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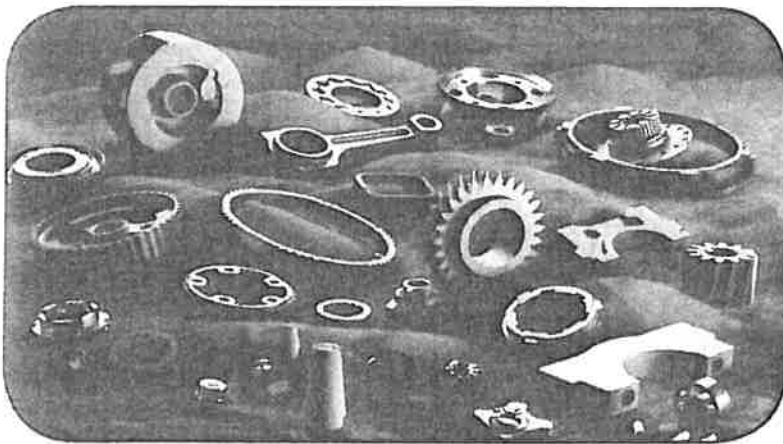


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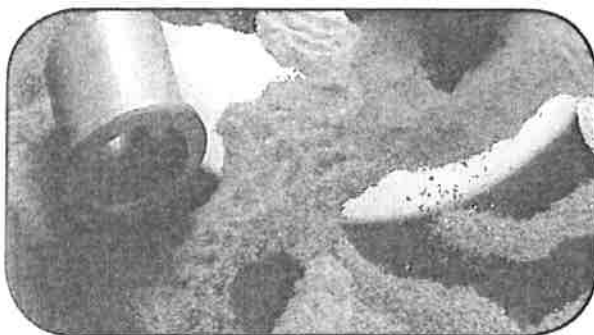


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Binder System for Fused Deposition of Metals

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Abstract

Fused Deposition of Metals (FDMe) is a technique developed to produce metallic components, based on the extrusion of metal/binder filaments to form layer by layer three dimensional objects. Filament materials must contain a high content of metallic powder to prevent shrinkage on thermal treatments like debinding and sintering, without compromising adequate rheological properties during the extrusion process. This research aims developing an FDMe system using metal/binder feedstocks in pellet/granule instead of filaments. The present work is focused on establishing a suitable binder system for fused deposition of carbonyl iron feedstocks. Binder systems based on Polyethylene Wax (PEW) or Paraffin Wax (PW), Polyethylene Glycol (PEG) and Polypropylene (PP) were investigated concerning their thermal and rheological properties. The rheological data showed that the binder systems containing PW presents lower viscosity than those having PEW. Thus, a binder system based on the former component was selected to assure appropriate rheological properties of carbonyl iron feedstocks with high content of solids for FDMe.

1. Introduction

Additive manufacturing techniques are quite flexible concerning tridimensionality and multimaterial layering. Parts are directly built, layer-by-layer, from a computer data description or computer aided design (CAD) files. In the last decades, several additive techniques have evolved to metal or ceramic processing which opens a new world of manufacturing and application possibilities [1, 2].

The additive technologies have gained relevancy on this domain since they can build freeform geometry and process materials such as metals that withstand mechanical efforts and temperature variations without significant degradation [3].

The use of additive manufacturing for metals is limited to particular cases due to the costs involved. In fact, the cost of a normal-sized part manufactured by an additive technology is dependent on height and construction volume [4, 5].

Fused Deposition of Metals (FDMe) is a technique developed to produce metallic components, based on the extrusion of metal/binder filaments to form layer by layer three dimensional objects. Filament materials must contain a high content of metallic powder to prevent shrinkage on thermal treatments like debinding and sintering, without compromising the adequate rheological properties during the extrusion process. This research aims developing an FDMe system using metal/binder feedstocks in pellet/granule instead of filaments.

2. Materials

2.1. Powder

Carbonyl iron powders supplied by Sigma-Aldrich (purity $\geq 97\%$ as Fe) were used as raw material for producing feedstock blends for Fused Deposition of Metals (FDMe). Figures 1 and 2 show the particle size distribution and the shape of powders measured by laser diffraction spectrometry (Coulter LS 130) and scanning electron microscopy (Hitachi SU-70), respectively. The carbonyl iron powders have a bimodal particle size distribution with mean diameter of $4.065 \mu\text{m}$ ($d_{10} = 1.283 \mu\text{m}$, $d_{90} = 7.813 \mu\text{m}$) and spherical particles. The true density of the powders, measured by helium pycnometry using an Accupyc 1330 instrument (Micromeritics), is 7454 kg/m^3 , while the tap density was evaluated by a vibration method is 3983 kg/m^3 . The particles pack to a density 53% of theoretical.

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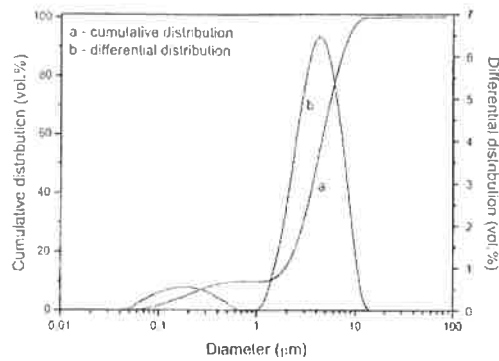


Fig. 1 Particle size distribution of carbonyl iron

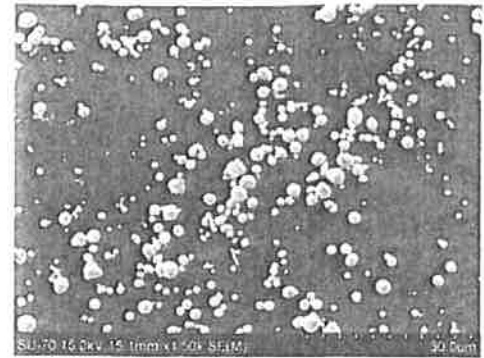


Fig. 2 SEM micrograph of carbonyl iron

2.2. Binder

Different binder systems were studied and developed in the aim of this work using the following constituents: polypropylene (PP, Borealis), polyethylene glycol (PEG, Panreac), polyethylene wax (PEW, Poliversal) and paraffin wax (PW, Poliversal).

The thermal characteristics of the organic materials were evaluated on a DSC 131 calorimeter (Setaram) from room temperature to 120°C (PEG, PEW, PW) or 400°C (PP) with an heating rate of 10°C/min in nitrogen atmosphere. Afterwards, they were then cooled down to room temperature at a rate of 10°C/min. At this conditions, the differential scanning calorimetry (DSC) curves show endothermic peaks due to melting around 150°C for PP, 70°C for PEG, 108°C for PEW and 75°C for PW, as well as a well-established exothermic peak around 93°C for PEW corresponding to its crystallisation temperature (Figure 3).

The binder systems based on PP, PEG, PEW or PW were prepared by weighing and mechanically mixing the solids constituents in the pre-defined ratio. Table 1 presents the binder constituents and their proportion (weight fraction) in the different binders (B).

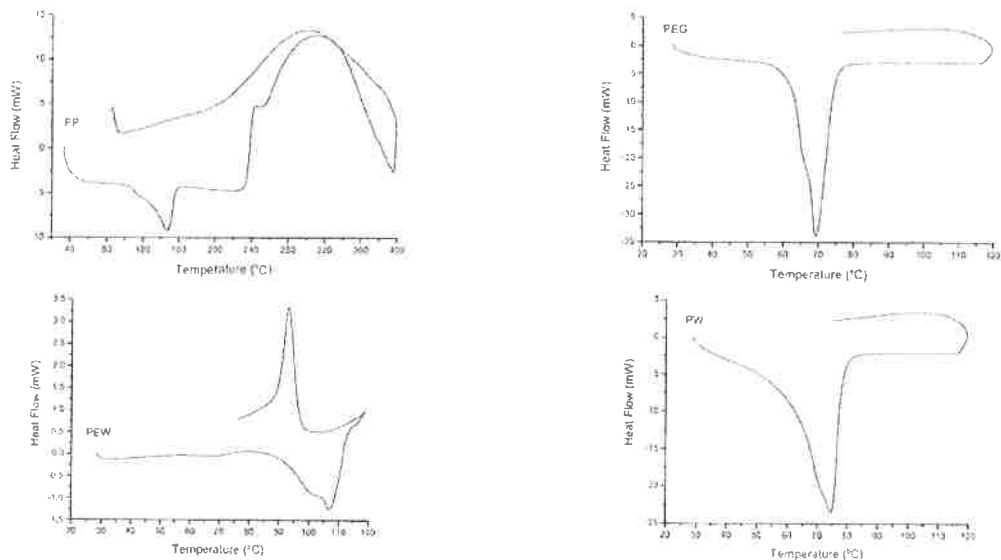


Fig. 3 DSC of the binder constituents: PP, PEG, PEW and PW

Table 1 Composition (wt.%) of the binder systems

Binder constituents	B1	B2	B3	B4	B5	B6	B7	B8	B9
Polypropylene	20	20	20	20	20	20	20	20	20
Polyethylene glycol	-	20	40	60	80	-	20	40	60
Polyethylene wax	80	60	40	20	-	-	-	-	-
Paraffin wax	-	-	-	-	-	80	60	40	20

3. Experimental

3.1. Fused deposition equipment

The fused deposition equipment (Figure 4) consists on a vertical single screw extruder with an L/D ratio of 6 ($L = 90$ mm; $D = 15$ mm) and a 2 mm diameter die. The heating of the barrel is ensured by two band heaters enabling processing temperatures up to 250°C. The part is built on a XY table driven by step motors to control trajectories and material deposition. The descendent movement along the Z axis required for the next layers is also driven by a step motor so that different layer thicknesses are possible. Processing temperatures and the building platform motion are controlled by a logical controller and a computer for parameter input (barrel temperature profile for the two heating zones, screw extrusion speed, material rate of deposition) and user interface.

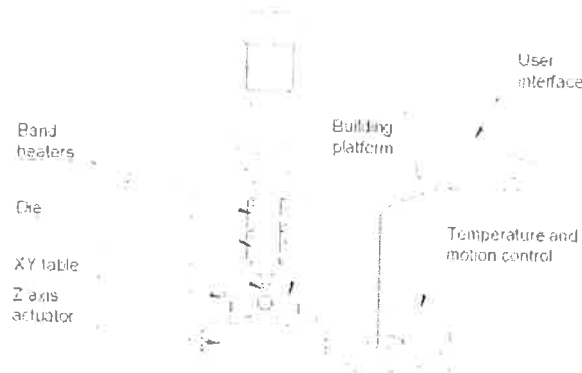


Fig 4. Fused deposition equipment schematics

3.2. Binders characterisation

The binder systems were tested concerning their thermal and rheological properties and also their extrusion behaviour. The thermal characteristics of binders B4 and B9 were evaluated by differential scanning calorimetry (DSC 131, Setaram). The tests were performed from rooming temperature to 400°C with heating rate 10°C/min in nitrogen atmosphere. These tests were important for establishing appropriated processing temperatures. The rheological analysis of the binders was carried out using a StressTech HR rotational rheometer fitted with plate-plate geometry (Reologica Instruments AB). Oscillatory rheological measurements were made over a frequency range from 0.01 to 100 Hz, with a gap of 0.5 mm, on pressed samples (discs of 25 mm diameter). The pressed samples were obtained from the homogeneous solid mixture of the constituents. This kind of rheological analysis allows studying the viscous and elastic responses of the different binders [6, 7].

The binders were extruded using the FDM extrusion equipment for testing the processing behaviour without the carbonyl iron powder. The extrusion conditions, namely the barrel temperature profile (two heating zones) had to vary according to the binder behaviour during extrusion. The barrel temperature varied between 155 and 185°C in zone 1 and between 180 and 187°C in zone 2 (see Table 2). The screw rotation speed remained constant at 10min⁻¹.

3.3. Feedstocks

The selected binder system was used to optimise and prepare the feedstocks. The optimal carbonyl iron/binder composition was evaluated by monitoring the torque variation during the mixing process of the carbonyl powders and the polymeric binder using a torque rheometer (Brabender Plastograph mixer). The powder/binder ratio was optimised as it is described elsewhere [8, 9]. After the optimisation of the powder/binder composition, various feedstocks were prepared. The binder system and the carbonyl iron powders were mixed in the Brabender Plastograph mixer during 20 min at 180°C. Preliminary tests of extrusion will be carried out with some feedstocks to evaluate their processing capability.

4. Results and Discussion

4.1. Binders characterisation and processing

Figure 5 shows the DSC results for binders B4 (PEW based) and B9 (PW based). It is possible to observe the characteristics endothermic peaks of PP, PEG and PEW or PW melting, however, at relatively lower temperatures. For binder B4 there are two more exothermic peaks around 285 and 385°C, corresponding to the decomposition/degradation of PEW and PP. Similarly, for binder B9 there are two exothermic peaks

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but at lower temperatures, respectively 265 and 375°C. In both cases, around 200-210°C the PEG should begin evaporating.

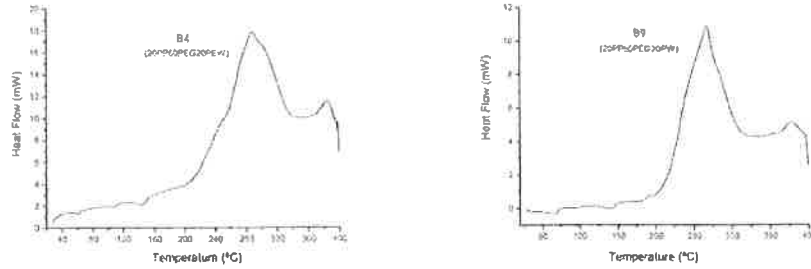


Fig. 5 DSC of binders based on polyethylene wax (PEW) and paraffin wax (PW)

The oscillatory rheological data are shown in Figures 6 and 7 depicting the complex viscosity (η^*) as a function of frequency for the binders containing two or three constituents, respectively. Both the storage (G') and the loss modulus (G'') of the different binder systems are shown in Figures 7a to 7c, being the binders grouped by their composition. Figure 7d shows the loss tangent ($\tan \delta$) for the studied binders.

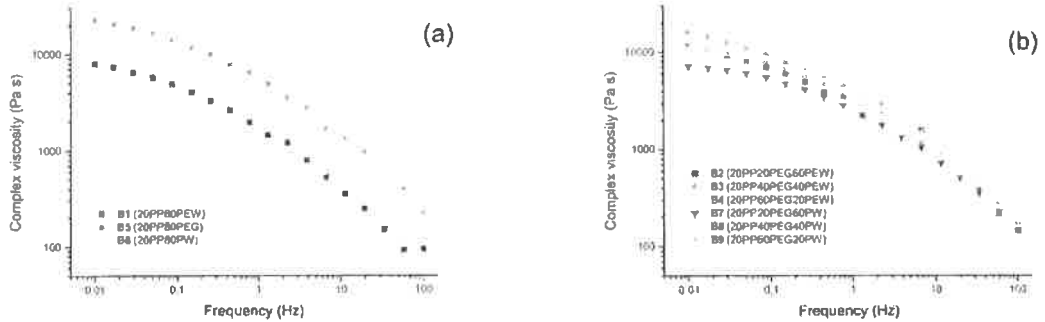


Fig. 6 Complex viscosity as a function of frequency for binders containing two (a) or three constituents (b)

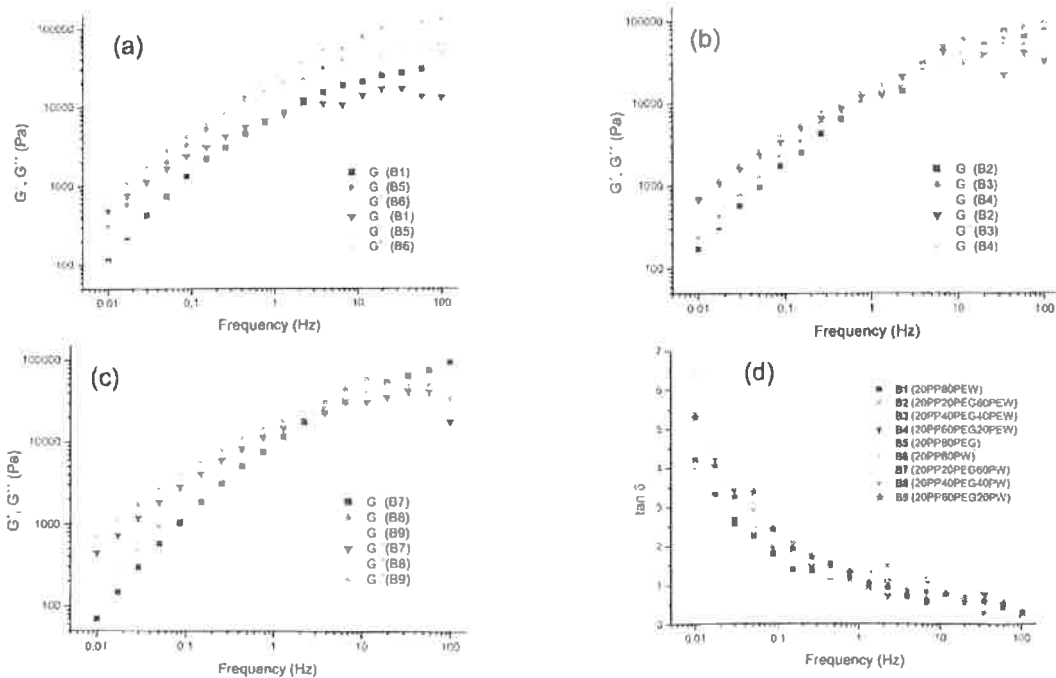


Fig. 7 Storage and loss modulus with frequency for binders with 80wt.% of one constituent (a), and PEW (b) and PW (c) based binders with 20-60wt.%; Evolution of the loss tangent with frequency for all binder systems (d)

Regardless of the binder system composition, it is possible to observe from Figures 6a and 6b that the complex viscosity decreases with frequency, revealing pseudoplastic flow behaviour for all binder systems. The binders with only two constituents, namely the PEG and PEW based binders, present the highest and the lowest values of complex viscosity over the entire frequency range; the PW based binder is the second one with highest complex viscosity values, however only at high frequency. About the binders with three constituents, the complex viscosity variation with frequency is more erratic for PEW than for PW based binders. Moreover, the last ones present lowest values of viscosity for almost the entire frequency range.

Figures 7a to 7c show that the storage modulus increases in the whole frequency range studied, while the loss modulus increases; with a slight tendency to decrease observed at 100Hz. This behaviour is similar for all the binders systems, however for the PEW (B1-B4) and PEG (B5) based binders there is an erratic behaviour of the loss modulus over a wider range of frequency, typically at the highest values, where the transition between the viscous and elastic behaviour occurs. Hence, at low frequency the behaviour of the binders is predominantly viscous ($G'' > G'$) while at high frequency is predominantly elastic ($G'' < G'$) and, consequently, the values of the loss tangent are higher or lower than one, respectively (Figure 7d). The behaviour transition occurs around 2Hz, except for the binders with 60% of PEW (B2) or PW (B7) and for the PEG based binder (B5) that occurs around 4 Hz. From Figure 7d it is also possible to conclude that the loss tangent of PEW based binders is lower than the PW based at low frequency, but at high frequency the opposite occurs, being the elastic behaviour dominant. Thus, the rheological tests allows to conclude that binders have viscoelastic behaviour and the PW based binders are more suitable for extrusion due to its higher fluidity.

Table 2 presents the extrusion behaviour of the binders as well as the extrusion temperature profile (see section 3.2). The binders with only two constituents, regardless of their nature (PEG, PEW or PW), do not flow. The binders based on PEW present some flowing problems, since the wax overheated due to viscous heating effects on the extrusion process. This is in according with the rheological results, since the viscous behaviour of these binders is dominant at high frequency. The binders based on paraffin wax flow without any kind of problems. Thus, based on the processing behaviour, the binders based on paraffin wax (B7-B9) are the most suitable for extrusion as expected given the oscillatory rheological tests. Combining both the rheological data and the extrusion behaviour, the binder selected was B7 containing PP (20wt.%), PEG (20 wt.%) and PW (60wt.%). The true density of this binder is 0.9668 kg/m³.

Table 2 Extrusion temperature profile and processing behaviour of the different binders

Extrusion temperature	B1	B2	B3	B4	B5	B6	B7	B8	B9
Barrel temp. zone 1 (°C)	159	155	159	158	159	185	155	159	185
Barrel temp. zone 2 (°C)	187	180	187	185	187	185	180	187	185
Extrusion results	No flow	Flow	Flow	Flow	No flow	No flow	Flow	Flow	Flow

4.2. Feedstocks optimisation and preparation

Figure 8 shows the behaviour of the mixing of carbonyl iron within binder B7 along time. There is a slight increase of the mixing torque for the first additions of solids, increasing significantly when the critical powder concentration is attained. This corresponds to 65vol.% of solids, being the mixing torque 11,5 Nm (Figure 9).

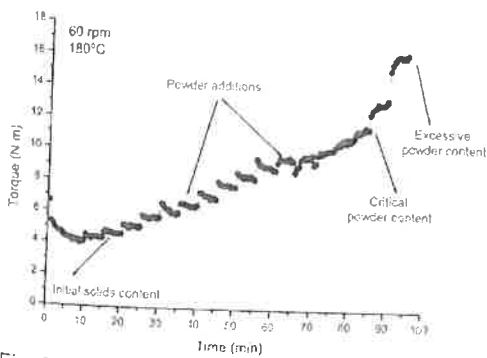


Fig. 8 Mixing torque as a function of mixing time

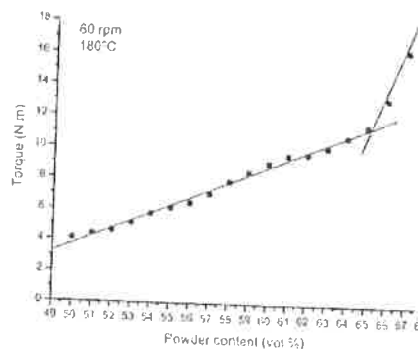


Fig. 9 Mixing torque as a function of powder content

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According to figure 9, the mixing torque for the 60 and 61vol.% feedstocks is similar, defining a possible value for the transition to a second regime, which was not considered in this work. Thus, it was decided to prepare a feedstock containing 61vol.% of carbonyl iron. However, as the mixing torque for this powder content is around 9 Nm, two more feedstocks were prepared with lower powder content, namely 59 and 57vol.% (mixing torque around 8,5 and 7,0 N m, respectively).

Conclusions

The thermal and oscillatory rheological properties of PEW and PW based binders were evaluated. The rheological results show that the complex viscosity of the binders reduced with increasing frequency, showing pseudoplastic flow behaviour. Moreover, the binders show viscoelastic behaviour, which is predominantly viscous or elastic, depending of the frequency range, lower or higher, respectively. Nevertheless, the complex viscosity of the PW binders is lower than those based in PEW, as well as the loss tangent for higher values of frequency, being these kind of binders more appropriate for preparing feedstocks to FDMe that requires high solids content to minimize shrinkage during thermal treatments. According these results, it was decided to select the binder B7 with 20wt.% PP, 20wt.% PEG and 60wt.% PW. The optimisation of the powder content enabled the conclusion that the critical powder concentration is 65vol%. Thus, a feedstock with 61vol% of carbonyl iron will be used in the fused deposition modelling tests.

Acknowledgments

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