# NET-SHAPE PROCESSING OF GRAPHITE WITH TAILORED POROSITY VIA POWDER INJECTION MOLDING OF MESOPHASE CARBON

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## Abstract

Mesophase carbon powder is an excellent precursor material for the production of fine grained graphite parts with superior mechanical properties. To provide a net-shape technique for complex as well as thick-walled carbon parts, a powder injection molding (PIM) process has been developed, making use of a water base binder system with agar as gelling agent. Since water can be removed by mere drying, the critical overlap of binder removal and pyrolysis / sintering of mesocarbon is avoided. This system also allows for an adjustment of shrinkage and porosity of the dried green body by varying the water and agar content. Thus, the porosity can be adjusted to meet the requirements of the mesophase powder employed. For the MCMB powder employed here, which exhibits little sinter activity, the densest possible green body is favorable, resulting in improved mechanical properties (flexural strength: 35 MPa, Young's modulus: 11 GPa).

## Introduction

Carbon mesophase is recognized as one of the most suitable precursor materials for the production of fine grained graphite parts with excellent mechanical properties. Until now, the most common processing method for these powders has been uniaxial or isostatic pressing. However, these techniques are limited to components of rather simple geometry. To avoid these drawbacks, this work focuses on a Powder Injection Molding (PIM) approach. This technique provides the opportunity of cost effective net shape processing of components with complex design. One of its main challenges lies in the selection of an appropriate binder system. If conventional binders are used, problems arise because the sintering / pyrolysis temperature of carbon mesophase (starting at 250 °C to 400 °C) is below the thermal degradation temperature of most organic binders (above 400 °C). The evaporation of enclosed gases leads to the deterioration of the product during the debinding process. With a water base binder system, which can be removed by drying at room temperature for the biggest part, this problem is reduced to a minimum.

## Experimental

### *Feedstock Preparation and Characterization*

For all feedstocks presented here, mesocarbon microbead powder (MCMB 6-G, Osaka Gas Chemicals, Inc.) with an average grain size of 6 µm was employed. One type of feedstock was compounded externally with a composition of approximately 64 wt.% MCMB powder, 30 wt.% water and 6 wt.% agar and additives. The exact processing conditions are not known. Proprietary compounds with varying contents of agar (TIC gums, Inc.) were prepared by stirring MCMB 6-G into a hot solution of agar and additives. After cooling, it was ground and fed into an extruder for homogenization and granulation. The desired water content could then simply be adjusted by drying or adding water. For characterization of the feedstocks, a high-pressure capillary rheometer (Goettfert Rheo-Tester 2000) was used.

### *Powder Injection Molding*

The water base feedstock was processed using a conventional injection molding machine (Arburg Allrounder 320 C 600-250), equipped with a special screw for powder injection molding. The molding process itself was straightforward and even longer dwell times of the material in the barrel of the machine didn't lead to substantial problems. Typical dimensions of the test bars molded were 5 mm x 20 mm x 100 mm. Injection pressure was in the range of 200 bars, injection speed 20 ccm/s, maximum barrel temperature 85 °C and cycle time typically around 60 seconds.

### *Thermal Treatment*

Debindering is the first, most critical and often most time consuming step of thermal treatment in the whole PIM process. With water-based systems, however, most of the binder can be removed in a mere drying process at moderate temperatures. In our case, it was carried out in a climatic chamber to ensure reproducible drying cycles, lasting about 15 hours. The dried green bodies were subsequently sintered in a tube furnace under argon flow. The heating profiles were calculated from prior thermogravimetric measurements of the feedstocks to obtain a constant mass loss rate. Finally, the samples were graphitized at 2000 °C for one hour.

## Results and Discussion

***Rheology***

In this water base binder system, water acts as filler, responsible for lowering viscosity and improving processability, while agar as backbone is necessary to provide sufficient green strength. As **Figure 1.** shows, lowering the water content by almost a quarter still renders processable feedstocks. Thus, depending on the complexity and wall thickness of the part to be molded, the viscosity can easily be adjusted within a wide processing window. All feedstocks examined exhibit a typical shear thinning behavior.

Varying the agar content also leads to a strong variation in viscosity (**Figure 2.**). Lowering the agar content decreases viscosity, however at the cost of less process stability, as indicated by the growing error bars. Moreover, the agar content must be kept at a level high enough to maintain sufficient green strength. Ideally, to reduce shrinkage and porosity and to facilitate drying and sintering, water and agar content are reduced to a minimum when working with MCMB powders. Agar with higher gel strength or additives enhancing it may help in this respect. Experiments to optimize feedstock composition are currently under way.

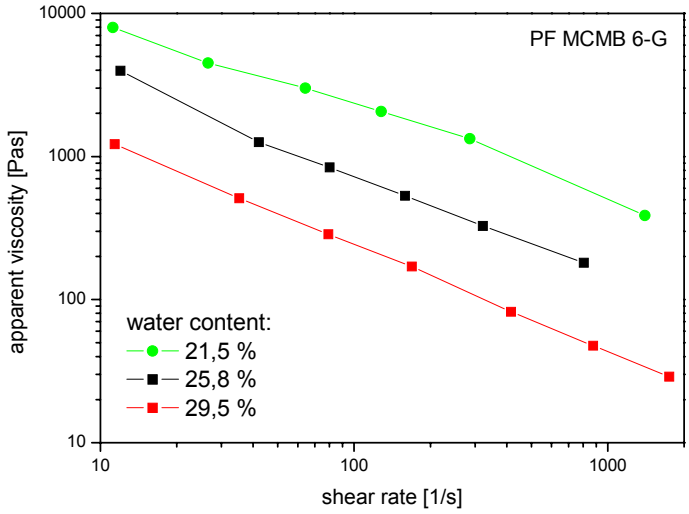


**Figure 1.** Dependency of the rheological properties on the water content. As expected, lowering the water content leads to a distinct increase in viscosity. All samples were prepared in the same way and had an agar content of 6 wt.%.

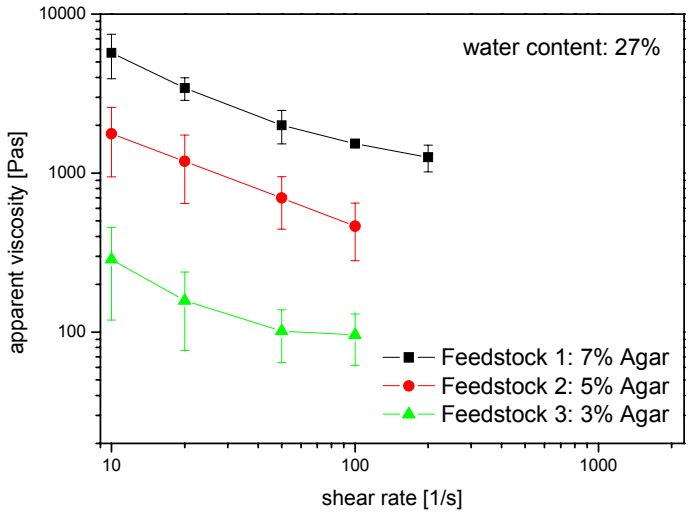


**Figure 2.** Dependency of the rheological properties on the agar content. Lowering the agar content decreases viscosity, however at the cost of less process stability, as indicated by the growing error bars.

***Drying and Shrinkage***

As already mentioned, the water content not only influences viscosity but also shrinkage during drying. In **Figure 3.**, mass loss and volume shrinkage of an injection molded sample were measured simultaneously under ambient conditions and plotted over time. In stage 1, both lines are congruent, which means that the green body shrinks homogenously and the water removed does not leave any porosity behind. In stage 2, a gap between the two lines develops, corresponding to the development of porosity. This is due to the fact that the particles – covered by a thin gel coat – start to touch each other so shrinkage starts to cease while water is still being removed from between the particles. In stage 3, all particles touch each other, so only the gel coat itself can shrink while loosing water.

A change in water content of the feedstock should mainly influence stage 1 drying and overall shrinkage, but not the porosity. The most critical point during drying is the transition from stage 1 two stage 2, where agar as backbone is still soft and stresses develop easily due to particles starting to touch. Non-uniform drying at this point makes the green body very susceptible to crack formation. A higher agar content leads to better green strength and makes drying easier. However, it will lead to increased porosity, not necessarily during drying, but in the subsequent thermal debinding step, when the agar is removed. Since MCMB powder only shows little sinter activity, this porosity will remain and deteriorate the mechanical properties of the final part.

From our experience with sintering of MCMB powders, a high heating rate is beneficial for improved mechanical properties, which can only be achieved, if most of the binder is removed before sintering starts. This is one of the main advantages of a water base binder when using MCMBs as precursor. Compared to pressed samples, mechanical properties are clearly inferior (flexural strength: 35 MPa, Young's modulus: 11 GPa, compared to 62 MPa / 18 GPa respectively for graphitized specimens), but significantly better than those achieved with polymer binders or by gel casting.

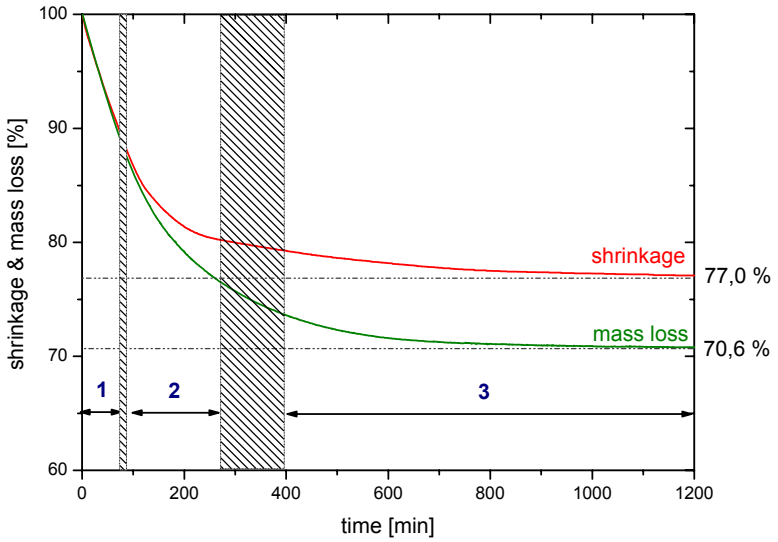


**Figure 3.** Bourry diagram for feedstock PF MCMB 6-G with a water content of 30 wt.%. Mass loss and shrinkage were measured simultaneously, the opening gap between the two lines denotes the development of porosity.

## Conclusion

Powder injection molding of mesophase carbon with water base binders appears as a very promising way to produce net shape graphite components with good mechanical properties, comparable to standard graphite qualities, but without the restrictions of the conventional forming technologies. To further improve strength and stiffness of this material, the goal is to get green bodies as dense as possible. Moreover, adding more sinteractive mesophase powder to the rather stable MCMB should also enhance properties, however at the cost of a more critical sintering behavior. Both routes are followed at the moment.

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