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Effect of powder particle morphology on the sintering behaviour of polymers

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The sintering behaviour of several amorphous and semicrystalline polymeric powders was studied. The coalescence of particles of polystyrene, PMMA and polyethylene of various molecular weights was photographically followed. The coalescence of the amorphous materials was found to depend on the common parameters affecting sintering including particle size and polymer viscosity. However, unexpectedly fast sintering was observed for the crystalline polyethylenes. The dominating factor in their coalescence, unaccounted for by the Frankel expression, is the internal particle morphology which increases the total particle surface energy. The polyethylene particles were actually found to be aggregates of small nodules, less than 1 μm in diameter, interconnected by a very fine fibrillar network. It is concluded that some semicrystalline high viscosity polymers, known to be unprocessable by common methods, do sinter due to their highly developed internal particle morphology.

1. Introduction

High temperature coalescence of polymeric particles is an important step in polymer processing. The free coalescence of particles in contact is of special interest in some sintering processes of powders. The coalescence–sintering process is driven mainly by the action of surface tension to lower the system free energy through decreasing its total surface area [1]. As the sintering of two spherical particles progresses material transport occurs resulting in gradual growth of the contact neck between the particles. It was shown that most of the changes involving viscous flow take place within and in the vicinity of the contact zone [2, 3]. A theoretical model attempting to describe the early stages of viscous coalescence of two spherical particles was derived by Frenkel [4]. This model shows that the sintering rate increases with surface tension (γ), and decreases with increasing viscosity (η) and initial particle radius (a). The Frenkel expression is the following

$$\left(\frac{x}{a}\right)^2 = \frac{3}{2}\left(\frac{\gamma}{a\eta}\right)t$$

where x is the neck radius and t is the sintering time. The contribution of the viscoelastic behaviour of polymers was recognized and appropriate modifications to the Frenkel equation were proposed [5, 6]. The change of x/a with sintering time at various temperatures was followed for several amorphous and crystalline polymers [2, 5–8]; all confirming various modified versions of the Frenkel expression.

The sintering of polymers was also studied regarding the effects of powder characteristics and process parameters on the density and mechanical behaviour of the resulting sintered products. It was first suggested [9, 10] that merely by using smaller particles a better densification of the green compacts occurred during sintering, improving their properties. However, more recently, Haldin and Kamal [11] and Truss *et al.* [12] have demonstrated and concluded that other factors such as the particles' morphology may play a more important role than just particle size. These authors have studied the sintering of ultra high molecular weight polyethylene (UHMWPE) powders obtained from various sources and differing among other things, in their morphology. The one which had an open fibrillar structure (the fibres being ~ 1 μm in diameter) was found to be superior [12], as to the properties of the sintered products, compared to other powdery particles which consisted of aggregates of small nodules. In some materials [11, 12] very fine fibres were seen linking the nodules. The enhanced sintering behaviour of the particles characterized by an open fibrillar structure was suggested to stem from the interlocking of the particles through the precompaction step and to an effective reduction in particle size as a result of the large number of particle/particle contact points.

The objective of the present work is to investigate the effect of powder particle morphology on sintering behaviour by comparing several polymeric powders.

2. Experimental details

Commercial powders of several polymers were used in this study including ultra high molecular weight polyethylene (UHMWPE, Hoechst Hostalen Gur

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TABLE I Measured material parameters and sintering time*

Material	Viscosity, η (poise)	Particle radius, a (mm)	$a\eta$ (approx.)	Sintering time* (min)	
				180° C	200° C†
RMWPE	2.1×10^4	0.1	0.2×10^4	0.3‡	–
HMWPE	1.4×10^6	0.8	2×10^6	90	30
UHMWPE	9×10^6	0.3	3×10^6	25	8
PS	7×10^4	0.1	0.7×10^4	15	7
PMMA	1.8×10^6	0.15	0.3×10^6	–	210

*Time required to attain $x \simeq a$.

†Sintering temperature.

‡Estimated from low temperature sintering experiments.

412), high molecular weight polyethylene (HMWPE, BASF Lupolen 5261Z), regular molecular weight polyethylene (RMWPE, Dupont Sclair 8507G rotational moulding grade), general purpose polystyrene (PS, Israel Petrochemicals Galirene HH-102) and polymethylmethacrylate (PMMA, ICI Diakon MG-102). The powders were fractionated to attain a narrow particle size distribution.

The powder particles morphology was studied by scanning electron microscopy (SEM, Jeol T-200). Specimens were prepared by dipping a sample holder, on which an adhesive tape was mounted, in a powder, followed by shaking off the excess, leaving only a small number of particles. All specimens were sputter coated with gold. To prevent beam damage to the unique UHMWPE structure the microscope had to be operated at a low voltage of 5 kV compared to the normal operating conditions of 25 kV.

Melt rheology of the various polymers was studied using an Instron melt rheometer equipped with a capillary 2.54 cm long and 0.127 cm in diameter ($L/D = 20$). Flow curves over a wide range of shear rates were constructed.

The isothermal sintering process of an isolated pair of particles was continuously followed using the following technique (a modification of the method described by Rosenzweig and Narkis [13]): a small number of particles were scattered on a freshly washed glass slide which was then mounted in a Mettler FP 52 microfurnace connected to a Mettler FP5 temperature control unit. The furnace was installed in a Wild optical microscope equipped with a camera. Two approximately equal size particles (in contact) were carefully selected and positioned at the centre of the viewing field. The furnace temperature was rapidly raised to a desired value and was then kept constant during the whole sintering process. Photographs were taken at desired intervals without interrupting the observed process. Since the particles were in contact also with the glass substrate, which may affect the free sintering process, several experiments were conducted in which the powder particles were suspended in silicon oil. Surprisingly, the sintering rates were found equal in both methods thus, the "dry" one was used throughout this study.

3. Results and discussion

The isothermal sintering of two particles (approximately equal in size), making a point contact between themselves, placed in an isothermal furnace was followed by using a hot stage optical microscope. The particles were used in their natural form (as-received) without any prior treatment or compaction. A deviation from free sintering conditions could be caused by the supporting glass substrate. However, the substrate effect was found negligible since the sintering rate was not altered when the particles were suspended in an inert liquid medium. The materials chosen for this study included three types of polyethylene powders which differed mainly in their molecular weight (approximate weight average molecular weights are the following: RMWPE = 1.5×10^5, HMWPE = 5×10^5 and UHMWPE = 4.5×10^6) and as will be shown they also differ in their morphology. In addition PS and PMMA powders were chosen for comparison purposes. The sintering experiments were conducted at two elevated temperatures, 180 and 200° C, except for the RMWPE which was sintered at 150° C (the sintering of this polyethylene at higher temperatures was too rapid to be followed with the present experimental setup).

Optical micrographs comparing the initial and an advanced stage of the sintering process of selected polymer particle pairs are shown in Fig. 1. It should be noticed that only the PS and PMMA particles are spherical whereas those of the PE are rounded in shape. The difference in particle size of the various powders should also be noted, though the particles of each pair are approximately identical. The "coalescence period" (defined arbitrarily herein as the time required to attain $x \simeq a$) determined for the various powders is summarized in Table I. The results obtained for PS and PMMA are in good agreement with published data [2, 7] (literature data for the other powders are not available). Two additional material parameters including particle diameter and melt viscosity are given in Table I. The viscosity (at $\dot{\gamma} = 0.3\,\mathrm{sec}^{-1}$) was calculated from the low shear rate range of the flow curves as shown in Fig. 2. Although the flow curves had to be determined at a temperature of 220° C, which is higher than the sintering temperature (180, 200° C) they are applicable for comparison purposes of the viscosity effect on the sintering process. The viscosity of the UHMWPE seems to be too low in comparison with the HMWPE viscosity (molecular weight ratio of ~ 9) presumably due to deviations from a simple shear flow mechanism.

Using the Frenkel expression [4] as a guiding model,

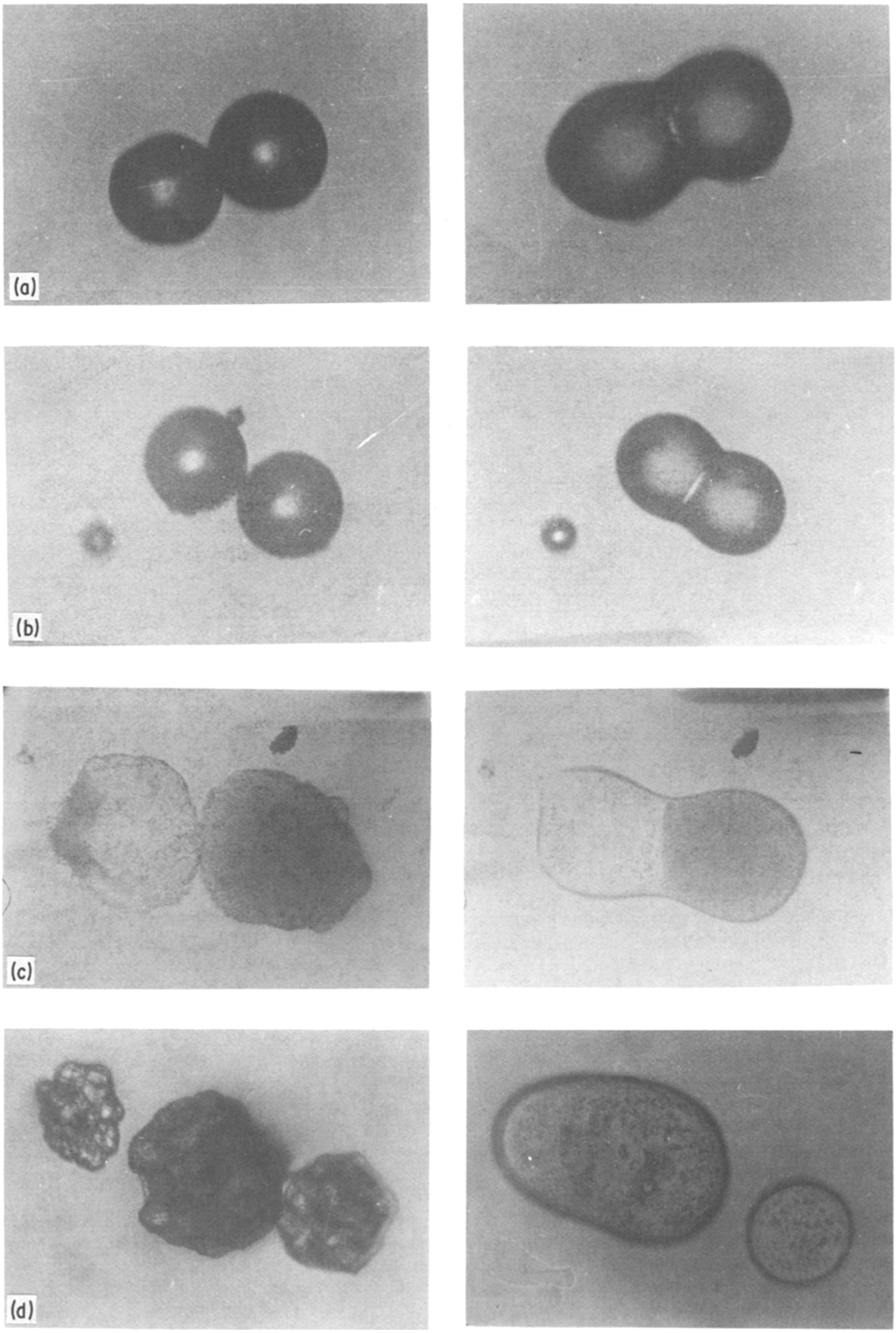

Figure 1 Optical micrographs of polymer particles before and during sintering at 200° C: (a) PS, (b) PMMA, (c) HMWPE and (d) UHMWPE.

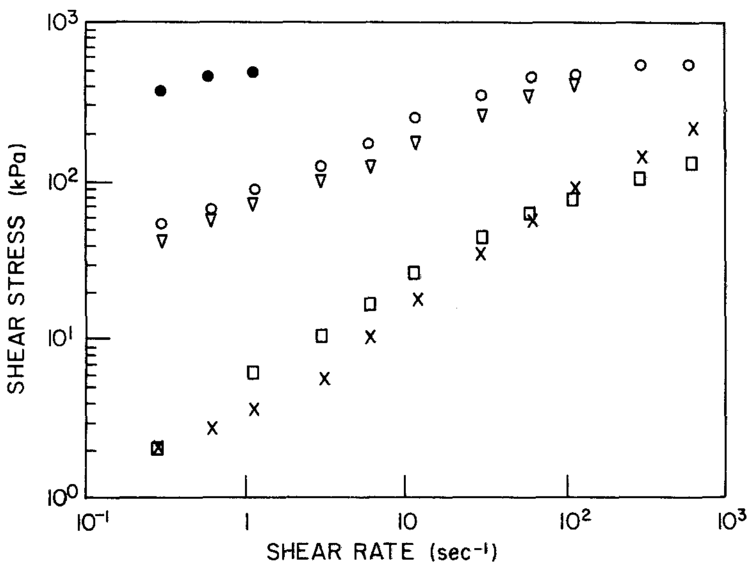

Figure 2 Flow curves of UHMWPE (●), HMWPE (▽), PMMA (○), PS (□) and RMWPE (x) at 220° C.

and assuming roughly the same surface tension for all the materials [14], it is expected that the sintering time (required to attain $x \simeq a$) is proportional to ($a\eta$), (see Table I) and should be in the following order: RMWPE < PS < PMMA < HMWPE < UHMWPE. As can be seen in Table I, the measured values of the sintering time do not follow this expected order. The most outstanding polymer for its low measured sintering time is the UHMWPE. Its sintering time is of the same order of magnitude as that of the PS inspite of its two-fold higher viscosity. In an attempt to elucidate this unexpected behaviour an additional parameter, the particle morphology, was investigated.

The PS and PMMA particles constitute solid spheres having quite a smooth, though irregular, surface (see Fig. 3). The HMWPE particles were found to actually be aggregates of either nodules about 1 μm in diameter (see Fig. 4a), or elongated, noodle shape, microparticles, about 1 μm in width and up to several tens μm in length (Fig. 4b). Some regions of the HMWPE particles exhibit open surface area enabling observation of their very porous internal structure, as seen in Figs 4a and b. The surface of some other regions is quite closed as if covered by a thin layer (see Fig. 4c). Further observation of the internal structure reveals that most of the subparticle units are in intimate contact, closely packed, and some are interlinked by very thin short stretched fibrils (see Fig. 4d). In conclusion, the HMWPE particles are aggregates of microstructural units which are closely packed. A very intriguing structure was observed in the UHMWPE particles. At a low magnification these particles are seen (Figs 5a and b) as rounded irregularly shaped porous solids. However, at higher magnifications a very intricate morphology was revealed leading to the conclusion that the UHMWPE particles consist actually of a structural hierarchy. The smallest resolved structural units are nodules less than 1 μm in diameter. These nodules aggregate and form larger structural units which exhibit a very wide size distribution, some consist of only several nodules, (Fig. 5c), and some of probably hundreds (Fig. 5b). Groups of these aggregates form the powder particles. Based on the observed hierarchic structure one may speculate that the smallest resolved nodules in the present work consist of even smaller units the size of which depends on the polymer molecular weight (the nodule diameter is about 500 nm compared to a calculated value of 50 nm for the end to end distance). Additional structural units, which were just briefly mentioned in the literature [11, 12] are the very fine fibrils linking the nodules of their aggregates (seen in Figs 5c–f). In some regions the fibrils are stretched in a certain direction (Fig. 5c), as if pulled out from the nodules, forming a structure resembling strings of pearls. In other regions, as seen in Figs 5c and d, the fibrils form a three-dimensional web-like network in which the nodules are situated at the web junctions. These fibrils can easily be damaged by the impinging electron beam; thus to prevent their scission the microscope had to be operated at its lowest voltage (some damaged fibrils can still be seen in the micrographs). The porous structure of the UHMWPE particles could have been formed due to a hydrodynamic shear field prevailing during the polymerization process. These fibrils presumably consist of highly oriented UHMWPE chains which may contribute to the high degree of crystallinity of the as-polymerized UHMWPE powder

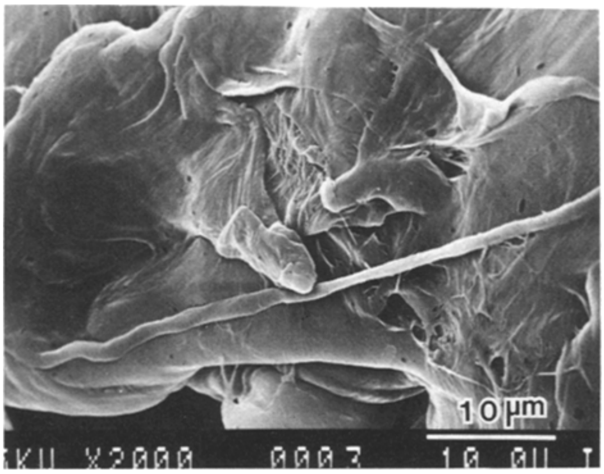

Figure 3 Scanning electron micrograph of a PS particle.

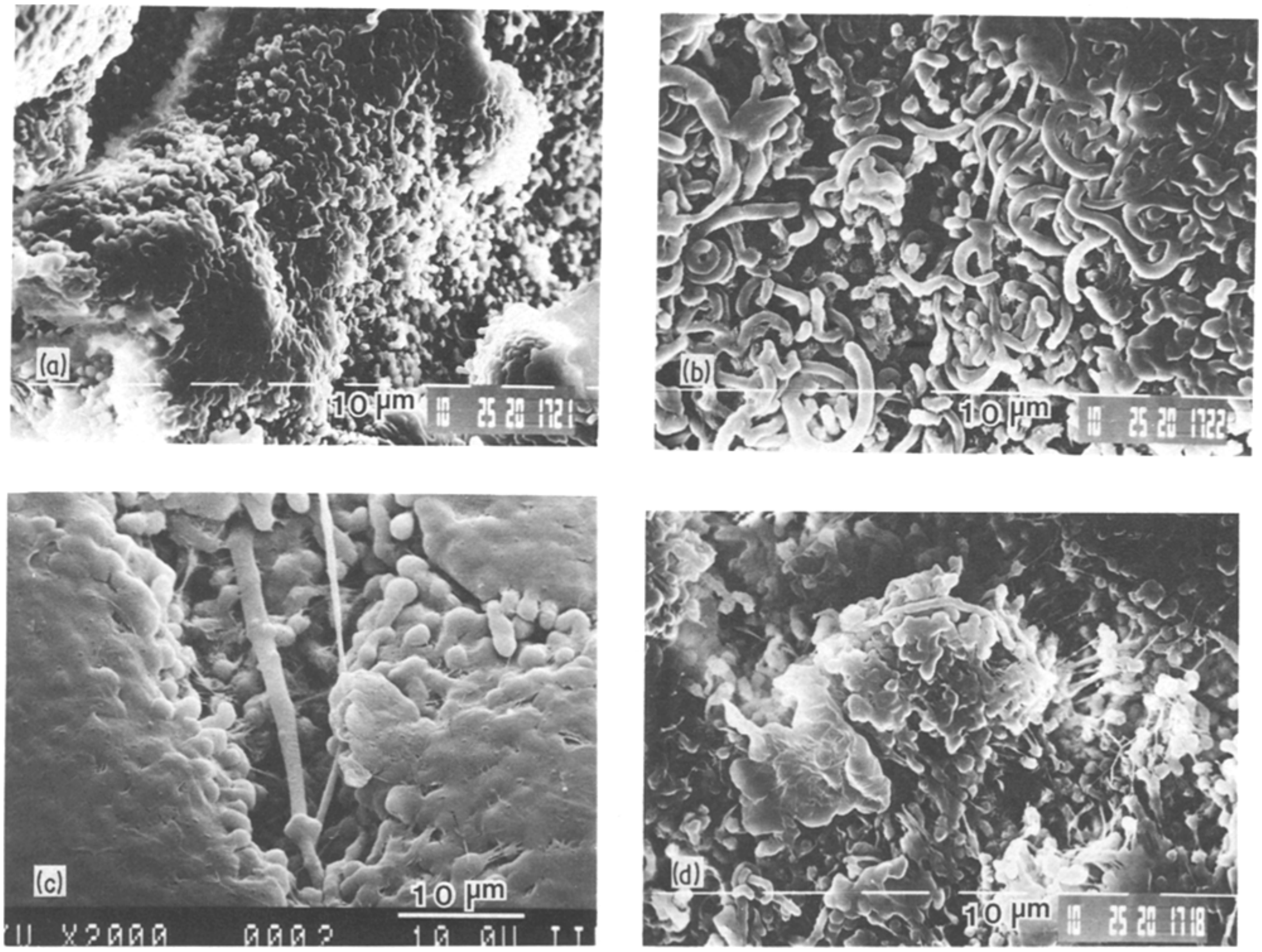

Figure 4 Scanning electron micrographs of HMWPE particles.

[15]. It is proposed that upon stretching, while the polymer is in the reaction medium, the nodules deform inhomogeneously forming micronecks along which the fibrils are stretched (see Fig. 5f). The very localized deformation results in the breakdown of large nodules into smaller ones, which are then linked by the fibrils. In conclusion, the UHMWPE particle is an aggregate of nodular units interconnected by a fibrillar network, forming a porous structure having a high surface area to volume ratio.

It is concluded that the sintering behaviour of polymer powders is controlled by their particle morphology in addition to the parameters included in the Frenkel's model; in some cases the former can be the predominating factor. The UHMWPE particles, structured as described above, and having a very high melt viscosity, are an excellent example where morphology predominates viscosity. Truss *et al.* [12] have attributed the relative better sintering behaviour of a certain grade of UHMWPE (Allied Chemical AC 1225) to its fibrous morphology. However, the fibres observed were one order of magnitude thicker than the presently described fibrils. Truss *et al.* [12] propose that since fibres of one particle are in contact with those of another one, the size determining the sintering time is the effective size of a fibre. The latter is almost a factor of 100 smaller than the powder particle hence, the sintering time should be considerably shorter than normally expected. In the present system an effective particle size to be considered is that of the nodule ($< 1\,\mu$m). Another contribution to the sintering process, which should not be underestimated is the retraction of the highly oriented fibrils. The unexpected enhanced sintering of UHMWPE thus could stem from the presence of the very small primary particles, the nodules, interconnected by the highly oriented fibrils, which cause densification upon their retraction. Another semicrystalline polymer, too viscous for processing by conventional thermoplastic fabrication methods, is PTFE. Inspite of its very high viscosity PTFE is processable by sintering, again, due to its developed particle morphology [6]. It is clear that amorphous polymeric particles, at a comparable viscosity, will not coalesce even during very long contact periods.

The foregoing conclusions can now be implemented in the interpretation of the sintering of the semicrystalline polyethylenes and the amorphous PS and PMMA. Hence, the fast sintering of the RMWPE relative to the other polyethylenes is mainly a result of its lower viscosity. UHMWPE sinters faster than HMWPE inspite of its higher viscosity due to its higher developed morphology. The PS sinters faster than the PMMA due to its much lower viscosity; the particles of these two polymers constitute "structureless" solid materials. By comparing ($a\eta$) values for the PMMA and HMWPE one would expect HMWPE to sinter slower, by a factor of ~ 5, however, as shown in

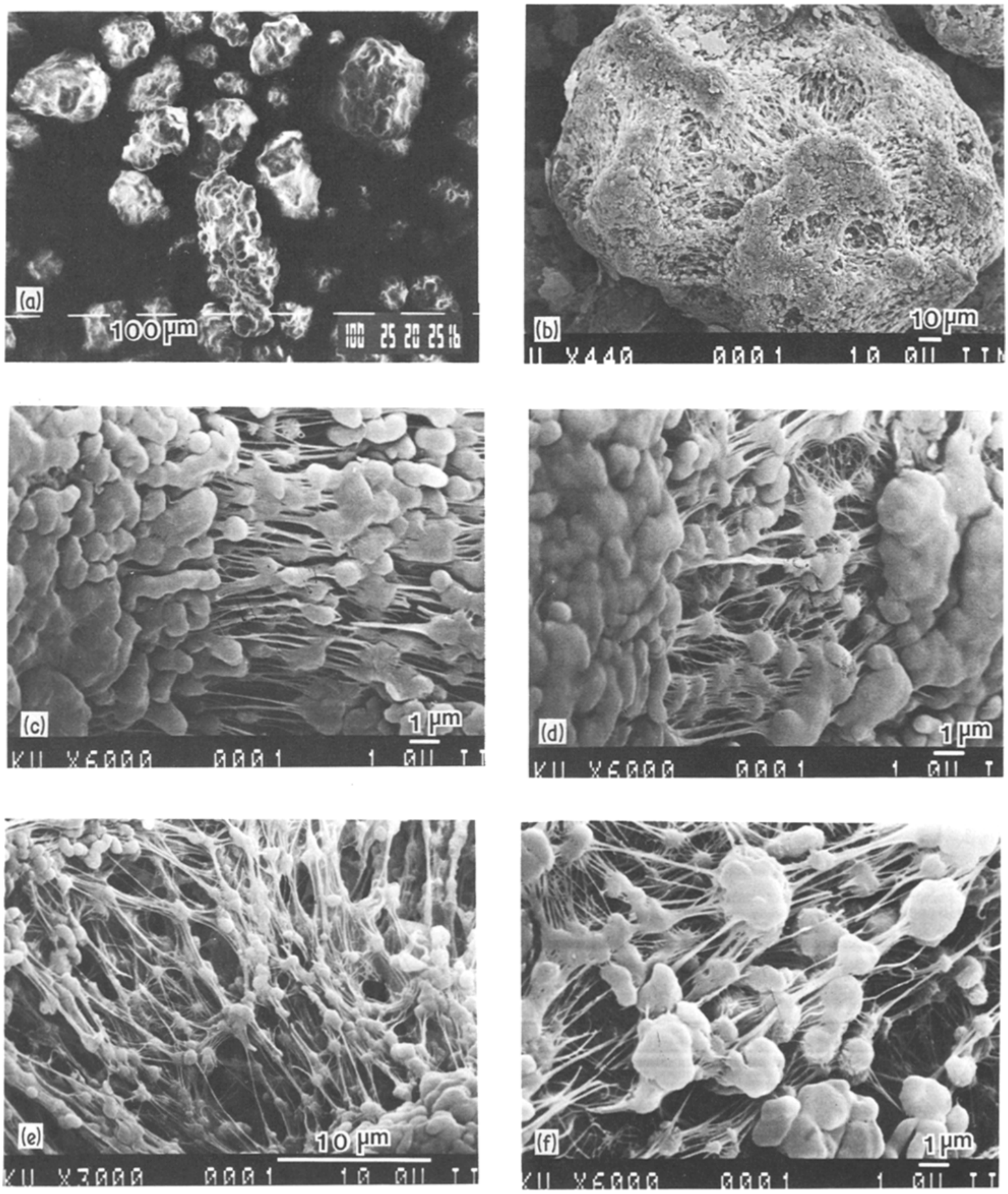

Figure 5 Scanning electron micrographs of UHMWPE particles.

Table I, the opposite is true and HMWPE sinters faster than PMMA by a factor of 7. The dominating factor here, unaccounted for by the Frenkel expression, is the developed structure in the HMWPE particles; even more pronounced is the comparison between UHMWPE and PMMA. Finally, based on ($a\eta$) values, the PS and RMWPE particles should sinter at similar rates. However, RMWPE was found to sinter faster (a factor of ~ 45) suggesting the existence of internal structure within its particles. This proposed particle morphology could not be observed under the microscope presumably due to a solid thin layer encompassing the particle.

In summary, the analysis of the sintering process of semicrystalline polymeric powders is more complicated than for spherical amorphous particles, which can be analysed by the Frenkel model. In practice, high viscosity polymers, unprocessable by common methods can be sintered if they are semicrystalline and their particles consist of a highly developed internal morphology.

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