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# Development of PEG/PMMA based binders for Ti - Metal Injection Moulding

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**Abstract.** As the world is moving towards green manufacturing, there is an increasing demand for the use of clean and environmentally friendly binder systems in metal injection moulding (MIM) industry. One example of these developed binders is polyethylene glycol (PEG) - polymethyl methacrylate (PMMA) based system. We have systematically evaluated and optimized this binder system, and reported some interesting new results. In this article, we reported the effect of PEG molecular weight on rheological properties of the feedstock and its water debinding behaviour. We also investigated the effects of different surfactants on MIM feedstock rheological and mechanical properties, and identified a potential surfactant that enhances compatibility between the binder components and metal powders. Furthermore, we reported an interesting problem – 'voids formation', which is associated with PEG crystallization. To minimize this void formation a crystallization inhibitor is incorporated in the PEG/PMMA system, thereby eliminating the void formation while maintaining the clean nature of this system. This paper is concluded with some new thoughts with regard to binder design.

## 1. Background

Due to environment friendly nature, water soluble binder systems have received much attention in recent years. Among water soluble binders, polyethylene glycol (PEG) is the most common used water soluble binder component because of its non-toxicity, solubility in water at low temperatures and commercial availability [1, 2]. The physical properties of PEG are very similar to wax; it can be in a form of liquid or solid at room temperature depending upon its molecular weight [1].

Polymethyl methacrylate (PMMA) is often employed as the backbone polymer in PEG based binder systems because of excellent compatibility. Moreover, PMMA is a clean polymer and leaves little residue upon decomposition. This is important when MIM of reactive metals such as titanium is employed [3]. In spite of numerous literature reports on this binder system [4-6], no commercial feedstock based on this binder system is available.

To facilitate the use of water soluble systems in Ti-MIM, we have extensively studied PEG based binder systems and have reported some interesting new findings. These new findings will shed new insight on the use of such binders in MIM industry and therefore has industrial applications. It should be noted that these developed binders can be used for other powders injection moulding such as stainless steel, copper, tungsten powders etc. We expect the MIM practitioners and customers would benefit from our studies.

## 2. Optimization process

**2.1 Effect of PEG molecular weight.** Rheological properties of the feedstock are essential to MIM. As the main component of binder controls the flow properties of feedstock, inherent properties of PEG have a significant effect on the overall properties of feedstocks. Intriguingly, the effect of PEG molecular weight on rheological properties of the feedstock and its water debinding behaviour has not been well investigated. In general, PEG polymers with an average molecular

weight in the range of 500 to 4000 g/mol are chosen for feedstock formulation based on the knowledge that primary component having lower molecular weight should be chosen for easy removal during debinding stage. However, no experimental relationship exists in the literature [1]. Therefore, it was one of our objectives to establish a relationship between PEG molecular weight, rheological properties and debinding behaviour of the feedstocks [7].

To study the effect of molecular weight, four different PEG molecular weights: 1500, 4000, 10,000 and 20,000 were selected for feedstock formulation (designated as Feedstock *A*, *B*, *C* and *D* respectively), while other parameters e.g., contents of backbone polymer and surfactant, powder loading were kept constant. The results reveal that the feedstock formulated from the high molecular weight PEG as the primary binder component leads to a high yield stress. However, the shear sensitivity of feedstocks increases with PEG molecular weight due to more adhesion with metal powders provided by the molecular chain lengthening, Figure 1.
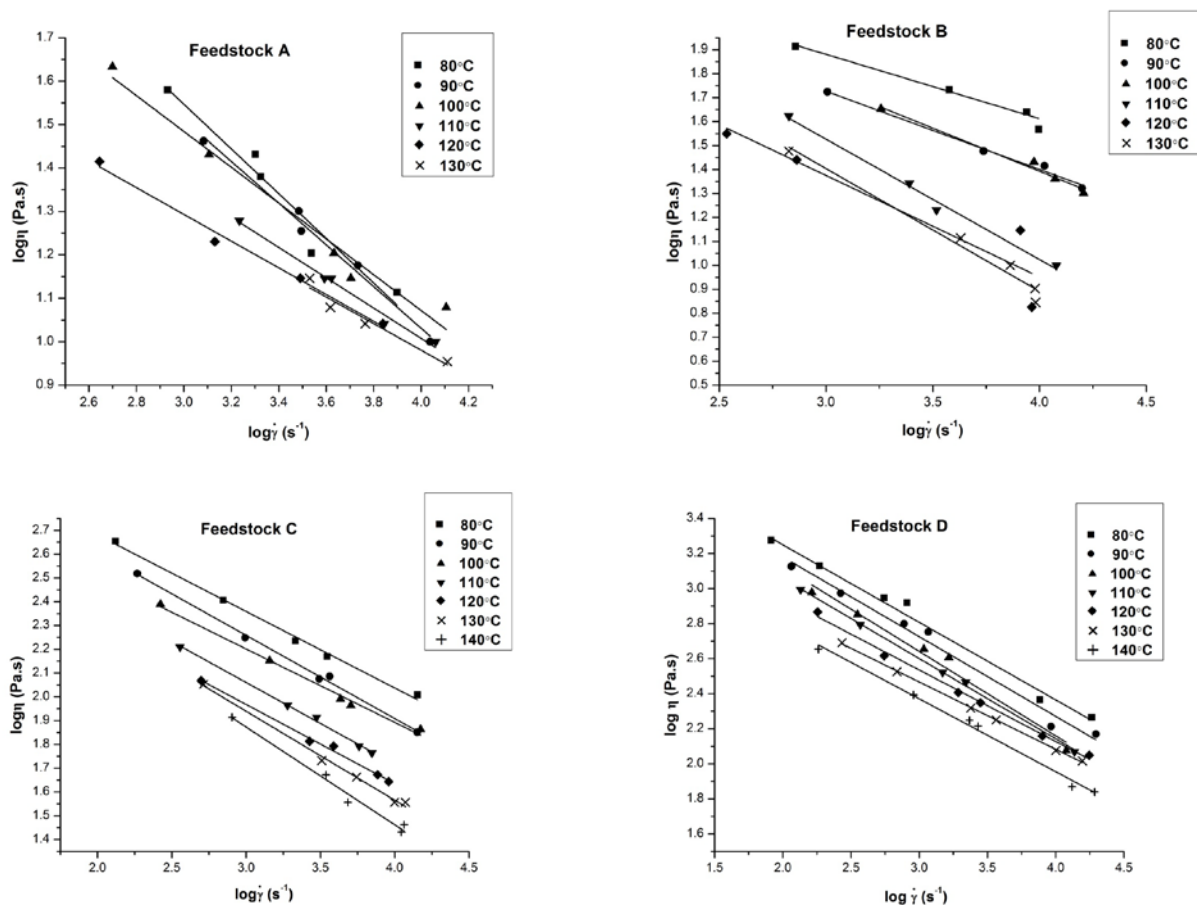


Fig.1 Plot of double logarithm of viscosity *vs*. shear rate. Taken from ref. [7] with permission.

It can be seen from Fig. 1 that as PEG molecular weight increases, feedstocks show more consistent shear rate dependency. The flowability of feedstocks is dependent on the bonding between metal powder and polymeric binder. Increasing PEG molecular weight would increase the interaction between powder and polymeric binder, as a result of increased number of hydrogen bonds on the longer PEG molecule chains. This enhanced interaction gives rise to increased adhesion of binder onto the metal powders, which in turn, results in better flowability.

Unfortunately the potential benefit of higher molecular weight for rheology is compromised by the poor water debinding performance. The increase in molecular weight decreases the mobility of the PEG chains in water (solubility) because chain lengthening also increases the adhesion with metal powders. As water penetrates into the samples, the dissolution of higher molecular weight PEG molecules is slower than the speed of water penetration, and therefore, the sample volume expands.

Such swelling ultimately leads to cracking. In other words, there would be upper limit of the PEG molecular weight that can be used for feedstocks formulations, Figure 2.
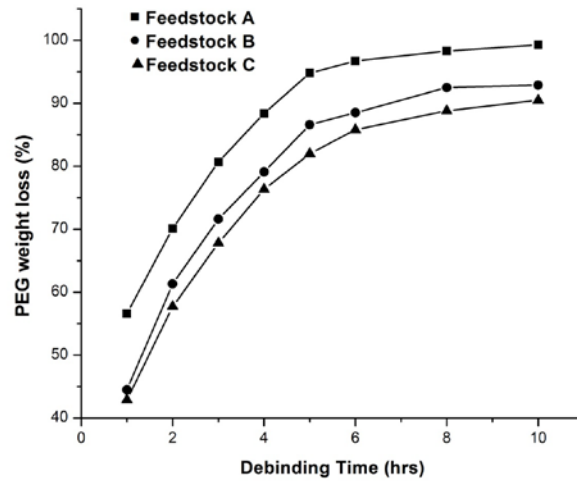


Fig. 2 PEG removal rate in feedstocks. The water bath temperature was 50°C. Samples made of Feedstock *D* experienced severe swelling and cracking within 30 min of debinding. Taken from ref. [7] with permission.

Surprisingly, difference between Feedstock *B* and *C* removal rate is not significant, given the viscosity difference and implies that PEG-10000 molecules have sufficient mobility for easy extraction. Based on the rheological properties and water debinding analysis, PEG-10000 seems the best choice. Although higher molecular weight PEG may increase the overall viscosity, the overall improvements in feedstock properties overshadows this one drawback.

**2.2 Compatibility improvement**. Surfactants are generally added in binder systems to further enhance the interaction between metal powders and the binder components by improving properties such as surface wetting, spreading, adsorption and binder strengthening as described in Ref.[8]. In other words, surfactant can improve the compatibility of binder and powders by increasing adhesion between binder and powder particles, thereby leading to a better moulding operation. Therefore, the surfactant acts as a bridge between the powder and the binder. The surfactant is thus critical to the binder system and MIM process [9]. Furthermore, it can also reduce the friction between powder and die wall by acting as a lubricant and enhance miscibility between binder components [10]. The most commonly used surfactant in Ti-MIM is stearic acid (SA).

The reports on feedstocks comprising of surfactants other than SA in MIM are few and far between. Similarly, the effects of nature of surfactants on rheological properties of feedstock are largely missing, particularly in the case of Ti-MIM. Only few reports can be found in MIM literature that uses surfactants other than SA; palm stearin is one such example. Owing to the importance of surfactant, a series of experiments were carried out to study the effects of different types of surfactant on the properties of Ti-MIM feedstock. These tests produced some interesting results. The detailed results can be accessed in Ref. [11]. In a nutshell, lower viscosity of feedstock and a higher green strength of injection moulded samples can be achieved using a liquid surfactant, Figure 3 and Table 1 respectively.
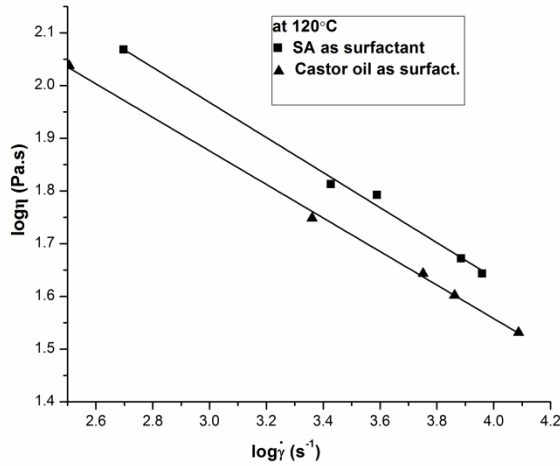
Fig. 3 Double logarithm of viscosity vs. shear rate plot of different feedstocks at 120 °C. Taken from ref. [11] with permission.

Table 1: Green strength comparison of two feedstocks with different surfactants.

|  | Feedstock having SA (MPa) | Feedstock having castor oil (MPa) |
|---|---|---|
| Average | 7.36 | 8.15 |
| Standard dev. | 0.17 | 0.18 |

It can be seen from Fig. 3, a lower viscosity of feedstocks can be achieved when SA is replaced by a liquid surfactant, castor oil. In this case, almost 5% reduction in viscosity was achieved. It can be argued that this reduction in viscosity might not be of importance for low solid loading feedstocks. However, an approximately 10% increase in flexural strength can be achieved using castor oil as surfactant, Table 1. To this end, the resultant improvement in quality becomes quite significant.

This improvement in properties is attributed to the higher interaction between Ti-metal powder and the binder system in the case of feedstock containing castor oil as surfactant. The reason of this higher interaction lies in the chemistry of castor oil [11]. The surfactants contain one polar group and a non-polar hydrocarbon chain. The polar group latches onto the metal powder surface via dipole-dipole attractive forces and the non-polar hydrocarbon chain keeps it in the binder matrix [12]. The more this attractive force, the better will be the powder dispersion. SA chain has only one polar ester functional group present. In contrast, the castor oil chain has at least three polar ester functional groups in addition to a hydroxyl group, which enhance the dipole-dipole attractive forces. Therefore, in the case of castor oil feedstock, a better powder dispersion and higher powder - binder interaction can be achieved, which ultimately leads to lower viscosity, good rheological properties, and a higher green strength of moulded samples.

**2.3 Improvement in the quality of PEG/PMMA binder system.** As mentioned before, the PEG/PMMA binder system has been widely reported in MIM literature and has been adopted for Ti-MIM as well. A few reports have shown that excellent mechanical properties can be achieved due to the clean nature of PMMA [4, 13]. However, during our extensive research on this binder system, it was found this binder system is not free of problems [14]. The main problem is the formation of shrinkage voids during solidification, Figure 4.
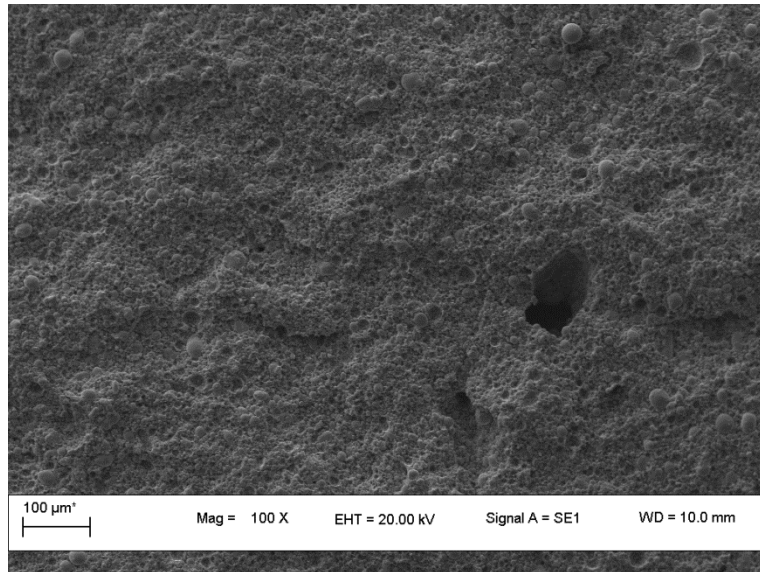
Fig. 4 Morphology of a void occurred during solidification of feedstock consisting of PEG/PMMA binder system. The irregular internal surface and a wormhole type appearance imply a typical solidification defect.

This void formation is an intrinsic property of PEG/PMMA binder system and is a result of hindrance to volumetric shrinkage (caused by PEG crystallization) by rigid PMMA chains upon cooling. It is arguable if PEG is not allowed to crystallize, this void formation can be minimized or somewhat eliminated. Hence, it is suggested that this binder should be used for micro-metal injection moulding (μMIM) only. In μMIM, cooling rates are inherently high due to smaller sample thickness, giving less time for PEG to crystallize as has been reported in Ref. [14].

The application of higher cooling rates to limit PEG crystallization hence void formation may work for μMIM or thin walled samples. In the case of conventional metal injection moulding, cooling rates can only be increased up to a certain point. It should be noted that too high a cooling rate will result in thermal stresses within the sample, which will eventually lead to shape distortion during sintering stage. Therefore, it becomes important to find other ways to retard PEG crystallization. One method which we have employed is the incorporation of polyvinylpyrrolidone (PVP) into PEG/PMMA binder system [15]. This method has proven to be very successful in minimizing void formation by limiting PEG crystallization, Figure 5.
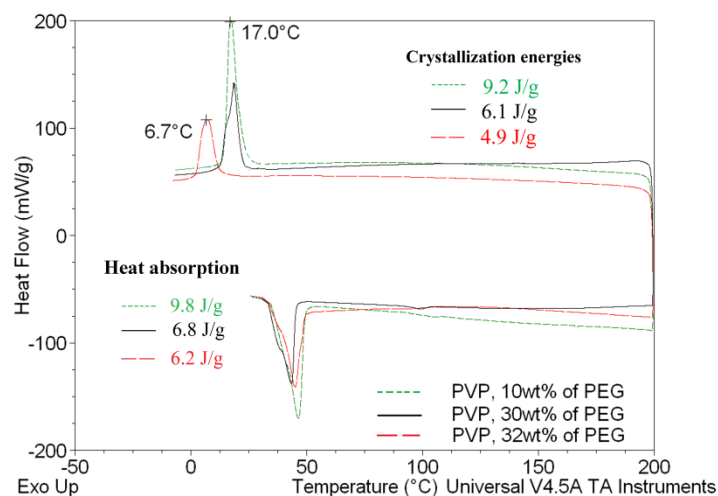


Fig. 5 Reduction of PEG crystallization temperature with increasing PVP content. Redrawn from ref. [15].

As shown in Fig. 5, the heat absorption of PEG decreases as the PVP content is increased. The lowest PEG melting energy is observed when the PVP content is 32 wt/wt% of PEG. The benefits of PVP inclusion into PEG/PMMA binder system are not limited to void formation only; it also improves the rheological properties of feedstock containing lower molecular weight PEG. As

mentioned above, binders containing lower molecular weight PEG usually have poor rheological properties and tend to separate from the powder at higher shear rate due to the lower interaction between the powder particles and binder system arising from smaller molecular chains [7]. The longer chains of PVP molecules increase the number of contacts with the metal powder, thereby increasing the shear rate dependency. Moreover, PVP is water-soluble polymer [16]. It can be extracted simultaneously along with PEG during water debinding. Therefore, it does not increase the overall production time.

The importance of reducing PEG crystallization is reflected in final mechanical properties of the sintered samples, Table 2.

Table 2: Comparison of sintered samples mechanical properties for two feedstocks consisting of stainless steel powder 17-4PH (From Epson Atmix Corporation, Japan) with powder loading of 60 vol.%. Redrawn from ref. [15]

| Feedstock (consisting of unaltered PEG/PMMA binder) | | Feedstock (containing 30 wt.% PVP in PEG/PMMA binder) | | ASTM minimum mandatory tensile properties requirement |
|---|---|---|---|---|
| Ultimate Tensile Strength (UTS) [MPa] | Elongation ($\epsilon$) [%] | Ultimate Tensile Strength (UTS) [MPa] | Elongation ($\epsilon$) [%] | |
| 921 | ~2 | 953 | ~7 | Ultimate tensile strength = 795 MPa Elongation = 4% |
| 950 | ~3 | 966 | ~7 | |
| 875 | <1 | 950 | ~6 | |
| 900 | <1 | 970 | ~8 | |

The ultimate tensile strength (UTS) and elongation values of Feedstock (containing PVP in PEG/PMMA binder) listed in Table 2 fulfill the ASTM B883-10 specifications [15]. Although the UTS values of Feedstock (consisting of unaltered PEG/PMMA binder) are within the standard limit, the elongations are well below the minimum requirement of 4%. These low elongation values suggest the presence of defects within the sintered samples. It should be noted that the same solvent, thermal debinding and sintering processing parameters were applied to both feedstocks. It is noted that a lower cost stainless steel powder was used in our initial trials due to the limited availability of atomized titanium powder. Recently, this modified binder system has been tried for Ti-MIM, and the final sintered parts have shown significant improvement in mechanical properties. The full details will be published elsewhere.

## 3. Impact of water debinding on final impurity contents

Control over impurities uptake during MIM processing defines the final mechanical properties in the case of reactive powders - Thermal debinding and sintering steps are considered the most crucial steps in this regard. However, proper removal of primary polymers during first stage of debinding (which in most cases is solvent debinding) is also very crucial. To highlight the importance of solvent debinding, PEG example is presented here. PEG is a crystalline polymer (chemical structure: $HO-[CH_2-CH_2-O]_n-H$) with an open helical structure. The molecular chain of PEG with the average molecular weight of 4000 g/mol approximately contains carbon 54.41wt.% , oxygen 36.5 wt.% & hydrogen 9 wt.% respectively. PEG thermal decomposition behaviour is shown in Figure 6.
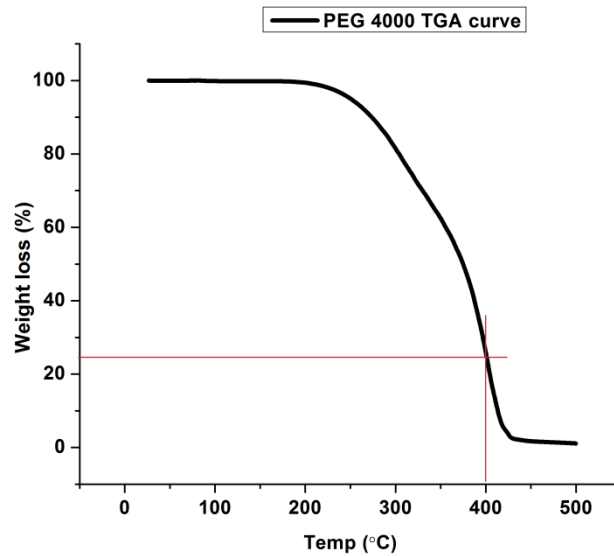
Fig. 6 PEG thermal decomposition behaviour under argon atmosphere.

Titanium reacts readily with impurities at a temperature over 400 °C. If we neglect impurity pick-up below 400 °C, the increase in the levels of impurity due to improper water debinding for a typical 67 vol.% Ti MPIF standard injection moulded part containing 1.3 g of PEG is estimated in Table 3.

Table 3: Estimated increase in impurity contents due to the improper first stage of debinding considering impurity pick-up after 400 °C only during thermal debinding.

| PEG [wt.%] removed after water debinding | Initial Impurity contents [wt. %] (GA-Powder) | | Approx. impurity contents after thermal debinding [wt. %] | | Percentage increase in impurity contents after thermal debinding [%] | |
|---|---|---|---|---|---|---|
| | Carbon | Oxygen | Carbon | Oxygen | Carbon | Oxygen |
| 0 | ~0.003 | ~0.13 | ~0.186 | ~0.253 | 6100 | 94 |
| 50 | | | ~0.0949 | ~0.1916 | 3000 | 47 |
| 75 | | | ~0.048 | ~0.1608 | 1500 | 23 |
| **90** | | | **~0.0159** | **~0.140** | **430** | **8** |

It should be noted that these calculations are based on assumptions that impurity is picked up only after 400 °C and that the sintering furnace will yield zero increment in impurity contents. However, in reality it is not the case. The carbon and oxygen pick-up may be far higher than stated here. Therefore, it is recommended here that in the case of titanium more than **90 wt%** of primary binder component should be removed during solvent debinding in order to keep impurity content in-check.

## 4. Summary

This paper highlights the important results obtained by systematic optimization and evaluation of PEG/PMMA based binder system. For instance, it is found that PEG molecular weight plays an important role on rheological properties and debinding performance of feedstocks. The results reveal that PEG with molecular weight of 10000 g/mol could be the best option as the primary binder component, contrary to the reported molecular weights in the literature (1500 to 4000 g/mol). Similarly, our results reveal that castor oil as surfactant leads to better overall properties of feedstocks compared to stearic acid. Although PEG/PMMA based binder system has a great potential due to its clean nature, it is susceptible to void formation during feedstock formulation. However, this problem can be averted by using a crystallization inhibitor such as PVP. The results has revealed that PVP incorporation into PEG/PMMA binder system improve the quality of MIM products without compromising the environment-friendly nature of the binder mixture. The

importance of solvent debinding has also been emphasized in this paper, and it is recommended that in order to keep impurity content in-check more than 90wt. % of primary component should be removed during solvent debinding. It is also noted that the results from these studies can also be used for other powders injection moulding.

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