Wick Debinding – An Effective Way of Solving Problems in the Debinding Process of Powder Injection Molding

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1. Introduction

Powder injection molding (PIM) has been shown itself to be a successful shaping technique for producing complex-shaped ceramic, metal or cermet parts. The process starts with preparing a high solid loading suspension, where ceramic or metal powder is mixed with a thermoplastic material. At high temperature the suspension is fluid and can be injected into molds by applying a pressure. Inside the mold the suspension takes the shape of the mold and then cools below the melting point of the thermoplastic material and solidifies into a green body. After the molding cycle the green body consists of solid particles held together by the thermoplastic phase, which serves as a binder.

The challenging and time-consuming operation in the powder-injection molding process is removing the binder from the green bodies prior to the sintering, without causing any deformation or cracks. The debinding process is difficult because green bodies contain relatively large amount of poorly volatile binder in the solid state, i.e. below the melting point. Debinding is usually achieved by slowly heating the green bodies, causing the binder to decompose and vaporize. This is the thermal debinding process. The difficulties are especially severe in low-pressure injection molding, since in this case the binder does not contain a backbone polymer that would hold the particles firmly in place during the debinding. Low-pressure injection molding (LPIM) is a variant of injection molding where relatively low pressures are used, typically less than 0.7 MPa, and the pressure is applied using compressed air instead of a screw (like in the more common high-pressure variant). The liquid medium in the feedstock is a low-melting-point wax, which is crucial for the low viscosity of the molten feedstock. The advantages of LPIM, in comparison with other ceramic injection techniques, include the lower cost of the molds, less die wear and less expensive and simpler equipment for the injection molding (Zorzi et al., 2003; Cetinel et al., 2010; Loebbecke et al., 2009; Gorjan et al., 2010). The method has also been shown to be appropriate for the shaping of microcomponents (Cetinel et al., 2010; Bauer & Knitter, 2002; Wang et al., 2008).

However, an effective way of reducing the formation of defects in the process of binder removal exists. That is, to introduce an additional debinding step – debinding in a wicking embedment (Curry, 1975; German, 1987; Wei, 1989; Liu, 1999; Bao & Evans, 1991; German,
1990) or wick-debinding. A wicking agent can be in the form of a porous solid substrate plate or in the form of a loose powder or granulate. The granular form offers a gentle physical support for samples, regardless of their shape, and thus prevents certain flaws, such as distortion and cracking. The capillary extraction is uniform over the entire surface of the green body, which ensures that debinded parts also have, as much as possible, a uniform structure after the wick-debinding. A solid plate does not offer so many benefits; however it has one advantage over the granular form of wicking agent, i.e., there are fewer practical problems when handling the compacts after the debinding. The wick-debinded parts do not have to be cleaned and are simply transferred to the sintering furnace.

![Fig. 1. Wick-debinding on a porous plate. The molten binder is extracted from the green body into the porous supporting plate.](image1)

![Fig. 2. Wick-debinding in an embedment of porous powder or granulate. The molten binder is extracted in all directions from the green body.](image2)

The wicking embedment can be utilized with great success in either the high- or the low-pressure injection molding. However, its use is more beneficial in the low-pressure variant, where the debinding is a more delicate operation.

2. Fundamentals

The basic principle of wick-debinding is the phenomenon called capillarity, which is a spontaneous flow of liquid into small pores. This effect occurs because of the attractive forces between the liquid and the solid surface of the pores and the surface tension of the liquid. The attraction of the liquid to the surface causes the adhesion of the liquid and the solid, which results in the liquid wetting the surface. The wetting is characterized by a wetting angle, which depends on the interactions between the liquid phase, the solid phase
and the atmosphere. The smaller the wetting angle the better is the wetting and the liquid easily spreads over the surface.

![Figure 3](image1.png)

Fig. 3. Sketch of a droplet of liquid on a solid surface showcasing the wetting phenomenon, characterized by the wetting angle (Φ). When a liquid wets a surface it spreads over it.

An interesting phenomenon occurs when the liquid is inside a small pore. When the liquid wets the surface of a small pore at a certain angle (Φ), the surface becomes concavely curved as is sketched in Fig 4. Any curved liquid surface causes a pressure difference across the interface (ΔP_c = P_V - P_L) between the liquid and the surrounding atmosphere.

![Figure 4](image2.png)

Fig. 4. The liquid, that wets the surface, inside a small, cylindrical pore forms a concave spherical surface that causes a pressure difference between the liquid phase.

The equilibrium pressure difference is described by the Laplace-Young equation:

$$\Delta P_c = P_L - P_V = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

where ΔP_c [Pa] is the pressure difference between the liquid phase and the air phase, γ [N/m] is the surface tension, and R_1 and R_2 are the principal radii of curvature. As the capillary surface is concave towards the atmosphere, the liquid pressure is lower than that of the atmosphere, possibly reaching negative values, which is called a tensile stress inside the liquid (Bouzid et al., 2011).

In the case of a small, cylindrically shaped, pore channel the surface of the liquid is symmetrical and R_1 = R_2 = R. On small scales gravity is not strong enough to significantly
influence the shape of the liquid surface so the surface has a spherical shape. If the wetting angle is considered the curvature in the small, tube-shaped, pore channel can be reasoned from Fig. 4:

\[
R = \frac{d}{2\cos(\Phi)}
\]  

(2)

Combining equations (1) and (2) we obtain a correlation between the capillary pressure, the wetting angle and the pore diameter:

\[
\Delta P_c = \frac{4\gamma \cos(\Phi)}{d}
\]  

(3)

From equation 3 it is clear, that the capillary pressure is inversely proportional to the pore diameter. Because the capillary pressure is larger for smaller pores, the liquid is forced to move from the larger to the smaller pores. So in the equilibrium state the liquid would fill the smallest pores of the system. The main idea of wick-debinding is to get a green body, heated to the temperature where the binder is molten, in contact with a material that has finer pores than the pores of the green body. Capillarity would then cause the binder to move from the green body into the material in the contact.

The wetting angle must be quite small for practical use. If the surface is not wetted by the liquid ($\Phi > 90^\circ$) then $\cos(\Phi)$ has a negative value, which means that the capillary pressure would be opposite and the liquid would not enter the porous media.

In any case, in a real system the porous media consist of pores of different sizes and shapes. Even for a green body made of packed monosized spherical particles there are voids of different sizes and shapes. However, real powders are composed of particles that are different in size and shape, which leads to an even more complex pore structure and a wider size distribution of pores. A labyrinth of interconnected voids is present in the green body and also in the wicking agent. Because of the complexity of real systems, the equation (3) is difficult to use directly. However, in real systems it has been experimentally observed that the liquid enters a porous body with a front (Bao & Evans, 1991; Somasundram, 2008) and a single value of characteristic capillary pressure at the front can be successfully used.

Another important thing to consider in the debinding is the kinetics of the process. It is important, from a practical point of view, that the process is reasonably fast. The kinetics of wick-debinding, besides capillary pressure, also depends on the resistance to flow through the porous media. Each individual channel has a certain resistance - a viscous drag that limits the velocity at which the liquid is flowing through.

The motion of liquid substances is generally described by the Navier-Stokes equations, which arise from applying Newton's second law to fluid motion. However, these equations are too complicated for practical use in describing debinding phenomena since the shape of the liquid surface would present boundary conditions that are too complex. However, with the development of computer software for liquid mechanics and because of the constant increase in computer power it is possible that accurate simulations of debinding will be developed in the future. Nevertheless, a simplified theoretical approach in dealing with the phenomena of debinding has produced satisfactory results.
The flow through an idealized single, long, circular, pore channel is described by the Hagen-Poiseuille equation (4), which is also an exact solution of the Navier-Stokes equations with certain assumptions, such as steady state, axisymmetric flow with no radial and swirl components of velocity.

\[ q = \frac{d^2 \Delta P}{32 \mu L} \]  

where \( q \) [m/s] is the flux or flow per area, \( \Delta P \) [Pa] is the pressure difference between the ends of the pore channel, \( \mu \) [Pa s] is the viscosity and \( L \) [m] is the length of the pore channel.

The smaller the pore, the larger the viscous drag. This generally means that small pores present a high resistance to flow. Again, like in the case of using equation (3), the Hagen-Poiseuille equation is due to the extremely complex shapes of pore channels in real systems, inappropriate for calculations, but nevertheless it demonstrates that despite the high capillary pressures, liquid transport through small pores can be slow. However, regardless of the complexity of pore channels, the flow of a liquid through porous material can be successfully described by a simple equation called the Darcy’s law:

\[ q = -\frac{K \nabla P}{\eta} \]  

where \( q \) [m³/(m² s)] is the volumetric flux, \( K \) [m²] is the parameter called permeability, \( \eta \) [Pa s] is the viscosity and \( \nabla P \) [Pa] is the pressure gradient.

The law was formulated in the 19th century by the French engineer Henry Darcy based on the results of water flow through sand (Richardson & Harker, 2002). It is a constitutive equation with a similar meaning for fluid flow as Ohm’s law for the electricity and Fourier’s law for the conductive heat transfer. Darcy’s law has been experimentally confirmed on many different material combinations and is considered well proven. It has also been derived from the Navier-Stokes equations.

The permeability \( K \) is a characteristic parameter of a porous substance that depends on the size, shape and interconnectedness of the individual pore channels and on the fractional porosity. The complex shape of pore channels makes a permeability difficult to calculate or predict from basic principles.

Many empirical equations have been used to determine the permeability from basic powder-compact properties, such as particle diameter \( (d) \), specific surface \( (S) \) and fractional porosity \( (E) \). Some of them are listed below (Bao & Evans, 1991; German, 1987):

\[ K = \frac{E^3}{5S^2(1-E)^2} \]  

\[ K = \frac{E^4d^2}{90(1-E)^2} \]
These permeability correlations have been tuned for a forced flow through the porous material, i.e., the flow of liquid that is pushed through the material by applying an external pressure. However, the permeability can be significantly different in the case of capillary extraction, where the liquid is sucked out of green body by capillary forces.

The wicking agent must extract the liquefied binder from the green body, which is itself a porous body. If the molten binder is removed from the green compact then a new surface must be formed in the interior of that compact. This new surface, which initially appears in larger pores, causes a capillary pressure in the opposite direction and resists extraction. A competition for the binder emerges between the two porous media. Only the smaller pores of the wicking agent might have a capillary suction that is strong enough to exceed the capillary pressure of the green body. The liquid then travels into the wicking agent only through these pores. In contrast, if the liquid were to be forced by the external pressure through the wicking agent it would travel mostly through larger pores, which present a smaller resistance.

The measured permeability, or that calculated from equations 6-8, could be significantly higher than in the case of capillary extraction. This means, that conventional methods of measuring permeability, such as measuring the forced gas flow through a sample of a porous material, cannot be used to determine the permeability for the capillary-extraction phenomenon. The mismatch between the forced flow and the capillary-extraction permeability is especially large in the granular form of the wicking agent. A characteristic case for porous material in the form of large granules with a fine porosity is schematically presented in Fig 5. If the fluid is forced through such a material the permeability would appear much larger than if this granulate was extracting the liquid from another porous material, for which a strong capillary pressure is required.

Fig. 5. In the capillary extraction the liquid flows only through smaller pores inside the granules, whereas in the case of liquid flow forced by external pressure the majority of flow would be between the granules.
Besides the kinetics of the capillary-extraction process it is crucial that the powder compact of green body retains its shape after the process has been completed and no flaws are introduced. One of the most critical moments in the process is the point when the binder melts. At this stage the compact becomes quite weak and soft. This is especially critical in the case of low-pressure injection molding, where only one component binder i.e., paraffin wax, is used. It is because of a characteristic known as the yield stress that the green body retains its shape. The suspension behaves like a rigid body below the yield stress and flows like a liquid above the yield stress. The yield stress is mostly governed by the particle size, shape, solid content and the inter-particle forces.

However, a large yield stress is undesirable for the molding step, since it results in a low moldability of the suspension (German, 1990). Suspensions with a high yield stress must have high powder content, which also increases viscosity, which is again undesirable in the molding step (German, 2003).

Fortunately, the yield stress of the molded green body can be significantly larger than the yield stress of the suspension before molding. This is because the particles rearrange during molding and solidification into a denser configuration - a consequence of the shrinkage of the binder after solidification. An increased attractive inter-particle interaction occurs in the denser form (Dakskobler & Kosmač, 2009). Ideally the process does not reverse during remelting. If the inter-particle forces are high enough, then the particle arrangement will not change; instead the expanding binder will be exuded from the body, while the particle arrangement remains intact. A series of photographs of a LPIM sample, taken with an optical microscope during heating from below to above the melting temperature of the binder, is shown in Fig. 6.

A molten paraffin binder exudes out of the green body. This happens without any disruption of the powder skeleton.

The extent of the exudation effect depends on the amount of low-melting point wax in the body. During the melting the volume of the wax increases by 15%. The effect is most pronounced in the low-pressure injection molding where the amount of wax is large - around 60 vol%. In high-pressure molding the amount of wax is around 10% - 30%. The large amount of wax is an important factor that explains why in LPIM extreme difficulties are encountered when a wicking agent is not used. In the HPIM process the yield strength during melting does not pose that big a problem, because the additional high-melting point polymer ensures that the particles are held in position. It has been shown that the yield stress of molded parts can also increase with the storage time after the molding (Novak et al., 2000; Cetinel et al., 2010).

Water from a humid environment can penetrate the green body and interfere with the bonds between surfactant molecules and the surface of the particles. The strength of the inter-particle forces increases, which leads to a significant increase in the yield strength. This effect can be made even faster, if the molded bodies are soaked in water (Novak et al., 2000).

Wicking embedment offers another benefit. It guarantees a gentle physical support for the parts. If the debinding takes place on a hard substrate there is danger that certain flaws will occur, as schematically presented in the sketch in Fig. 7. The suspended parts of the green
Fig. 6. Exudation of the paraffin-wax binder during heating above the melting point of the paraffin, as observed with optical microscope. The photograph a) shows the state before the melting, b) shows the first molten paraffin exuding from the green body, c) shows the situation 1 minute after the b) and d) shows state 10 min after the b).

Fig. 7. Green bodies with a complex shape can pose difficulties if they are debinded on a solid substrate. Small areas on which the green body rests on the substrate (1 and 2) can be deformed due to the large compressive stress. Suspended parts of the body can bend due to gravity or even crack at the point where the tensile stress is the highest (3). The wicking embedment can successfully reduce these flaws, since the support pressure is well spread over the green body's surface.
body could bend or crack and point pressure areas where the green body rests on the solid substrate can deform.

3. Overview of theoretical work

Because of the complexity of the capillary system in the porous green body and the wicking agent the accurate and general theoretical model is difficult to obtain. Since the systems can be quite different, the extraction can also show different behaviour. The existing theoretical models predict different behaviors during the debinding and many even contradict each other. The basis of all models is Darcy’s law and some form of capillary-pressure description. One of the first to theoretically describe the process of wick debinding for injection-molded samples was German (German, 1987), who in 1987 proposed a model, where he assumed that the binder is extracted from a molded compact as a continuous body in liquid form, leaving behind a binder-free region.

A partially debinded compact should, therefore, have a characteristic binder distribution with a binder-saturated region near the contact with the wicking powder and a region with no binder on the other side. A sharp border between these regions should be present – a sign of the trailing front of the molten binder. This model is simple and has frequently been used as a basis for research in wick debinding. Monte-Carlo simulations of binder removal based on German’s assumptions have also been conducted (Shih & Houring, 2001; Lin & Houring, 2005). These simulations focused on binder penetration in the wicking embedment and examined the case where pieces are not completely surrounded by the embedment.

However, German’s model has been criticized, on the basis of experimental data. Contradicting this model, many researchers observed that the binder is uniformly distributed inside the body at all stages of the debinding process (Liu, 1999; Bao & Evans, 1991; Vetter et al., 1994; Kim et al., 1999; Somasundram, 2008). There is also the question of how the air can enter behind the trailing front into the binder-free region if the molded pieces are completely surrounded by the wick (Somasundram, 2008). Furthermore, the debinding rate does not correspond well with some experiments (Vetter et al., 1994). It has also been observed that the permeability in a wick embedment can have important effects and can be a limiting factor, rather than the flow through a sample, as was suggested in German’s model [Vetter et al., 1994; Somasundram, 2008]. With more precise examinations of the binder-removal rate it has been confirmed that wick-debinding must take place via more than a single mechanism.

One clearly observable effect, for example, is a rapid decrease in the binder content at the beginning of the process. This has been attributed to the pressure arising from the thermal expansion of the binder [Somasundram, 2008, Gorjan et al., 2010]. Before the debinding process, molded parts contain binder in the solid state, then during the melting a large, and relatively sudden, expansion of the binder occurs. For example, the density of the paraffin drops by around 15% during melting (Gorjan et al., 2010).

With further studies of the kinetics of capillary extraction it has been found that the molten binder inside the body exists in different states, a differentiation based on the position inside the body. It can behave as a ‘mobile binder’ located in the larger voids between the powder
particles, which can flow due to the pressure gradient caused by the wicking embedment and as an 'immobile binder' located on the surfaces of the particles and inside the smaller voids, which cannot be moved due to the capillary suction – it is too strongly bonded to the powder and trapped inside smaller pores (Gorjan et al., 2010).

There can also be shrinkage during the debinding, which is inversely related to the ceramic volume fraction, with less shrinkage in green bodies with a high solid loading. Very little or no shrinkage occurs at a volume fraction of around 64% [Wright et al., 1990, Gorjan et al., 2010]. In order to avoid a large shrinkage a green body must be made with high a green density. A high green density is also beneficial for the sintering process; however, a high solid loading is detrimental for the molding step. It is always necessary to make a certain compromise.

Capillary extraction effectively removes only a part of the binder, because there is always a certain amount of the binder "trapped" inside the finest pores of the green body. This residual binder must be removed in the form of a gaseous phase. In the case of oxide ceramics the removal of the remaining binder can be achieved by controllably burning the binder. If the temperature during wick-debinding is raised above approximately 200°C then an organic binder starts to decompose due to oxidation reactions.

All of the binder can be removed if the temperature is increased above approximately 600°C, where even carbon burns. However, when all of the binder is removed from the body, the body becomes extremely brittle and weak. In this state it would be impossible to remove it from the embedment and clean it without causing serious damage. One solution is to further heat the system to the temperature where first stage of sintering starts. Pre-sintered or 'biscuit sintered' parts can then be safely removed from the embedment and since they contain no binder they can also be sintered without problems. However, practical problems can accompany this procedure. For example, if alumina parts are debinded a high temperature is required for the pre-sintering and at this temperature the wicking agent also starts to lose the fine porosity and can stick strongly to the surface of ceramic parts.

Another, economically even more acceptable option is to heat the samples after the capillary extraction to the temperature where the organic binder starts to decompose and then hold the parts at this temperature. It has been observed that at this temperature some amount of paraffin wax cures into a hard, brown-colored, non-volatile resin, which remains in the parts and is stable at the dwell temperature of around 200°C. This curing effect drastically improves the strength of the samples, which increases with the dwell time (Gorjan et al., 2011).

Parts processed in this way can be made sufficiently strong for handling without any risk of damage. They are also appropriate for green machining, like cutting, boring and grinding. Since they contain a very small amount of the binder, rapid heating inside the sintering furnace can be applied and the curing of the binder does not influence the strength of the sintered ceramic parts.

A procedure of debinding, where the benefits of wick-debinding are fully used, has also been developed, while the main drawback, i.e., additional cleaning and handling operations are avoided. According to the patent the debinding and sintering can take place in a single furnace (Gorjan & Dakskobler, 2011). This can be achieved by using a high purity-carbon granulate, which completely burns after its role as the wicking agent is completed.
4. Practice

In a practical use the wick-debinding process can offer significant benefits. Faster and safer debinding can be achieved in comparison with debinding a without the wicking agent. One of the most important factors in the debinding practice is to avoid the introduction of defects in green bodies. Potential defects include the loss of a compact's shape through distortion, warping, cracking and also the undesirable strong adhesion of the wicking powder on the surface of the debinded parts.

For example, in a low-pressure injection-molding, shaping technique it is almost impossible to debind samples without using a wicking agent. In HPIM the use of wick-debinding can be avoided, since the green body retains its strength after the wax has been melted due to the presence of polymer, which binds the particles together. Also in the case of HPIM, the wick-debinding reduces the possibility of flaws.

![Photograph a)](image1)

**Fig. 8.** Wick-debinding can significantly reduce the formation of flaws. Photograph a) shows the low-pressure injection molded sample, debinded without wicking embedment, while the photograph b) shows the sample which was debinded in the embedment of highly porous alumina wicking agent.

A major practical problem of wick debinding is the danger of causing defects when the parts are removed from the wick embedment and cleaned afterwards. Because the debinded parts
can be quite fragile, a gentle and manually intensive operation is required. If the debinded compacts are strong, then a more robust handling such as sieving can be applied. During this handling the breaking of parts can occur.

In the practice a wicking embedment must also satisfy some additional considerations besides having good capillary-extraction characteristics. It is the most practical if it is in the form of granules with a size of 50–200 μm. This size of granules ensures uniform contact with a green body and has, at the same time, good flowability. This flowability is crucial for easy handling. Smaller pores are powders tend to form dust, which is undesirable. Also, the granules are easier to clean from the surfaces of the parts after the debinding process. Each individual granule contains a very fine porosity, which is crucial for a highly efficient capillary extraction.

The correct temperature regime must be used in order to achieve debinding. A slow heating rate must be applied in order to give the wicking agent time for extraction. Typical debinding cycles last from 20 hours to several days.

The adhered wicking agent causes problems, because it would lead to a rough surface after the sintering. Therefore, it should be thoroughly cleaned from the debinded parts.

Fig. 9. Alumina wicking agent in the granular form. Photograph a), taken with optical microscop, shows granules of the wicking agent. Photograph b), taken with scanning electronne microscope show the surface of one granule. It can be seen, that the granula contains very fine porosity, which is a condition for efficient capillary extraction.
Fig. 10. Comparison of the properly debinded part (left) with the deformed part (right), which was deformed and had granulate wicking agent adhered to the surface. The defect was caused when the part was embedded into a too hot wicking agent, which had not been cooled enough after a thermal regeneration.

Fig. 11. Wick-debinded parts are loaded on a tray for the sintering process. Successfully wick-debinded samples contain an open porosity and are ready for a fast sintering cycle, in which complete burnout of the residual binder takes place.
After single or multiple uses the wicking agent accumulates a certain amount of organic phase – binder degradation products. This phase decreases the porosity of the wicking agent and thus its capillary-extraction ability. However, it can be regenerated by heating it to around 600°C, where all the organics burn. In practice, a wicking granulate with different amounts of residual organic phase can be used for debinding different parts. Small parts are debinded in the embedment, which is rich in organics, whereas the large parts are debinded using freshly regenerated granulate with a maximum capillary-extraction ability. As a result, the embedment can thus be consequently used for ever smaller parts.

5. Conclusion

Removing the organic binder from the powder-injection-molded parts with the use of highly a porous granular embedment has been shown to be an effective method. It offers many benefits, such as shorter debinding time due to capillary extraction. Also, it guarantees a gentle physical support for the parts and therefore reduces certain flaws, such as distortion and cracking. Wick-debinding also has an important drawback, such as the practical problems of cleaning the debinded bodies. These drawbacks are the reason, that wick debinding is avoided if possible. In the case of high pressure injection molding it is possible to avoid using the wick embedment because of the use of high melting point polymeric binders in addition to the low melting point wax.

However in the case of low-pressure-injection molding, where the debinding process is even more delicate the use of wick-debinding has a firm place. Furthermore, future improvements in wick-debinding and the developments of novel procedures can make this highly effective way of removing the binder from injection-molded parts easier to apply and more popularize in the industry.

6. References


This book is composed of different chapters which are related to the subject of injection molding and written by leading international academic experts in the field. It contains introduction on polymer PVT measurements and two main application areas of polymer PVT data in injection molding, optimization for injection molding process, Powder Injection Molding which comprises Ceramic Injection Molding and Metal Injection Molding, and some special techniques or applications in injection molding. It provides some clear presentation of injection molding process and equipment to direct people in plastics manufacturing to solve problems and avoid costly errors. With useful, fundamental information for knowing and optimizing the injection molding operation, the readers could gain some working knowledge of the injection molding.

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