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Removal of low molecular weight components during thermal debinding of powder compacts

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This paper discusses the thermal removal of a low molecular weight component in a stainless steel powder-binder compact. A two-component binder composed of stearic acid (SA) and polypropylene (PP) with widely different debinding temperatures was chosen as a model system. Thermogravimetric analysis was used to determine separately the debinding kinetics of SA. Strong evidence was found that the mechanism which determines the debinding rate is the diffusion of stearic acid in the polymer. The diffusion length is half the distance between neighbouring pores which allow the evaporation products of stearic acid to move out of the compact. The differences with debinding mechanisms in ceramic powder compacts are discussed. Upper thresholds of the activation energy of diffusion of SA in liquid and solid PP are calculated to be 70 and 122 kJ mol^{-1}, respectively. The diffusivity at $T = 167\,^{\circ}\mathrm{C}$ was estimated as 8×10^{-9} cm^2 s^{-1}.

1. Introduction

Before the sintering of injection-moulded powder compacts the binder must be removed in order to prevent cracking of the sample and contamination with binder residue. The debinding is the most crucial step in the powder injection-moulding process because the binder must be extracted without distorting the component. Most frequently the binder is removed by evaporation which may be accompanied by thermal decomposition. The binder is a multicomponent system of different organic products (polymers, waxes, oils) which vary in their removal temperature. Therefore, the debinding is carried out in a series of heating ramps and isothermal holds. Due to the rather complex heat treatment the debinding is the most time-consuming part in powder injection-moulding. Improvement and optimization of binder burn-out require an understanding of the basic mechanisms which govern the process. The low molecular weight components (waxes, oils) are removed at low temperatures and create channels for the gaseous evaporation products of the polymer to move out at high temperatures. Depending on the system, a volume fraction of 30 to 40% of low molecular weight components is sufficient to achieve a high enough permeability in the porous structure [1]. During this process the polymer is still rigid and imparts strength to the compact.

The present paper deals with the kinetics of removal of the low molecular weight components during the first stage of the debinding process. A two-component binder composed of a wax and a polymer is used as a model system. A suitable choice of the two constituents with respect to their removal temperatures allows the separate observation of debinding of one component. As a low molecular weight component, stearic acid (SA) was chosen which is widely used in powder processing as a wetting agent [2]. It provides a better homogeneity after mixing and lowers the viscosity during moulding. Stearic acid has a melting temperature of 73 °C. Polypropylene (PP) (grade Eltex P HV202 from Solvay, Belgium) was used as a polymer. The melting point of the PP, as given by the company, is $T_m = 161\,^{\circ}\mathrm{C}$. The experimentally observed value during mixing was $T_m \approx 170\,^{\circ}\mathrm{C}$. The kinetics of removal of stearic acid was determined by monitoring the weight loss of the compacts by thermogravimetric analysis (TGA).

2. Experimental procedure

The compacts for the TGA measurements were produced by mixing spherical stainless steel powder SS316L with stearic acid and PP in a twin-cam mixer. The particle size of the powder ranged from 8 to 58 µm with a mean value of 26 µm. The tap density was determined as 5.04 g cm^{-3} and the pycnometer density as 7.93 g cm^{-3}. The volume fraction of the metal powder was chosen to be 0.60. The ratio of the volume of stearic acid to that of PP was adjusted to 40%, which allows a debinding of the whole binder without deformation of the sample as was seen in further experiments. The mixing was carried out in air at 175 °C until the viscosity of the mixture did not decrease any more.

Subsequently, the granulated feedstock was fed into a stainless steel sample container and hot-pressed with a pressure of 7.5 MPa at 230 °C. This temperature provided the best pressed samples with a minimal amount of stearic acid loss. The disc-shaped samples

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had a diameter of 13 mm and variable thicknesses. The desired thickness for a specific experiment was achieved by grinding.

The samples were then inserted in the TGA apparatus. They were placed on a stainless steel foil and surrounded with a stainless steel ring to ensure that debinding occurred only from one side. During operation the measuring tube was flushed with high-purity nitrogen (99.999%) with a flow rate of 99 cm min^{-1}. The electrobalance was connected to a PC-AT to observe the weight loss during operation and for further evaluation of the data.

3. Results and discussion

Fig. 1 shows the reduced total mass $[m/m(0)]_{\text{tot}}$ of the compact with respect to time ($m(0)$ is the initial total mass) for isothermals in the temperature range of 137 to 270 °C. The samples were heated up to the specified temperatures in about 1 h. The beginning of the isothermal hold is marked in Fig. 1 by a dotted line. Only a part of the measured data is plotted in this graph because the partial overlap of the curves would obscure the general behaviour. The thickness of the samples was 1.75 mm for each of these experiments. It can be seen that the binder loss is thermally activated. While at a temperature of 137 °C the weight loss after a debinding time of 16 h is only small, the debinding has already finished at 217 °C after about 6 h. The nearly horizontal line of the latter indicates that only the removal of the low molecular weight component of the binder, stearic acid, has taken place. A significant debinding of the polypropylene starts at temperatures about 350 °C, as further experiments showed.

In order to fit the observed debinding kinetics of stearic acid to a certain mechanism, a general model must be established first for how the removal process proceeds step by step. It is reasonable to assume for a binder of two components that a system of interconnected pores exists throughout the partially debound compact. These pores develop, beginning at the sample surface, when the volatile low molecular weight component starts to debind. The assumption of a planar binder–vapour interface which retreats into the interior of the sample with continued debinding seems to be impossible for a multicomponent binder system, because only the volatile components are removed at low temperatures while the viscosity of the polymer is so high that it is supposed to remain in its initial place. Following this model, the removal of stearic acid is assumed to take place (see Fig. 2) by diffusion of the molecule through the polymer to an interface between a pore and the binder inside the compact (step 1) and evaporation (step 2) with subsequent flow of the gaseous products through the pores to the compact' surface (step 3). Finally, the decomposition products are flushed away by the nitrogen gas stream (step 4). The slowest step in the sequence 1 to 4 controls the overall debinding rate.

If the binder removal is controlled by the diffusion of the stearic acid in polypropylene (step 1), the following equation is a good approximation [3–5]:

$$\ln\left(\frac{m(t)}{m(0)}\right)_{\text{SA}} = \ln\frac{8}{\pi^2} - \frac{\pi^2}{4}\left(\frac{D_{\text{eff}}}{l^2}\right)t \qquad (1)$$

where $m(t)$ and $m(0)$ are respectively the instantaneous and removable mass of stearic acid, l is the diffusion length (cm) and t is the debinding time (s). D_{eff} is the effective diffusivity of the low molecular weight component in the polymer (cm^2 s^{-1}) given by

$$D_{\text{eff}} = DE/\tau \qquad (2)$$

where D denotes the real diffusion coefficient, E is the porosity of the compact and τ is the tortuosity factor. In Fig. 3, the kinetic data of debinding of stearic acid for different temperatures under the condition of constant sample thickness (d = 1.75 mm) are plotted according to Equation 1. The dotted line indicates again the beginning of the isothermal hold. For every temperature a nearly exact straight line is observed. Indeed, the debinding process proceeds much too slowly

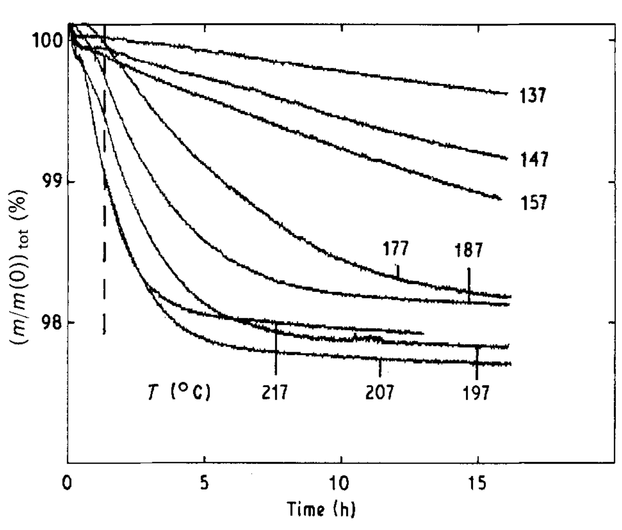

Figure 1 Reduced total mass $[m/m(0)]_{\text{tot}}$ of the compact ($m(0)$ is the removable total mass) with respect to time for isothermals in the temperature range 137 °C $\leqslant T \leqslant$ 217 °C. The thickness of the sample was 1.75 mm in all cases.

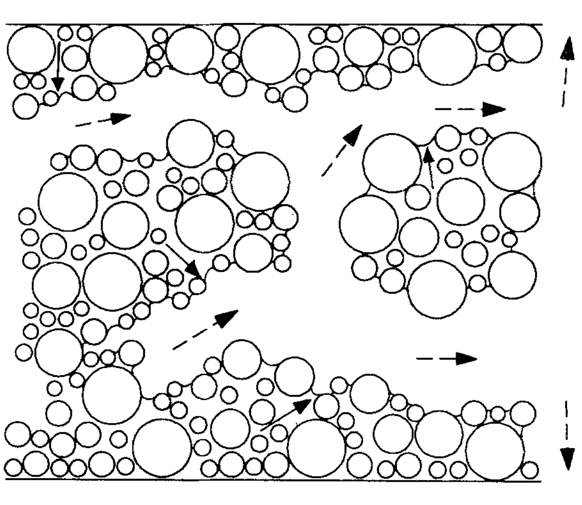

Figure 2 Sketch of the step-by-step model of low molecular weight component removal: diffusion in the polymer to a binder–pore interface (step 1), evaporation (step 2), flow through the pores to the surface (step 3), flushing away by a nitrogen stream (step 4) (the N_2 hits the surface in a vertical direction).

for the reaction steps 2 or 4 to have an influence on it. Even for high temperatures the extraction of the stearic acid takes several hours so that there is enough time for evaporation at a pore–binder interface (step 2) and for removal of the gaseous products from the surface of the compact (step 4). Debinding experiments at $T = 217\,^{\circ}\mathrm{C}$ with different flow rates of N_2 ranging from 0 to $200\,\mathrm{cm\,s^{-1}}$ yielded no different results.

Also step 3 is not supposed to affect the debinding rate because the diffusion coefficients D in the gas phase are of the order of 10^{-1} to $10^{-2}\,\mathrm{cm^2\,s^{-1}}$, whereas the diffusivity in the liquid phase is in general three to four orders of magnitude smaller [6]. For the diffusion coefficients of the plasticizer dibutyl phtalate in poly(vinyl butyral) at temperatures from 60 to 150 °C, even lower values ranging from 10^{-12} to $10^{-10}\,\mathrm{cm^2\,s^{-1}}$ were found [3]. Generally, a difference in D might be compensated by different diffusion lengths l. However, if the ratio of the diffusion coefficient D to the diffusion length l is assumed to be D/l^2 also for step 3, the big difference in D cannot be compensated for in the present compact by the comparatively small difference in l for steps 1 and 3, which are assumed to be about 65 μm in the solid phase (see below) and at most about the thickness of the sample, 1750 μm, in the gas phase, respectively. Furthermore, the drop in the stearic acid concentration controlled by the flow of the gases through the system of channels would also have to follow an exponential dependence with respect to time as shown in Fig. 1. This provides strong evidence that the removal of the low molecular weight component in the polymer is controlled by the diffusion of stearic acid in the latter.

Studies on a two-component binder compact formed together with alumina powder have shown that strong capillary forces, which lead to a redistribution of the binder during thermolysis, govern the debinding process in these compacts [3]. The graphical representation of $m(t)/m(0)$ for the low molecular weight component against time t should show a straight line then, whereas for a compact formed by SS316L stainless steel powder, Equation 1 is valid and therefore an exponential decay is observed. The capillary forces are apparently too small in the compact used in the present work. This is due to the $1/d$-dependence of the capillary forces and to the much bigger particle diameter d of the metal powder (here $d \approx 26$ μm) in comparison with that of ceramic powders (usually < 1 μm).

According to Equation 1 the factor $(\pi^2/4)(D_{\mathrm{eff}}/l^2)$ determines the slope of the straight lines shown in Fig. 3. These factors are plotted in Fig. 4 on a logarithmic scale against the reciprocal temperature $1/T$. The reaction regime is divided into two regions, where in both cases straight lines are obtained. This behaviour can be explained by the melting point T_{m} of polypropylene. During the mixing process of the binders with the powder the melting of PP was observed at a temperature of 170 °C. Therefore, for temperatures $T < 170\,^{\circ}\mathrm{C}$ the diffusion of SA proceeds in solid and for $T > 170\,^{\circ}\mathrm{C}$ in liquid polypropylene. The appearance of the two different phases of PP can decrease the factor $(\pi^2/4)(D_{\mathrm{eff}}/l^2)$ in two ways. First, the diffusion coefficient of stearic acid will be lower in the solid polypropylene. But also the diffusion length l might be different for solid and for liquid PP. It is reasonable to assume that the development of pores is more difficult in the solid polymer and therefore the diffusion length increases (see next paragraph). However, the observation that the phase transformation of the polymer from liquid to solid affects the debinding kinetics is another strong hint that diffusion of the low molecular weight component in the polymer is the mechanism which controls the debinding process.

From the slope of the straight line in the temperature ranges $T > 170\,^{\circ}\mathrm{C}$ and $T < 170\,^{\circ}\mathrm{C}$ activation energies of 70 and $122\,\mathrm{kJ\,mol^{-1}}$, respectively, can be

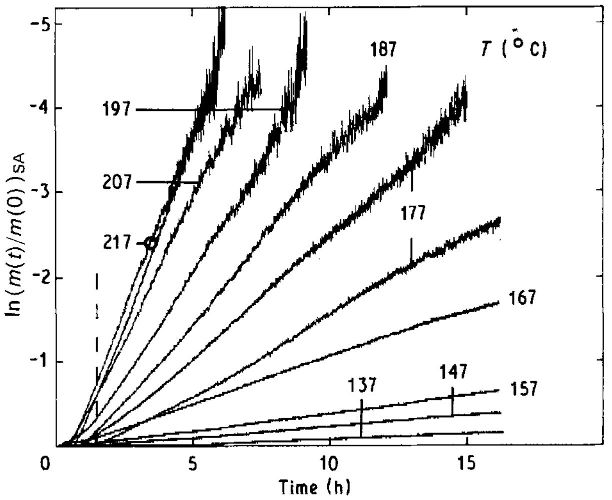

Figure 3 Reduced mass–$m(t)/m(0)_{\mathrm{SA}}$–($m(t)$ and $m(0)$ are the instantaneous and removable mass of stearic acid, respectively) of SA with respect to time for different temperatures plotted according to Equation 1. The straight lines provide strong evidence that the debinding is controlled by diffusion of the low molecular weight component in the binder.

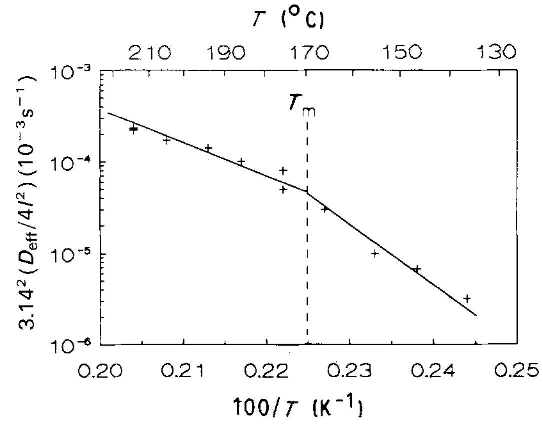

Figure 4 Factors $(\pi^2/4)(D_{\mathrm{eff}}/l^2)$ (slopes in Fig. 3 according to Equation 1; D_{eff} = effective diffusion coefficient of SA in PP; l = diffusion length) against the reciprocal temperature $1/T$ (T = temperature of the isothermal hold). The straight lines for temperature $T > 170\,^{\circ}\mathrm{C}$ and $T < 170\,^{\circ}\mathrm{C}$ with two different slopes are due to the change from liquid to solid PP.

calculated. In addition to the diffusivity these values might also be influenced by a temperature dependence of the diffusion length l. In order to get more information about this parameter l, debinding experiments were carried out with different sample thicknesses d in the range of $0.95 \leqslant d \leqslant 2.88$ mm at a constant temperature of 197 °C. In Fig. 5 the factors $(\pi^2/4)(D_{\text{eff}}/l^2)$ derived from the graphical representation of the debinding data according to Equation 1 are plotted against the sample thicknesses d (marked by crosses). The circles in Fig. 5 indicate the progress of $(\pi^2/4)(D_{\text{eff}}/l^2)$ with increasing d, starting at an arbitrary chosen common point at $d = 0.95$ mm, if the diffusion length l is considered identical with the sample thickness. It can be seen that in this case the factor $(\pi^2/4)(D_{\text{eff}}/l^2)$ should drop by a factor of about 9 if the sample thickness is increased from 0.95 to 2.88 mm.

Because the experiment provides only a decrease by a factor of 2, the diffusion length cannot be the sample thickness. It is suggested that the parameter l is half of the distance between two neighbouring channels. Evidence for this assumption has also been found for ceramic compacts [3]. The decrease in the factor $(\pi^2/4)(D_{\text{eff}}/l^2)$ with rising sample thickness means that it is more difficult for thicker samples to develop pores in the interior than for thin ones. This effect is understandable if the formation of a pore is associated with a movement of powder particles inside the sample over a small distance. This is confirmed by the observation that the samples with small thickness showed a considerable homogeneous swelling (without deformation of the surface) after debinding of the SA, while thick samples were much less affected. The strength of this effect must then depend on the packing density of the compact; it is much stronger in a compact with a high packing density of the powder particles as in the present work, where spherical stainless steel powder particles are used which is (for instance) reflected by the high tap density of 5.04 g cm^{-3} [2, 7] (64% of the pycnometer density). The diffusion length l is probably also affected by different debinding temperatures because the viscosity of the polymer is reduced and it should be easier to develop pores. The calculated activation energies may therefore contain also a contribution from the temperature-dependence of the diffusion length, and the given value represents an upper threshold for the activation energy of diffusion of stearic acid in polypropylene.

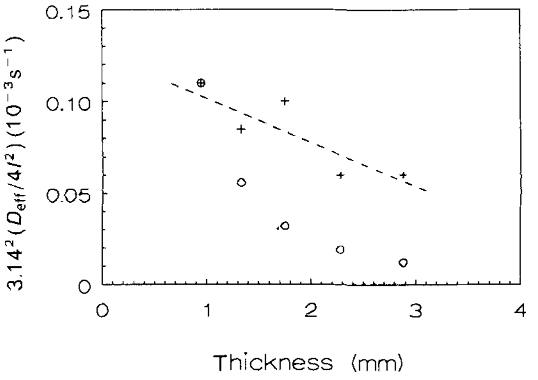

Figure 5 Factors $(\pi^2/4)(D_{\text{eff}}/l^2)$ (slopes in Fig. 3 according to Equation 1; D_{eff} = effective diffusion length of SA in PP; l = diffusion length) against the sample thickness (T = 197 °C). (+) Experimental results; (○) theoretical reaction progress if the diffusion length l is considered as identical to the sample thickness, starting at an arbitrary chosen common point at a thickness of 0.95 mm. The difference from the experimental results shows that the diffusion length is not identical with the sample thickness.

The identification of the diffusion length l also allows an estimation of the diffusivity $D(T)$. If the distance between pores is about five particle diameters, l becomes 65 µm. Accordingly, the effective diffusivity D_{eff} at a temperature of 167 °C which corresponds to a factor $(\pi^2/4)(D_{\text{eff}}/l^2) = 3.2 \times 10^{-5}\,\text{s}^{-1}$ is calculated as $5 \times 10^{-10}\,\text{cm}^2\,\text{s}^{-1}$. Using Equation 2 the real diffusivity D can be determined. The porosity of the compacts is 0.4. The tortuosity factor τ ranges generally from 3 for loose random-packed powder particles to 7 for dense random-packed [2]; a value of 6.5 was chosen with respect to the high packing density of the compacts in this work. Based on these estimates, the diffusivity of stearic acid in polypropylene $D_{\text{SA/PP}}$ (167 °C) is calculated to be $8 \times 10^{-9}\,\text{cm}^2\,\text{s}^{-1}$. This value is very close to the diffusivity of the plasticizer dibutyl phtalate (DBP) in the polymer poly(vinyl butyral) (PVB), $D_{\text{DBP/PVB}}$ (164°C) $= 1 \times 10^{-8}\,\text{cm}^2\,\text{s}^{-1}$, which has been measured by hot-stage Fourier-transform infrared spectroscopy [3].

4. Conclusion

The topic of the paper is the mechanism of removal of the low molecular weight binder components in powder-binder compacts. In order to be able to observe the removal of these separately, a two-component binder model system with widely different debinding temperatures was chosen composed of stearic acid and the polymer polypropylene. TGA was used to follow the debinding of stearic acid in the temperature range 137 to 217 °C, which is well below the burn-out temperature of polypropylene (≈ 350 °C). Spherical stainless steel powders with a mean particle size of 26 µm were selected to form the compact.

Strong evidence was found that the diffusion of SA in PP governs the debinding process. This is based on two points: first, the debinding kinetics can be plotted according to a diffusion equation and secondly, in the graphical representation of the factor $(\pi^2/4)(D_{\text{eff}}/l^2)$ for the different isotherms against $1/T$, two straight lines were found for temperatures above the melting point of polypropylene and below. Capillary forces which control the debinding of plasticizers in ceramic greenware are not strong enough in compacts based on stainless steel powders. This is due to the much bigger particle size (here 26 µm) in comparison with ceramic powders (usually < 1 µm).

Debinding experiments at constant temperature with increasing sample thicknesses showed only a relatively small decrease of the debinding rate. This observation gives evidence that the diffusion length is half of the distance between neighbouring pores which develop in the early stages of the debinding. The activation energies of 70 and 122 kJ mol^{-1} for the temperatures $T > 170$°C and $T < 170$°C, respectively, are therefore an upper threshold for the activation energies of diffusion of SA in liquid and solid PP, respectively, because the pore distance which determines the diffusion length might also be temperature-dependent. With the assumption that the pore distance is about five particle diameters, the diffusivity of SA in PP at $T = 167\,^{\circ}$C was assessed as 8×10^{-9} cm^2 s^{-1}.

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