

Study of Sintering of Poly(methyl Methacrylate)*

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Synopsis

Sintering of poly(methyl methacrylate) spheres to the blocks of the same material was studied at temperatures ranging from 127° to 207°C. The analysis of the data based on the empirical Ostwald relation indicates that the predominant mechanism responsible for this process is non-Newtonian viscous flow. The type of the flow changes with temperature of sintering, being pseudo-plastic at lower temperatures and tending to dilatancy at higher ones.

INTRODUCTION

Solid particles, when in contact with each other at elevated temperatures, tend to decrease the total surface area by coalescence. This process, called sintering, usually accompanied by a decrease of the total volume of the powder mass, is of great importance in the technology of materials. In this paper, an attempt is made to discuss the elementary processes taking place during sintering of polymer particles. Similar studies done before on metallic and oxide particles¹⁻³ revealed that the rate of increase of the neck radius x formed between two spheres of radius a , such as represented schematically in Figure 1, can be described by a general equation:

$$\left(\frac{x}{a}\right)^n = \frac{F(T)}{a^m} t \quad (1)$$

where t is the time of sintering, and $F(T)$ is a function of temperature only, characteristic of the flow predominant in the process.¹ The latter is characterized by the exponents n and m in eq. (1). Thus, when $n = 2$ and $m = 1$, the flow is viscous and Newtonian, when $n = 3$ and $m = 2$, the transport is via external phase. For (evaporation and condensation), when $n = 5$ and $m = 3$, there is volume diffusion flow; when $n = 7$ and $m = 4$, there is surface diffusion flow.

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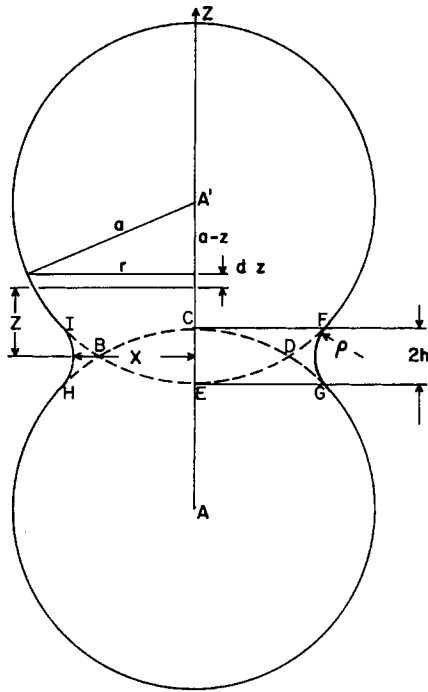


Fig. 1. Schematic representation of sintering of two globular particles.

These flows are caused by the capillary tensile stress in the neck area whose value can be approximately expressed by the equation

$$\sigma = \frac{\gamma}{\rho} \quad (2)$$

where ρ is the radius of neck curvature and γ is the surface tension of the solid, considered to be isotropic. As shall be shown below, the viscous flow mechanism is of most interest in our problem. Frenkel⁴ was the first to consider welding of two spheres by Newtonian viscous flow. His analysis resulted in the equation

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

where η is the viscosity of the medium. This equation, a special case of general eq. (1), was verified experimentally by Kuczynski³ for glass spheres.

No such studies have been done on polymer spheres. Dillon, Matheson, and Bradford⁵ spread a thin layer of synthetic latex solution containing 20 parts per million of solid on a plane collodion film and observed the sintering of latex globules during the drying of the solution. They found that, at a given time of sintering, the square of the neck diameter was proportional to the sphere diameter. From this observation, they concluded that

Frenkel's eq. (3) was fulfilled. However, this may not necessarily be a correct conclusion because the relation they found can be obtained from a more general equation

$$\left(\frac{x^2}{a}\right)^p \sim t.$$

If p differs from unity, the flow, as will be shown later, is non-Newtonian. Unfortunately, Dillon et al.⁵ did not study the time relation to ascertain the value of the exponent p , nor the temperature dependence of the process.

EXPERIMENTAL

The spherical powder of poly(methyl methacrylate) of high purity was kindly donated by the du Pont Experimental Station. The size of the globules ranged from submicroscopic to about 0.3 mm. The method of sintering of the spheres to the flat blocks of the same material was adopted. Some powder was sprinkled on the metallographically polished surface of a block previously prepared from the same batch of powder by hot pressing. These specimens were heated at temperatures ranging from 120° to 207°C for time intervals extending from 5 min to 100 hr. After each heat treatment, the diameters of the spheres sintered to the block were measured under the microscope, then the globules were removed from the block with a small spatula, and the diameter $2x$ of the always circular stump of the neck was measured. The removal of the sphere was watched through the microscope to assure that the observed stump corresponded to the measured sphere. The profiles of some necks between the spheres and the blocks

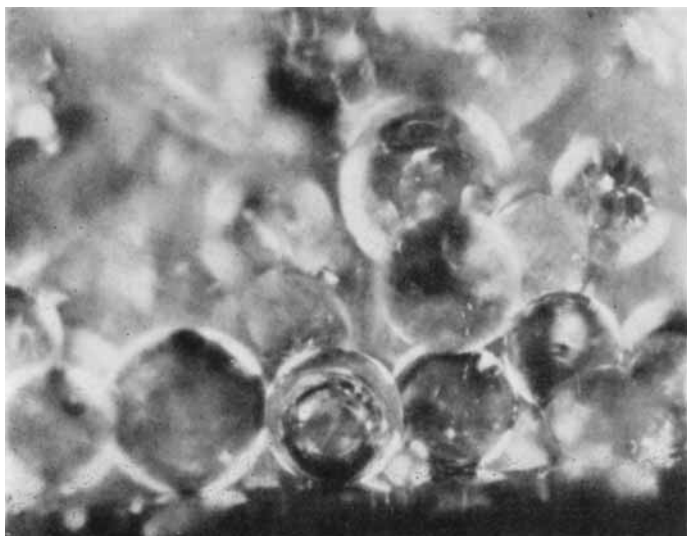


Fig. 2. Spheres of poly(methyl methacrylate) sintered to a block at 170°C for 15 min.

93×

resting on the edge of the block could be observed directly. A photomicrograph presented in Figure 2 reveals the details of the geometry of the neck during sintering.

RESULTS AND DISCUSSION

In order to establish the dominant sintering mechanism, the relationship between neck diameter and time has to be established. This was accomplished by measuring the neck radius x as a function of time for spheres of the same diameter. As the relationship expected is of the form of Frenkel's eq. (2), the plot of $\log x^2/a$ versus $\log t$ should yield the exponent p . Such a plot, reproduced in Figure 3, reveals that up to about 150°C the exponent p is constant and approximately equal to 2.5; above that temperature, p decreases continuously to 0.27 at 207°C . In some samples, not indicated in Figure 3, heated below 140°C , the value of p at the beginning of sintering was found to be as high 5, but always changed to 2.5 after prolonged sintering. This could be due to the bad contacts of rather small necks developing at low temperatures, caused by some surface imperfections. The exponent $p = 1/n$ as a function of temperature is represented in Figure 4.

Varying the particle radius a in similar experiments enabled us to establish that $x \sim a^{0.51}$, very close to the relation predicted by Frenkel ($x \sim a^{0.5}$) and observed by Dillon et al.⁵ This relation holds for all temperatures investigated. The experimental results can be combined in one empirical equation:

$$\left(\frac{x^2}{a^{1.02}}\right)^p = F(T)t \quad (4)$$

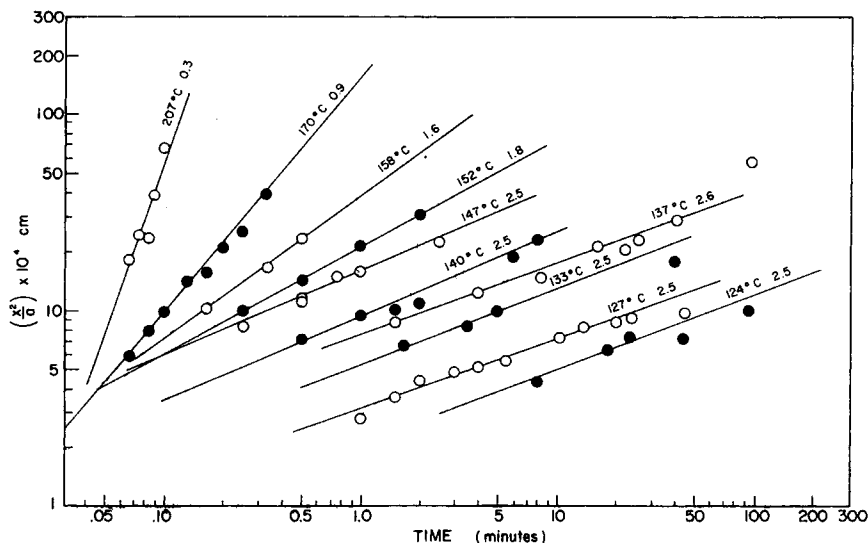


Fig. 3. Variation of the ratio x^2/a with time for spheres of poly(methyl methacrylate) sintered at indicated temperatures.

where $F(T)$ is a function of temperature only, and p varies with temperature in a manner described above.

For $p = 1$, accepting that the exponent of a is a close enough approximation to unity, the empirical eq. (4) reduces to the Frenkel eq. (3). This and the form of eq. (4) suggest strongly that the most likely mechanism of sintering of this polymer is viscous flow, but not necessarily Newtonian.

Equation (4) can be derived theoretically assuming that the flow of polymer is generally described by the Ostwald empirical relation:

$$\sigma = K(\dot{\epsilon}_s)^n \quad (5)$$

where σ is the shear stress, $\dot{\epsilon}_s$ is the shear strain rate, and K is a function of temperature only. If the exponent n in the above equation is equal to 1, the flow is Newtonian, and the function K is the true viscosity η .

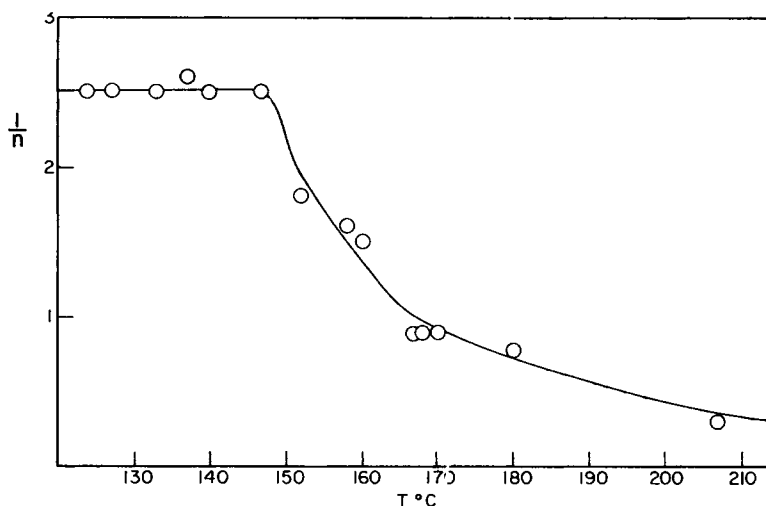


Fig. 4. Variation of exponent n with temperature.

The geometry of the system is represented schematically in Figure 1. It can be shown⁶ that if $x/a < 0.3$, $\rho \approx h \approx x^2/4a$. The neck between two spherical particles grows by displacement of the matter from the lenticular volume $BCDE$ in Figure 1 into one obtained by rotation of the "triangle" DFG around the AA' axis. As the material is nearly incompressible, the total volume of the system remains constant. Assuming steady state conditions, the flow equation can be obtained by equating the rate of surface energy change during sintering, dE_s/dt , to the rate of its dissipation by viscous flow, dE/dt . In view of the smallness of ρ , it is quite obvious that

$$\frac{dE_s}{dt} = 4\pi\gamma x \frac{dx}{dt} \quad (6)$$

This energy is dissipated in viscous flow. The energy increase per unit volume due to the shear stress σ is $\sigma\dot{\epsilon}_s$. Thus, the rate of energy dissipation per unit volume is $\sigma\dot{\epsilon}_s$. The total dissipation rate is

$$\frac{dE}{dt} = 2 \int_h^a \sigma\dot{\epsilon}_s dV. \quad (7)$$

The limits of this integral are adequately explained in the sketch represented in Figure 1. From the geometry of this figure, one can easily find that $dV = \pi(2az - z^2)dz$. The strain rate $\dot{\epsilon}$ is a gradient of the velocity:

$$\dot{\epsilon} = - \frac{d}{dz} \left(\frac{dz}{dt} \right)$$

and, as a solid, is practically incompressible:

$$\frac{dz}{dt} / \frac{dh}{dt} = \frac{h}{z} \text{ or } \frac{dz}{dt} = \frac{h}{z} \frac{dh}{dt};$$

and, because $h = \rho$,

$$\dot{\epsilon} = \frac{\rho}{z^2} \frac{d\rho}{dt} \quad (8)$$

which is not the shear strain rate. By an argument similar to that used by Eshelby,⁷ we obtain $\dot{\epsilon}_s = 2\dot{\epsilon}$. Introducing eq. (8) into eq. (7), we obtain

$$\frac{dE}{dt} = \pi K 2^{n+2} \rho^{n+1} \left(\frac{d\rho}{dt} \right)^{n+1} \int_\rho^a \left(\frac{2a}{z^{2n+1}} - \frac{1}{z^{2n}} \right) dz$$

which, after integration, yields

$$\frac{dE}{dt} = \pi K 2^{n+2} \rho^{n+1} \left(\frac{d\rho}{dt} \right)^{n+1} \left[- \frac{a}{nz^{2n}} + \frac{1}{(2n-1)z^{2n-1}} \right]_p^a$$

Because $\rho \ll a$, only the term containing the highest power of ρ in the denominator will be retained:

$$\frac{dE}{dt} = \frac{\pi K}{n} a 2^{n+2} \rho^{1-n} \left(\frac{d\rho}{dt} \right)^{n+1}$$

and, as $\rho = x^2/4a$,

$$\frac{dE}{dt} = \frac{\pi K}{na} 2^{2n-1} x^{3-n} \left(\frac{dx}{dt} \right)^{n+1}.$$

This rate should be equal to the rate of surface energy decrease given by eq. (6). Comparison of these two equations after some simplifications gives

$$x^{-1+2/n} \frac{dx}{dt} = 2^{-2+3/n} \left(\frac{n\gamma}{K} \right)^{1/n}$$

and, after integration,

$$\left(\frac{x^2}{a} \right)^{1/n} = \frac{1}{2n} \left(\frac{8n\gamma}{K} \right)^{1/n} t. \quad (9)$$

This equation, with $p = 1/n$, is equivalent to eq. (4) found experimentally. For Newtonian flow, $n = 1$, it reduces to

$$\frac{x^2}{a} = \frac{4\gamma}{\eta} t \quad (9a)$$

which is equivalent to Frenkel's equation as corrected by Eshelby.⁷ The constant n has rheological significance. If $n < 1$, the flow is pseudo-plastic. If $n = 1$, the flow is Newtonian. If $n > 1$, the flow is dilatant. (At large strain rates, large stresses have to be used to further increase $\dot{\epsilon}$.) According to Figure 4, the mechanism of sintering of poly(methyl methacrylate) spheres up to 170°C is the pseudo-plastic flow. Up to 150°C, n remains reasonably constant and approximately equal to 0.4. Above that temperature, it increases steadily to become 1 at about 170°C. Above this temperature, the polymer changes to a viscous melt. The long chains curled by entropy forces float among short ones, and the structure of the liquid becomes anisotropic. The dilatant behavior is probably due to this anisotropy. The short chains act as sort of low viscosity liquid which surrounds the longer chains of lower mobility. Such a model corresponds closely to the models of deflocculated pastes in which dilatancy is commonly observed.

Equation (9) can be transformed into yet another one closely related to Frenkel's eq. (9a). Strain rate at $z = \rho$ according to eq. (8) and the definition of ρ is

$$\dot{\epsilon} = \frac{2}{x} \frac{dx}{dt}$$

Taking the derivative of both sides of eq. (9) written in a logarithmic form, we obtain

$$\frac{2}{x} \frac{dx}{dt} = \frac{n}{t}$$

Thus,

$$\dot{\epsilon} = \frac{n}{t} \text{ and } \dot{\epsilon}_s = \frac{2n}{t} \quad (10)$$

Using relation (5) and the definition of viscosity η , we can write

$$K = K_0(\dot{\epsilon}_s)^{n-1} = K_0 \left(\frac{2n}{t} \right)^{n-1} \quad (11)$$

which, together with eq. (9), gives

$$\frac{x^2}{a} = \frac{2\gamma}{K} t \quad (12)$$

This equation is formally identical to Frenkel's equation (9a); however, it should be kept in mind that, in a general case, K is not constant but depends on stress and strain rate.

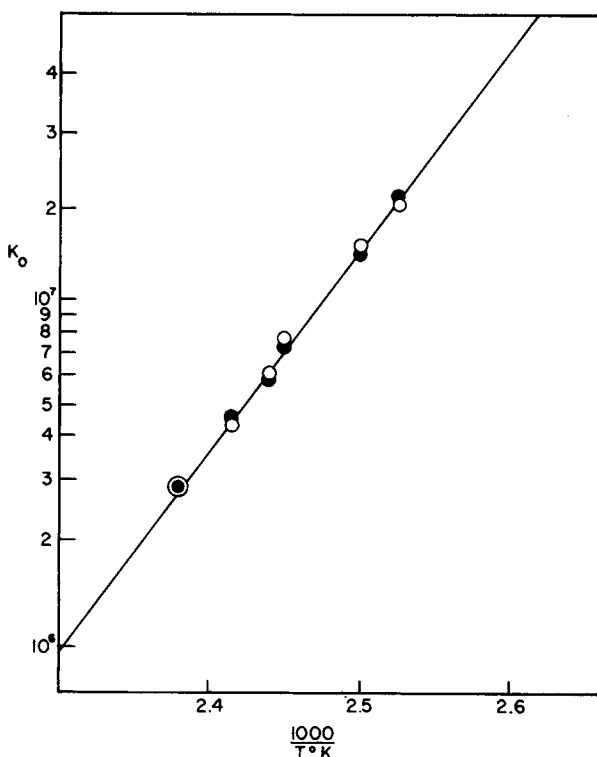


Fig. 5. K_0 as a function of reciprocal absolute temperature: (○) constant x^2/a ; (●) constant time t .

Before closing, a few remarks should be made on the temperature dependence of the sintering process. Two parameters, n and K in eq. (9), are functions of temperature. Parameter n characterizes the type of flow in our analysis and, as was pointed out, changes only with the structural changes in polymers. These occur above 150°C , when appreciable melting of polymer takes place and manifests itself by a steady increase in n with temperature. Some general remarks on this effect were made above. Below 150°C , n is constant and changes in the rate of deformation with temperature are expressed by parameter K_0 . From the definition of viscosity η given by eq. (11), it is obvious that K_0 must have the form

$$K_0 = K_0^* \exp(Q/RT)$$

where K_0^* is a constant and Q is the activation enthalpy of viscosity. K_0 is independent of stress and strain rate. That this indeed is the case can be ascertained from Figure 5, where $\ln K_0$ is plotted against the reciprocal of absolute temperature. The values of this parameter were calculated from the curves of Figure 3 with the help of eq. (9) at constant x , which is equivalent to constant stress conditions, as well as at constant t , which is equivalent to constant strain rate. All the points lie on the same straight line as

should be expected if K_0 was independent of stress and strain rate. The curve in Figure 5 yields the following relation:

$$K_0 = 4.7 \times 10^{-8} \exp\left(\frac{28000}{RT}\right).$$

It should be noted that activation energy is independent of stress, which is in variance with the results of Sherby and Dorn⁸ who from creep measurements of poly(methyl methacrylate) samples at low temperatures found that the activation enthalpy of creep decreases linearly with applied stress. They also observed that the activation enthalpy at stress equal to zero is about 48 kcal/mole, or even greater at higher temperatures. The temperatures in their experiments never exceeded 100°C.

The actual viscosity coefficient K depends on stress, as is evident from eq. (11), which can be rewritten in form

$$K = K_0^{1/n} \sigma^{1-1/n}.$$

For $1/n > 1$, viscosity decreases with increasing stress, as indeed has been observed by Sherby and Dorn.⁸ Moreover, the activation enthalpy of viscosity is $1/n$ times greater than the activation enthalpy of K_0 . According to our observations, below 150°C, $1/n \sim 2.5$; therefore, the activation enthalpy of viscosity is about 71.5 kcal/mole, fairly close to the values obtained by Sherby and Dorn⁸ near 100°C. For dilatant flow, $1/n < 1$ and viscosity increases with increasing stress, which indeed is characteristic of this type of flow. For Newtonian flow, $1/n = 1$ and $\eta = K_0$, which indicates that viscosity is stress independent. The calculated values of viscosity in the temperature interval 120°–150°C decreases from 10^{10} to 10^8 poises in good agreement with the viscosity spectrum of this polymer.⁹

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