Coalescence phenomenology of spherical polymer particles by sintering

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Liquid drops in contact with each other tend to decrease their total surface area by coalescence. Surface tension is the main driving force in the coalescence process[1]. Sintering is a term describing the high temperature coalescence of solid particles such as metals, ceramics and polymers. High temperature sintering (with or without compaction) is an essential stage in some plastic processing techniques. A simplified theoretical model attempting to describe the early stage of viscous coalescence was derived some 35 years ago by Frenkel[2]. This model accounts for the effects of surface tension and viscosity on the sintering process with time. An advanced experimental technique for investigation of the sintering process recently developed by the authors[3] has produced reliable data enabling critical testing of the Frenkel theory for polymers. Good agreement between theory and experience is reported here even in stages far beyond the region claimed to be covered by the theory. In previous publications[4-6] researchers have not been able to verify Frenkel's theory even in the early stages of sintering for polymers, probably due to inappropriate experimental techniques.

The tendency of a pair of spherical particles to decrease its total surface area by viscous sintering in the early stages of the process was formulated by Frenkel[2] by equating surface are with some average visocus friction energies:

$$x^2 = Kt \qquad (1)$$

x is the neck radius formed between two particles and t is the sintering time. K is a function of particle radius, surface tension and Newtonian viscosity.

Kuczynski *et al.*[4] studied the sintering behaviour of poly(methyl methacrylate), PMMA, spherical particles with a flat block of the same material. They proposed a non-Newtonian viscous flow sintering mechanism (sintering region $x/a \leqslant 0.3$; a = sphere radius) where the non-Newtonian behaviour changes with the sintering temperature, being pseudoplastic at the lower temperatures and dilatant at the higher ones after passing through a certain temperature at which the behaviour is Newtonian. A generalized Frenkel equation was proposed:

$$x^{2p} = K't \qquad (2)$$

where the deviation of p from unity indicates a deviation from Frenkel's theory. The range of p values reported by Kuczyski *et al.* is from 2.5 at 150°C to 0.27 at 207°C. A significantly narrower range of p values from 1.12 at 175°C to 0.55 at 203°C was recently reported by Narkis[5] by following the progress of the sintering of groups of PMMA particles placed as single layers on flat aluminium surfaces. A viscoelastic mechanism especially at the lower sintering temperatures was discussed by Lontz[6].

'Pure' sintering can be visualized by observing two equal particles making a point contact between themselves placed in an isothermal space (no additional contacts). Such ideal conditions can hardly be met in practice, but the authors have been able to develop a new technique, enabling continuous observation of a pair of particles undergoing sintering in a hot stage optical microscope. Such a pair is characterized by a common contact between the particles and an additional contact between one of the particles to a surface. Whereas previous techniques could be described as intermittent methods, having clear drawbacks, the new continuous technique approaches the conditions necessary to produce data adequate for critical testing of the theoretical models.

The sintering behaviour of PS (polystyrene) particles by coalescence is shown in *Figure* 1 starting with two spheres and ending with a single sphere consisting of the two. The contact neck between the particles is shown to be well-rounded, an experimental fact unaccounted for by Frenkel's model. In *Figure* 2 the total length of the pair undergoing sintering and the diameters of the contact neck, upper and lower particles are plotted against time.

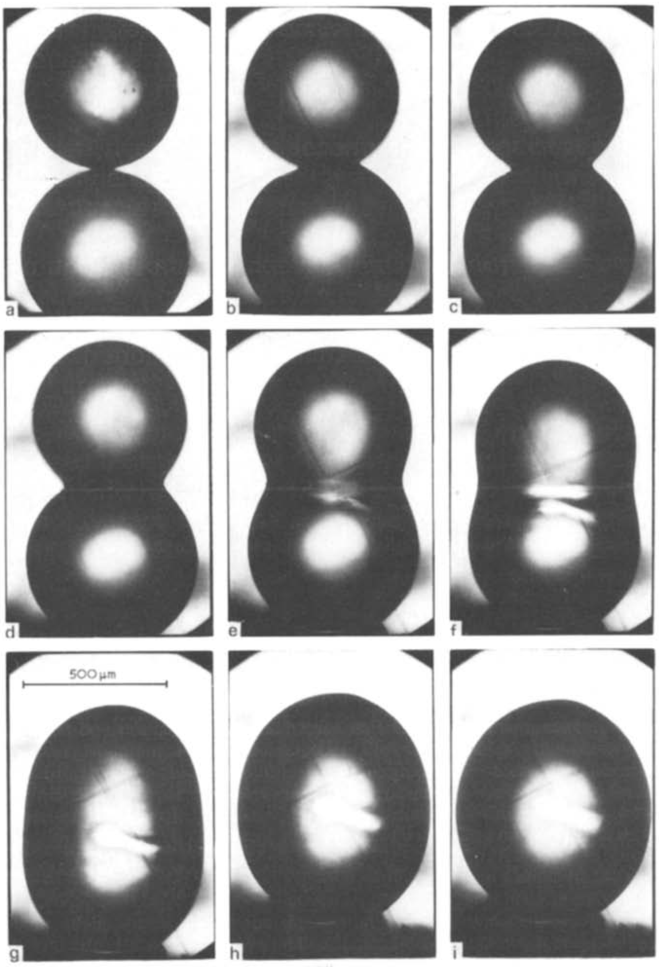

Figure 1 Progress of sintering of PS spheres at 180°C: (a) 0; (b) 8; (c) 14; (d) 20; (e) 32; (f) 41; (g) 55; (h) 69; (i) 79 min

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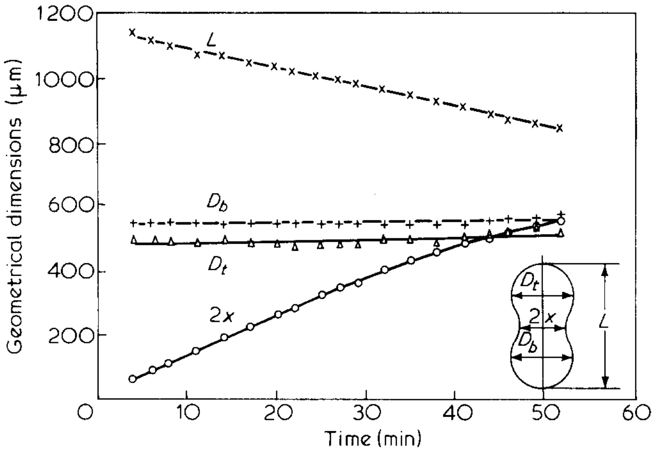

Figure 2 Dependence of typical geometrical dimensions upon sintering time (PS at 180 °C). L, total length; D_b,,diameter of bottom particle; D_t, diameter of top particle; $2x$, diameter of contact neck circle

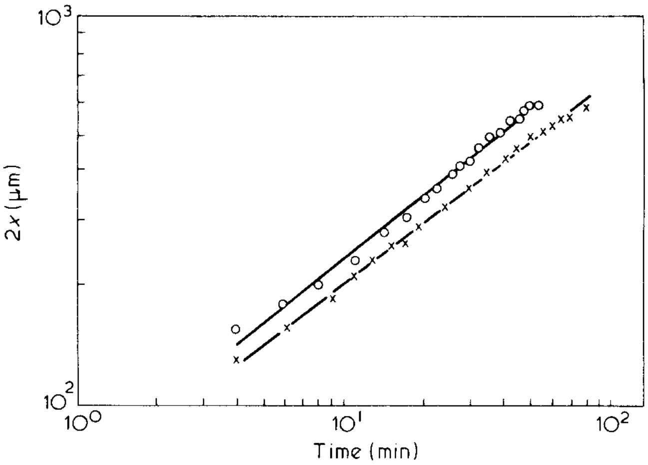

Figure 3 Linear dependence of log $2x$ vs. log t, ●, PS, 180°C, slope = 0.56; x, PMMA, 200°C, slope = 0.53

This Figure clearly shows that with increasing time the total length decreases and the contact neck diameter increases parabolically while the particles diameters do not change appreciably over a wide range of the sintering process. This behaviour, typical of all the experiments with PS and PMMA, shows that during a significant part of the sintering period most of the changes involving viscous flow take place within and in the vicinity of the contact zone. Thus widening of the neck is at the expense of the total length with little change in shape of most of the particle. In this regard, however, it is important to point out that Frenkel, in order to maintain a constant volume model of the sharp neck corners had to assume increasing particles diameters with sintering progress.

A Frenkel-type log–log plot is shown in *Figure* 3 where the neck diameter is plotted against time for pairs of PS and PMMA particles. The linear dependence shown is typical of all the experiments with PS and PMMA spheres. The values of the slopes are 0.56 for PS and 0.53 for PMMA, in surprising agreement with predicted value of 0.5 from Frenkel's theory. A temperature range from 160°C to 220°C was covered for sintering of the PMMA spherical particles giving slopes of 0.49 for 160°C and 0.63 for 220°C, respectively. This slight effect of temperature on the slopes and their proximity to the predicted 0.5 value support Frenkel's Newtonian viscous flow model. This conclusion is consistent with typical sintering conditions, namely low shear rates. Interpretations in terms of a wide non-Newtonian flow behaviour and especially dilatancy can be ascribed to artefacts and not to the natural flow mechanism involved.

The sintering process for polymeric particles by coalescence is a process of highly complicated viscous flow trajectories with moving boundaries. It is thus surprising to observe good agreement between Frenkel's simplified model and the experimental results. A fundamental sintering model based upon solutions of continuity and momentum equations with proper boundary conditions is presently being developed and will be reported at later date.

Acknowlegement

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Interpretation of radial distribution functions for non-crystalline polymers

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In investigations of the structure of non-crystalline polymers using radial distribution functions (*RDF*s) there has been a tendency to assume that a marked periodicity of about 5 Å extending to 20 Å and beyond is evidence of significant chain parallelism (for example see references 1 and 2). In this communication we show, first from experiment and then from model calculations, that such a periodicity is evidence only for a well defined closest distance of approach between chains.

*RDF*s are calculated from scattering data using the

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