Observation and Analysis Technique for Studying Sintering of Polymeric Particles

INTRODUCTION

Sintering is a common term describing high-temperature coalescence of solid particles such as metals, ceramics, and polymers. High-temperature sintering is an essential stage in some plastic processing methods including rotational molding, fluidized bed coating, and slush molding. In some cases polymer sintering is accompanied by chemical reactions, usually of the crosslinking type (powders of crosslinkable polyethylene, epoxy, and polyimide).

Amorphous polymer particles contacting each other at a temperature above their glass transition temperature tend to decrease their total surface area by coalescence. Surface tension is the main driving force playing a role in the coalescence process. A simplified theoretical model describing the early stages of viscous sintering was formulated by Frenkel.[1] This model accounts for the effects of surface tension and viscosity on the sintering progress with time. The sintering progress is determined by measuring the time and the increasing diameter of the contact circle between a spherical particles pair starting from a point contact.

Experimental sintering studies of contact diameter dependence upon time, temperature, and particle size were conducted by Lontz (PTFE cable strands),[2] Kuczynski (PMMA particles on PMMA block),[3] and Narkis (PMMA particles placed in aluminum dishes).[4] The practical conditions of all these sintering experiments deviate from Frenkel's theoretical conditions in which an isolated pair of identical spheres is undergoing sintering. In addition, samples were taken out intermittently from the sintering oven, cooled down to room temperature, and then inspected and analyzed. The technique described herein offers the advantage of continuous observation of a particles pair undergoing sintering by using a hot stage/optical microscope setup. In addition, the investigated pair is characterized by a common contact between the particles and a single contact only of one of the particles to a surface. Such experimental conditions are expected to afford a much better empirical simulation to theoretical models thus giving adequate tools for critical testing of the models' validity.

RESULTS AND DISCUSSION

Two similar-size spheres were introduced to a glass capillary tube sealed at one end. A presintering step consisted of heating the tube and its content (PMMA, 160°C, 7 min; and PS, 140°C, 7 min) in order to form a minimum practical neck engabling further handling of the particle pair. Typical contact neck diameters of presintered pairs were usually about 10% of the particle diameter. The presintered pair (in some experiments groups of particles were presintered) was taken out from the tube after cooling and one of its spheres glued gently with an epoxy adhesive to an aluminum carrier attached to a microscope glass slide. The slide was introduced to a Mettler FP52 microfurnace connected to a Mettler FP5 temperature control unit. The pair's position in the furnace could be changed, thus enabling the study of gravitational effects on the sintering process. The microfurnace was installed in a Wild optical microscope equipped with a Nikon microflex photographing device. Heating periods of the furnace to the selected sintering temperatures were short, and about 140 sec was required to stabilize the temperature at 180°C. Photographs were taken at desired intervals without intercepting the sintering process. Photographed frames were projected on a screen and the desired measurements performed.

The polymers studied in the present work were PMMA (Diakon MG-102 poly(methyl-methacrylate), ICI) and PS (Galirene HH-102 polystyrene, Israel Styrene Polymers) having diameters in the range of 500 to 590 μm.

The sintering behavior of PMMA particles at 180°C is shown in Figure 1. The contact neck between the particles is shown to be well rounded, an experimental evidence in contradiction with Frenkel's model in which sharp contact corners were assumed.[5] In Figure 2. the total length of the PMMA pair undergoing sintering and its contact neck top and bottom diameters are plotted against time. This figure shows clearly that with increasing time the total length decreases and the

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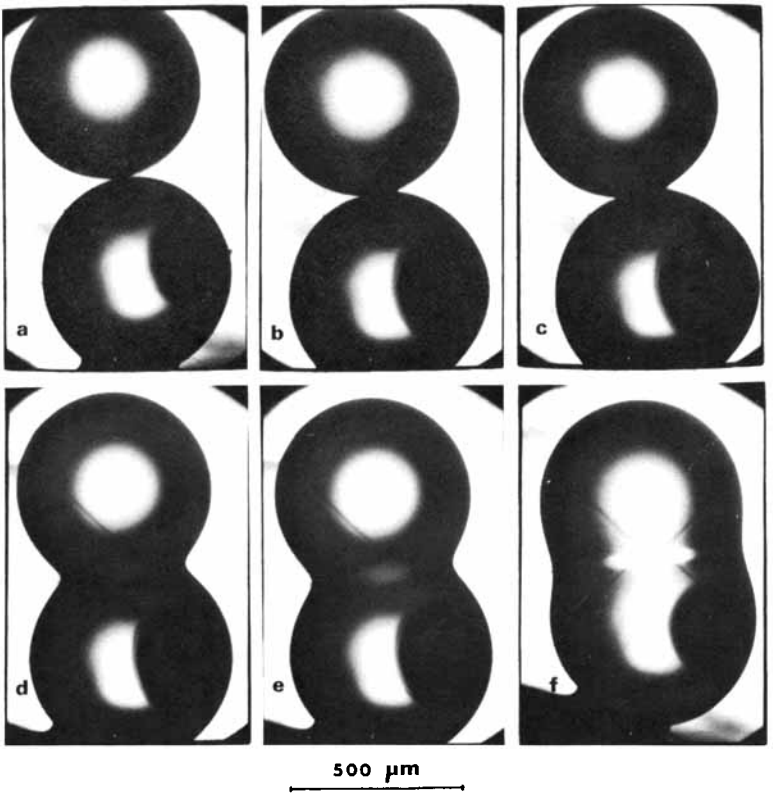

Fig. 1. Progress of sintering of PMMA spheres at 180°C: (a) 0; (b) 15; (c) 40; (d) 240; (e) 300; (f) 550 min.

contact neck diameter increases while the particle diameters do not change appreciably over a wide range of the sintering process. Viscous flow is thus taking place mostly within and in the vicinity of the contact zone, an experimental evidence again in contradiction with Frenkel's model in which the whole pair volumes was assumed to participate in the sintering process.

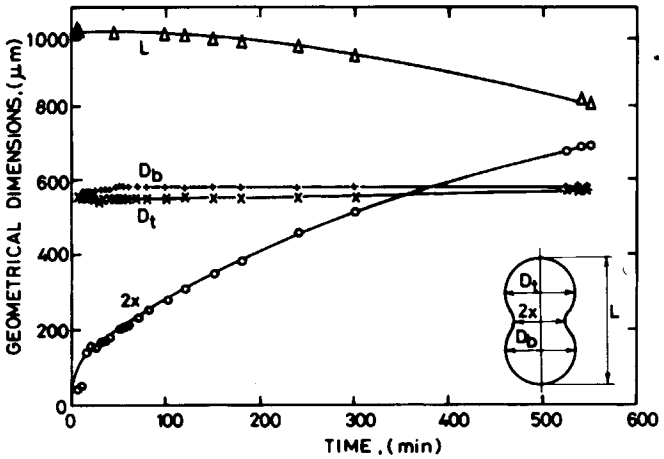

Fig. 2. Dependence of typical geometric dimensions on sintering time (PMMA at 180°C). L = total length; D_b = diameter of bottom particle; D_t = diameter of top particle; $(2x)$ = diameter of contact neck circle.

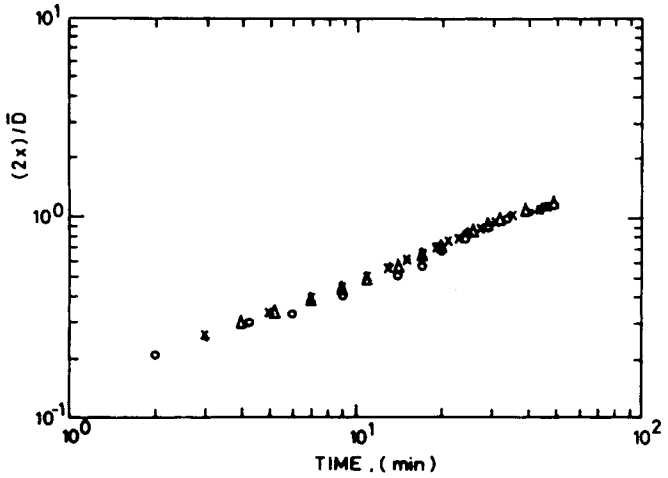

Fig. 3. Reproducibility studies of the dependence of $(2x/\bar{D})$ on time for four independent sintering experiments (PS at 180°C).

The present technique, in addition to being informative and of significant scientific potential, is characterized by its reproducibility. Figure 3 shows the logarithmic dependence of $(2x/\bar{D})$ upon time for four independent sintering experiments of PS particles $[\bar{D} = (D_b + D_t)/2]$ at 180°C. The average slope of four straight lines describing the four experiments is 0.572 (slopes range between highest and lowest values is 0.012). The average slope found for PS sintering (0.572) is in good agreement with Frenkel's predicted slope (0.5). Similar results were also found in PMMA sintering experiments using the present technique. In other publications, however, using different sintering methods, significantly higher slopes were reported,[2-4] which disagreed at least partly with Frenkel's model describing Newtonian viscous sintering.

In future publications, theoretical models based upon experimental facts and fundamental continuity and momentum equations will be presented and compared to experimental data generated by the present technique.

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