and the second DSC runs.
[g] Degree of crystallinity determined by Raman spectroscopy.
[h] Syndiotactic content determined by Raman spectroscopy.

F-LMW and Sicron, in accordance with the results of Maron and Filisko [25]. Syndiotactic contents, although directly related to crystallinity, did not exactly parallel the indices of crystallinity, possibly because of the presence of some isotactic structures. No reliable results could be obtained from the double scan thermal analysis method, probably because of degradation occurring within the melting range. In any case, the differences in heat of fusion between the first and the second DSC runs did not follow the sequence of crystallinity as calculated from Raman spectra. Finally, the low crystallinity of the products was qualitatively confirmed by powder X-ray diffractometry. No evidence of distinct peaks was observed on the photographic films.

3.2. Particle characteristics

The pictures of the powders are illustrated in Fig. 1 and the particle characteristics are given in Table 3.

Particle size and shape appear very different, depending on the manufacturing process of the powders. Pevikon is produced by emulsion polymerization, the powder consists of very fine particles slightly anisotropic and partially agglomerated. It exhibits the largest specific surface area. The three other samples are produced by suspension polymerization. Their particles are in fact discrete agglomerates, very close in size and shape. However, large differences in specific surface area were obtained.

3.3. Compression characteristics

The main compression parameters obtained when tableting the PVC powders at a fixed pressure or at a fixed porosity are summarized in Tables 4 and 5, respectively. Values for porosity at maximum pressure, for elastic recovery as defined by Eq. (3) and for the crushing force of the finished compacts are also given. In contrast, friction parameters (index of lubrication R, work of friction, ejection force) are not reported because they indicate low friction and did not differ significantly from one product to another, although the die was not lubricated before compression.

The compression cycles obtained at 135 MPa were also used to draw the complete Heckel plots (not shown) and to calculate the yield pressures at compression P_y and the corresponding values at decompression P_{yd} (Table 4).

The various products display quite different compression characteristics. Compared with common excipients compressed at the same applied pressure, PVC powders offer a higher resistance to volume reduction as attested by high upper punch work values [26]. Plasticity indices are rather low, showing that a high elastic component is present in the deformation of PVC particles. The degree of volume reduction at maximum pressure varies a lot among products, low porosities being reached as is usually the case for plastically deforming materials. On the other hand, strain recovery is very important for all samples as evidenced by both the high values of porosity at ejection and elastic recovery. But the greatest differences among products was found for the mechanical strength of the finished compacts, only F-HMW and above all Pevikon giving firm compacts.

Similar trends were observed when considering parameters obtained upon compression at a nominal porosity at ejection of 20% (Table 5). Again, F-HMW was the most difficult PVC to densify (high applied pressure and upper punch work). Interestingly, the same porosity at maximum pressure (although not the same pressure was applied for all products) and elastic recovery (because of same porosity at ejection) were calculated for three of the samples (Pevikon, F-HMW and Sicron). The same crushing force ranking was found as compared with the first series of compacts, because the differences between products were large enough not to invert the sequence, whether the compacts are prepared at a fixed pressure or at a fixed packing fraction.

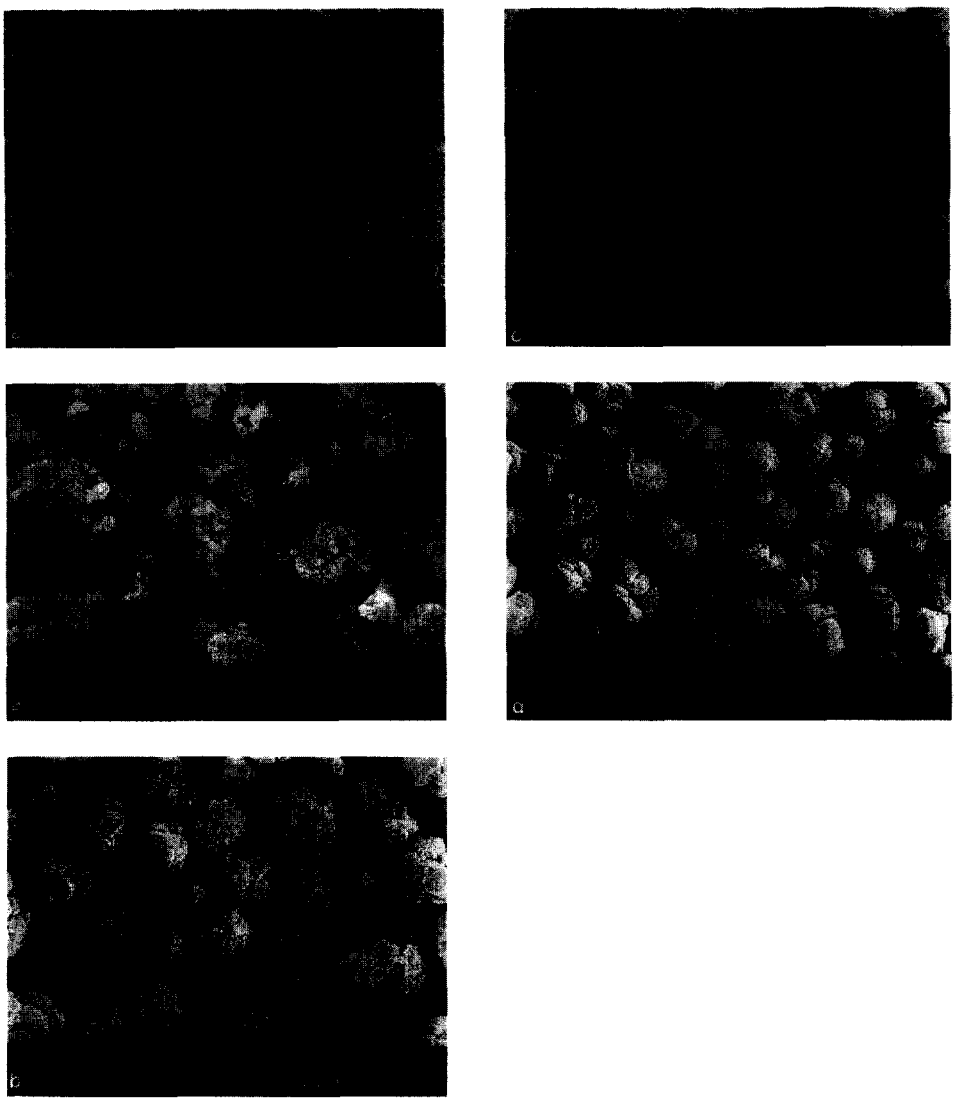

Fig. 1. Scanning electron micrographs of PVC powders: (a) Pevikon (at two magnifications), (b) F-HMW, (c) F-LMW, (d) Sicron

Low values of both yield pressures, P_y and P_{yd}, were found, typical of volume reduction by plastic flow. P_y values were very close to those found by Roberts and Rowe [27] for another PVC grade.

The absence of fragmentation upon compression was theoretically confirmed by calculating the critical particle size below which even the most brittle materials will flow. According to Kendall [28], the critical size d_{crit} for transition from ductile to brittle behaviour is given by:

Table 3
Micromeretic data of the four PCV powder grades

PVC sample	d_p (μm)[a]	n[b]	K[c]	S_w (m^2/g)[d]
Pevikon	3.4	1.88	0.78	3.075
F-HMW	118.4	1.34	0.97	1.770
F-LMW	104.4	1.42	0.98	0.398
Sicron	82.5	1.52	0.89	0.356

[a]Mean projected diameter.
[b]Elongation ratio.
[c]Circularity.
[d]Specific surface area.

Table 4
Compression properties and characteristics of the compacts prepared from the four PVC grades at 135 MPa

Parameter	Pevikon	F-HMW	F-LMW	Sicron
Upper punch work (J)	9.9	12.1	10.5	10.7
Plasticity (%)	71.7	75.8	62.8	71.7
Porosity at maximum pressure (%)	4.9	9.0	3.3	~0
Porosity after ejection (%)	17.0	21.3	13.0	15.7
Elastic recovery (%)	10.9	12.0	8.3	15.1
Crushing force (N)	222	101	0	47
P_y (MPa)	69	81	65	55
P_{yd} (MPa)	131	146	125	94

Table 5
Compression properties and characteristics of compacts prepared from the four PVC grades at a nominal porosity at ejection of 20%

Parameter	Pevikon	F-HMW	F-LMW	Sicron
Upper punch pressure (MPa)	97	160	163	76
Uper punch work (J)	8.0	13.3	11.8	7.3
Plasticity (%)	73	73	69	75
Porosity at maximum pressure (%)	8.9	8.3	3.3	8.8
Elastic recovery (%)	11.0	12.9	16.1	11.4
Crushing force (N)	165	74	0	21

$$d_{crit} = \frac{32ER}{3P_y^2} \quad (4)$$

where E is the Young's modulus of elasticity, R is the fracture energy or fracture toughness, and P_y is the yield pressure. Taking $E = 2.5$ GPa [29], $R = 1.4$ kJ/m^2 [29] and $P_y = 70$ MPa, we obtain a d_{crit} value of 7.6 mm, far beyond the size of the PVC samples tested.

3.4. Relationship between material- and particle-related properties and compression characteristics

It was of interest to establish a correlation between the compression characteristics of the PVC powders and factors related either to the material (Table 2) or to the particles (Table 3). When looking at the material-related factors, we can observe that the strong tablets were obtained with the high molecular mass PVCs (Pevikon and F-HMW). Many molecular theories have been proposed to explain the molecular mass dependence on strength. For instance the model proposed by Mikos and Peppas [30] predicts that for glassy polymers with molecular masses higher than the critical value correspondis to the onset of entanglements, the fracture energy and strength increase with molecular mass. Such a model assumes that fracture occurs through a homogeneous body. In the case of particulate systems, producing porous bodies upon compression, fracture may occur around the particles and no dependence on molecular mass is to be expected. The situation would be different with polymer powders compacted at temperatures above glass transition where chain interpenetration is possible. Examination of the scanning electron micrographs of the cross-section of diametrally ruptured compacts (Fig. 2) shows in fact that breaking occurred round the grains indicating a weak interparticulate bond and not across the grains. The pictures also show the plastically deformed grains compared with uncompressed grains (Fig. 1) and confirmed the absence of fragmentation during compression.

Very little data is available on the dependence of compact strength on the polymer molecular mass with particles of the same size. Rime [31] could not prepare compacts from poly(methyl methacrylate) with molecular mass of 12 300, but strong compacts were obtained with PMMA with molecular mass of 105 000 and 722 000. Size fractions of 63–125 μm were used. Two other papers report on ethylcellulose powders. Upadrashta et al. [32] noticed a decrease in the crushing strength of compacts with increasing molecular mass (420–840 μm size fractions). A similar observation was made by Lin and Lin [33] for coarse particles, but not for fine powders where no dependence was visible. It is noteworthy that in this latter work, no narrow size fractions were used and that in all these articles the compacts were not compared at identical packing fractions.

In this context, it seems improbable that the differences observed with the PVC samples tested can be assigned a molecular mass effect, without any further information on the type of rupture of the compacts. Moreover, the differences in molecular mass of the samples are not large enough to support such a theory.

Differences in mechanical strength are to be assigned to the particle morphology of the products, in turn related to their manufacturing process. A parallel was observed between the specific surface area of the powders as measured by BET and the strength of the compacts. Strong compacts are the result of increased interparticulate contact area. A special mention has however to be made concerning the morphology of PVC powders in connection with their manufacturing process, which is very important in PVC. Pevikon is prepared using aqueous emulsion polymerization. This process produces PVC lattices, i.e. colloidal dispersions of spherical particles ranging in size from 0.1 to 3.0 μm [23,34,35]. The lattices are then dried, thus inducing a partial agglomeration of the particles and then milled to the appropriate size range (usually 1–20 μm). The powders are quite heterogeneous with discrete primary and secondary particles (Fig. 2).

The morphology of PVC powders produced by suspension polymerization is very different and is complicated owing to the insolubility of PVC in the liquid vinyl chloride and to the high density of the polymer as compared to that of the monomer. An idealised model of a PVC sub-grain morphology is shown in Fig. 3.

Discrete constituents of PVC powder, usually named 'grains', are in the 50–250 μm range and they are made up of more than one polymerized monomer droplet (sub-grains). These sub-grains, after polymerization is complete, may or may not retain the complex submicroscopic structure formed during the process, i.e. agglomerates (ca 5 μm) of primary particles (ca 1 μm). The latter contain microdomains of 0.1 μm diameter. The extent of contraction of the polymerizing droplets will influence the morphology of the sub-grains. Only in the case of total contraction, the sub-grains will have no porosity. If contraction is prevented, the final poros-

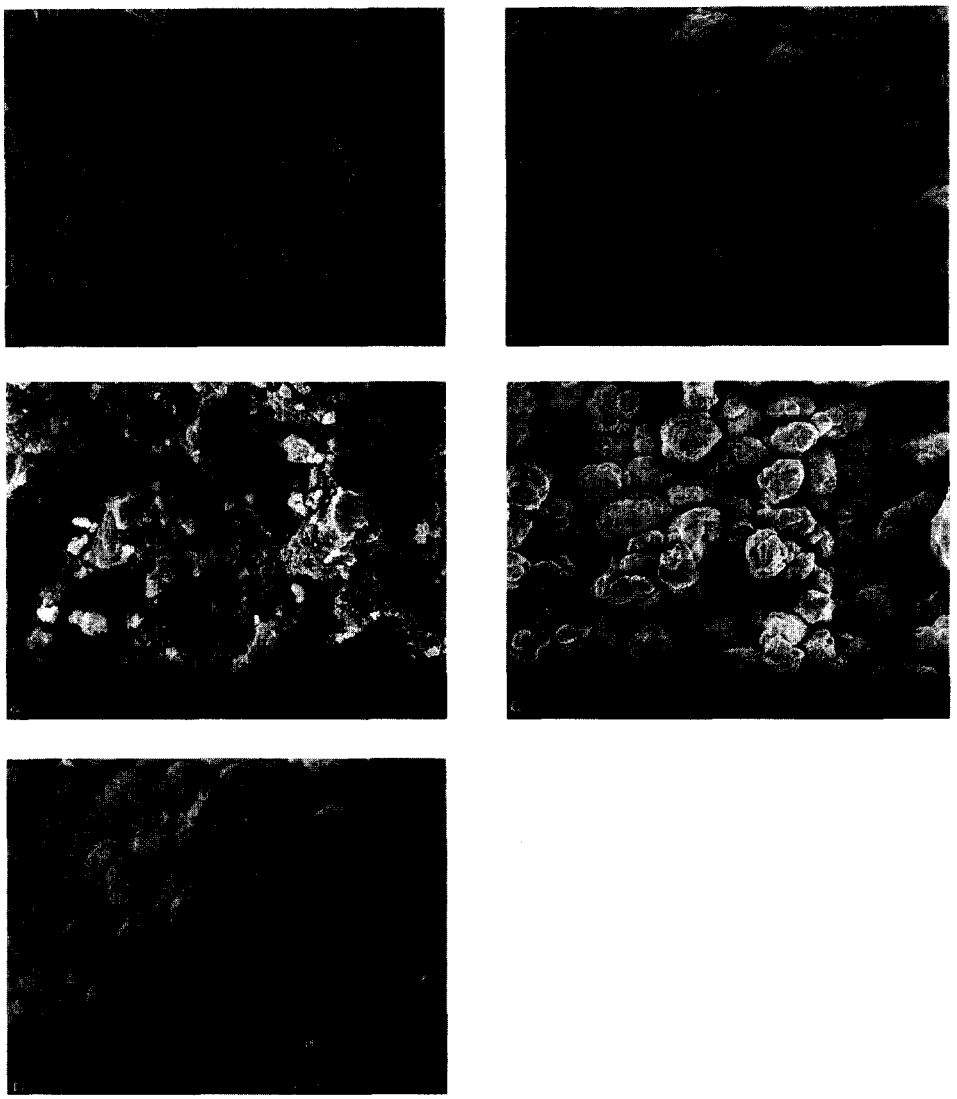

Fig. 2. Scanning electron micrographs of the cross-sections of ruptured compacts: (a) Pevikon (at two magnifications), (b) F-HMW, (c) F-LMW, (d) Sicron

ity can be as high as 39%. Thus the differences in morphology probably explain the varying specific surface area measured for the three PVC powders prepared by suspension polymerization.

4. Conclusion

PVC is a rigid plastic polymer, in the glassy state at room temperature. Upon compression, particles deform plastically and show high elasticity. The high differences in tableting properties between the products tested do not seem to be due to any material-related properties. In particular, no effect of the molecular mass on the strength of the compacts was observed because rupture occurred round the grains and not across them.

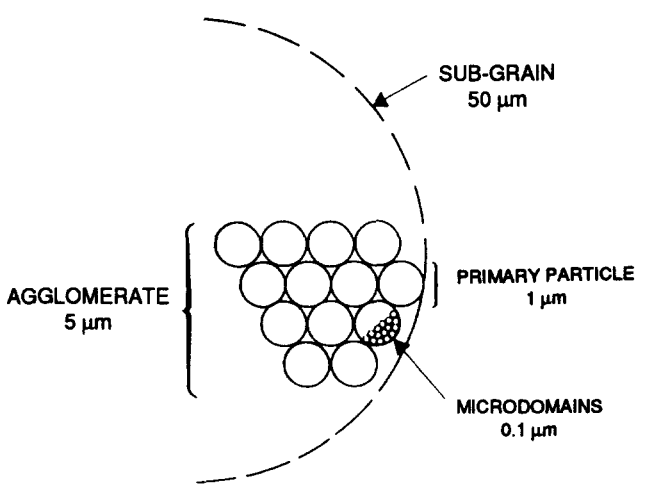

Fig. 3. Schematic representation of a sub-grain of a PVC powder

Among the particle-related characteristics a relationship could be established between the compact strength and the powder specific surface area, as measured by low temperature nitrogen adsorption. The compacts strength was thus only dependent on the interparticulate and intraparticulate contact area, which in turn is directly related to the morphology of the constituents of the PVC powders. In this sense, the peculiar and complex morphology of the PVCs, whether prepared by emulsion or suspension polymerization, makes this material a special case in polymer powder tableting.

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