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Polymer powder production for laser melting through immiscible blends

Dietmar Drummer[a]*, Martha Medina-Hernández[a], Maximilian Drexler[a], Katrin Wudy[a]

[a]*Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nuremberg, Germany*

Abstract

Availability of polymer material in powder form with a defined particle size and spherical morphology is the first major hurdle in procuring suitable materials for laser melting. Obtaining the correct particle size and morphology is vital as the powder properties influence both processing ability and the final characteristics of the part. The exploitation of the immiscibility of special polymer blends during extrusion or kneading process represent a path to generate powder with desired morphology and particle size. Key issues to consider are: the feasibility to separate the mixture, properties and processing limitations of the constituents. In this paper it is studied the resulting morphological structure of PA12-PEG and PA12-Polyvinil Alcohol (PVA) blends. PA12 is by far the most widely used polymer in laser melting and, PEG and PVA are water soluble, these factors make the investigation of their blends and possibilities to control their morphology a pretty interesting path to produce quality powder for laser melting.

Ke words: Powder production, particles morphology, immiscible blends

1. Introduction

Selective laser melting (SLM) is a rapid prototyping process that allows to generate complex 3D parts by solidifying successive layers of powder material on top of each other. Solidification is obtained by fusing or sintering selected areas of the successive powder layers using thermal energy supplied through a laser beam. The

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* Corresponding author. Tel.: +49 9131/85 29700; fax: +49 9131/85 29709.
E-mail address: info@lkt.uni-erlangen.de

development of new polymer powders suitable for selective laser melting process is complex as a lot of different materials properties have to be fulfilled. Ideally powders should have a high sphericity to facilitate flow, reduce the surface area to volume ratio and improve packing efficiency; these powders should also have a size distribution between 1 and 100 µm and a mean diameter bigger than 10µm [1-3]. The powder flowability is an important and not negligible parameter during development process, the ratio of tap and bulk density should be typically under a limit of 1.25 (high flowability) to be regarded as a useful powder with sufficient powder density [4], and equally important are the optical, thermal and rheological behavior.

Current techniques to produce polymer powder are, for example, through mechanical action like cryogenic grinding or solid-state shear pulverization [5, 6]. The powder produced via these techniques presents the inconvenient of very irregular particle morphology and it can be a negative dominating factor in terms of how material responds to a flow additive. Another technique to produce powders is via the spray drying of a polymeric solution; this method has been used for long time in micro-encapsulation of food ingredients and pharmaceutical products [7-10], the particles produced are substantially spherical and usually hollow, therefore it is formed a free flowing powder. On the other hand, the use of solvents is being studied as a potential way to produce polymer powder [11, 12], this method can overcome the disadvantages associated with use of high temperatures, as in the case of spray drying and milling. General observations with the use of supercritical fluids [11] have been that the external shape of the resulting particles is relatively insensitive to process variables, and that the particle morphology depends more strongly on the properties of polymer itself. For example, if the polymer is semicrystalline such as polyesters, particles are found to be spherical, and if the molecules have stiff chains as polyamides, fibrous forms are likely to be formed. The major drawback to overcome is the low product yields.

The objective of this work is to offer a new path of study in the production of polymer powders. A rough schematic representation of the idea is shown in figure 1. The morphology of immiscible polymer blends has been largely studied [13-16]. The melting and mixing process can generate morphologies ranging from disperse drops to fibers to lamella to co-continuous structures. It is not uncommon to generate the morphology of spheres or spheroids dispersed in a polymeric matrix and this issue can be used to produce spherical shape powder particles. The final morphology of a polymeric blend is a result of materials properties, operation parameters and their mutual interactions. Although the amount and properties of the constituents play an important role in its determination, microstructure is not an intrinsic property of a blend. Rather, microstructure is controlled by the blend's deformation history.
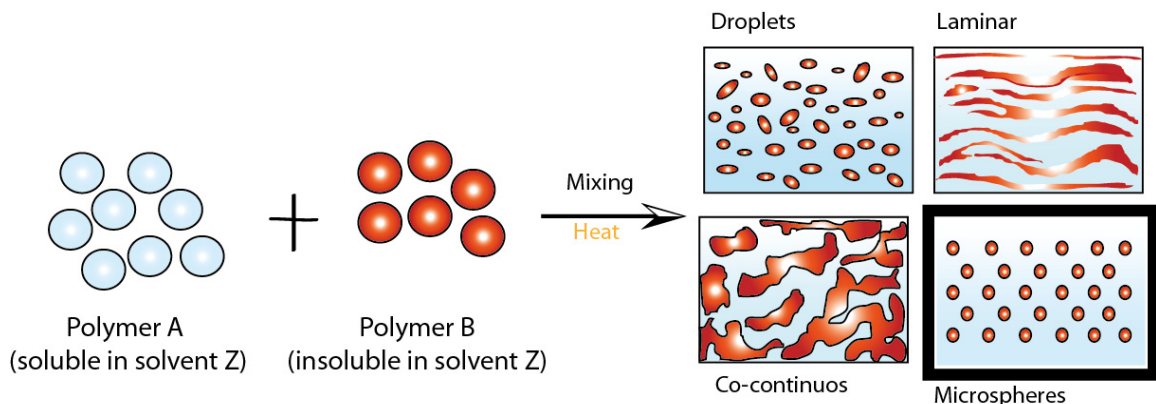

Figure. 1 Key elements of proposed method to produce spherical shape powders, it is shown the common produced morphologies of immiscible polymer blends.

The initial mechanism of morphology development [17] involves the dragging of a large particle of the dispersed phase along a hot surface such as the mixer walls. This dragging action results in the formation of sheets or ribbons of the dispersed phase. These sheets or ribbons become unstable due to the effects of shear and interfacial tension. Holes develop in the ribbons which grow in size and concentration until a fragile lace structure is formed. The lace

structure breaks into irregularly shaped particles which are the broken up to into nearly spherical particles. The most important deformation/disintegration process takes place during the first several minutes of mixing.

The size and the shape of this dispersed phase are much controlled by the interfacial tension, rheological properties, and the complex strain field of the mixer [13], in many situations the droplet shape is very close to an ellipsoid. After cessation of a steady flow, or after applying a step strain, the deformed droplet shapes are not stable. Driven by interfacial tension, droplets either retract back to spheres or break up into smaller fragments, for typical polymer blends and small deformations this relaxation time can be on the order of seconds, for highly extended droplets, total breakup by end pinching would take a very long time [13].

After studying several polymer/ rubber blends in a co-rotating twin screw extruder, Wu [18] found that the formation of dispersed phase during melt blending can be described by a master curve relating the Weber number to the viscosity ratio as in the following equation:

$$D_{Wu} = 4(\eta_r)^{\pm 0.84} \frac{\sigma}{\eta_m \dot{\gamma}}$$

(1)

Where D_{Wu} is the predicted diameter of dispersed phase according to Wu's theory, $\dot{\gamma}$ is the shear rate, σ the interfacial tension, η_m the matrix viscosity, η_d the dispersed-drop viscosity, and $\eta_r = \eta_d / \eta_m$. The plus (+) sign applies for $\eta_r > 1$, and the minus (-) sign for $\eta_r < 1$. Thus the dispersed drops are the smaller, when the interfacial tension is the lower and the viscosity ratio is the closer to unity. The Wu equation was developed for blends with a fixed composition at 15% of the dispersed phase, it considers the coalescence phenomena but not the concentration effect. At higher dispersed phase concentrations, the particles formed in the break-up process will frequently collide and coalescence of the droplets may occur. The size of the dispersed particles is then the result of the balance between break-up and coalescence behavior in the applied flow-field. As the volume fraction approaches 0.5, the discrete phase takes on complex shapes, and co-continuous structure may develop [13].

2. Experimental

2.1 Materials

It was used polyamide 12 (PA12) from EMS-GRIVORY (Grilamid L20G), Poly(ethylene glycol) (PEG8000) and Polyvinyl alcohol (PVA) Mowiflex TC 253. It was also used polybutylene terephthalate powder (PBT) pulverized via cryogenic grinding with a median particle size of 200 μm, and PA12 powder from EOS with a diameter median size of 60μm.

2.2 Preparation of blends

Section I. Applying shear stress (Kneading machine Typ 350, Fa. Branbender).
The pellets were pre-mixed with a concentration of 20% wt of PA12 for all samples. In the case of the PA12/PVA mixtures, two mixing temperatures were chosen, 190°C and 225°C, the first is just 12 grades over the melting point of PA12 ($Tm_{PA12} = 178°C$) and the second is the upper temperature operation limit of PVA to avoid its degradation. The rotation speeds of mixer were 50 and 100 rpm. In the case of PA12/PEG mixture the operation temperature was 190°C and the rotation speed 100 rpm. The mixing time was settled in 15 minutes.

Section II. Zero shear stress
Due to difficulties associated with mixing polymers of very different viscosities, as the case of PA12 with PEG, it was studied the possibility to modify just the form of the particles through the interfacial tension property, starting from already produced powders and using PEG as a fluid matrix. Separately powder of PA12 and PBT were mixed in melted PEG at approximately 70°C, and then heated up until the powder turn from milky opaque to transparent color, removed from the heating plate and cooled down at room temperature.

2.3 Morphological analysis

The blends composed of PVA were put in demineralised water (approximately 50gr/ liter), after the PVA was dissolved (stirring at 70°C) it was taken a drop of the sample and put it on a microscope glass to form a film, then the samples were analyzed by optical microscopy (transmitted polarized light). In the case of PEG blend, the samples were collected from the machine and put immediately in water, after certain time, the polyamide was partially separated through decantation, a drop of this mixture was taken and analyzed under the microscope.

2.4 Thermal analysis

Differential scanning calorimetry (DSC) was employed to discard possible compatibility between PVA and PA12. The samples were first heated from room temperature to 200°C to erase previous thermal history, then cooled from 200°C to 20°C and heated again up to 200°C, the cycle was performed at a rate of 10°C/min.

3. Results and discussion

3.1 Section I (Kneading). PA12/PVA

The PA12 had mostly a good dispersion and distribution in the PVA matrix. After dissolving the mixture in water, it formed a kind of milky solution from which it was not possible to separate the Polyamide through centrifugation and filtration would take too much time. Thus it was formed a solution of very fine polyamide particles, this was corroborated by the microscopy results presented in figure 2, similar results were found for all used parameters, the samples were taken after dissolving the mixture in demineralised water, so that the structure of PVA is not appreciated by the microscope, and the white spots correspond to the dispersed polyamide.
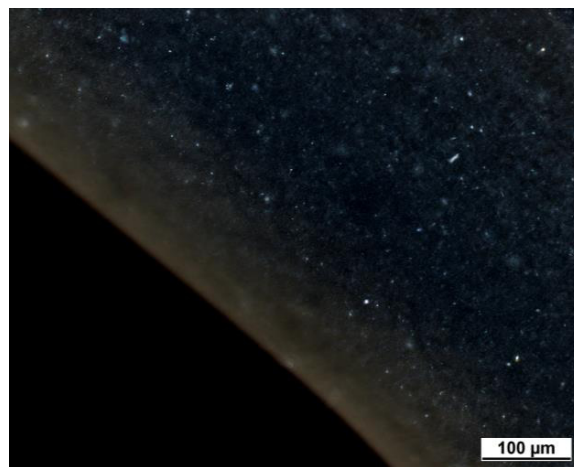

Figure 2. PA12 microstructure in PVA film.

For the PA12/PVA blends there were not significant effect on the particles size, in regard of powder requirements for laser melting, at least in appreciation of the micrographs and due to difficulties to separate the phases through centrifugation or filtration, we could suggest that the mean diameter size for the particles of the mixture PA12/PVA was lower than 10µm for all used operation parameters. In respect of morphology, it is quite difficult to assure that spherical shape particles were formed, conversely the few "big" observed particles (mostly smaller than 50µm) seems to have random shapes with just a certain small percentage of spheroids. Figure 3 shows crudely the break up stage of the PA12 phase. Under shearing or extensional flow, the initial molten pellets undergo transient affine deformation to form sheets or threads. The latter break up into small particles due to the interfacial instability.
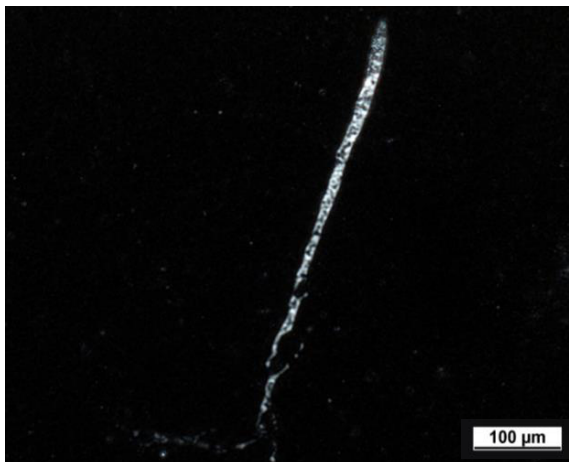
Figure 3. Morphology development of PA12 dispersed phase in PVA matrix (thread's breakdown).

Even when there were formed many very small particles in this blend (PA12/PVA), compatibility of materials is not supported by their thermal behavior. Theoretically the glass transition temperature of compatible blends is shifted from that of their original components to an intermediate value [19]. The results obtained by the scanning calorimetry (Figure 4) did not show changes on the Tg of the rough PVA Mowiflex TC 253 (Tg=62°C) and, therefore, interpolymer interactions are no probable.
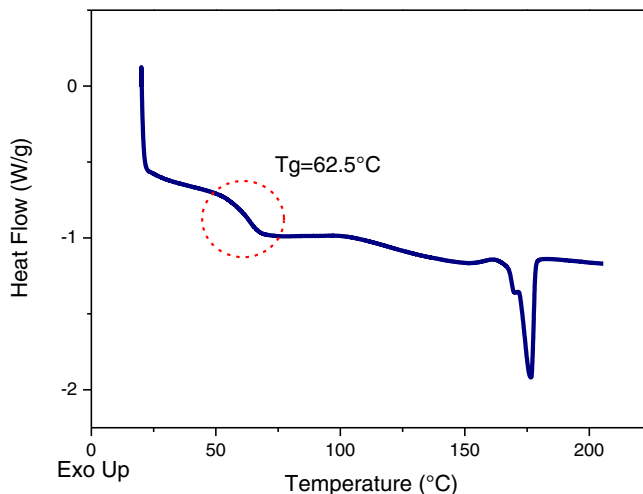

Figure 4. DSC second heating curve for the film of the mixture PA12 /PVA .

These results are not bad at all for the purpose of powder for Laser melting. It is known that one important factor for laser melting processing is the flowability of the powder, and thereby it is quite important to choose an appropriate drying method when the powder is obtained from a solution and, the spray drying of a polymeric emulsion has been found a viable path to obtain good powder characteristics for laser melting process [8]. It is then the blend of PA12 and PVA an option to produce a polymeric emulsion with fine PA12 particles.

3.2 Section I (Kneading). PA12/PEG

On the other hand, in the case of PA12/PEG, most of the PEG flowed away from the machine during the first 5 minutes of mixing, this due to its high fluidity at 190°C, the material that flowed from the machine was collected in a recipient and immediately dissolved in water, then analyzed by Microscope. Figure 5 corresponds to the micrographs of the collected mixture after been partially separated through decantation. There were found several round particles and also some small fibers, it was also noted a significant difference on particles size distribution. It worth mentioning that PA12/PEG blend has been analyzed in other work [20] (although with different molecular weights), the authors found two patterns in the size distribution and mostly spherical shape particles.
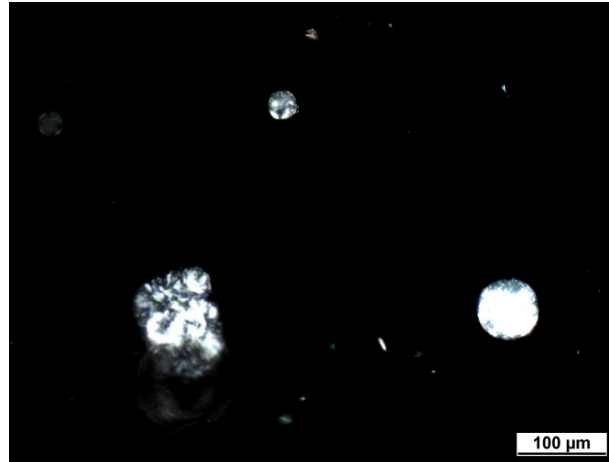

Figure 5. Collected mixture of PA12/PEG during the first 5 minutes of mixing at 190°C and 100 rpm

It is known that the elongational flow is very effective in deforming spherical particles [21] but also it is known that the interfacial tension between components of the mixture retract the deformed droplets into a spherical shape. The blend of PA12 in PEG matrix showed a fast retraction of PA12 particles into a spherical shape, the case for PA12/PVA blends seems to be not the same.

3.3 Section II. Zero shear stress.

The absence of shear stress produces spherical morphology of the dispersed phase [13, 21]. For both materials (PA12 and PBT) all observed particles had spherical shape after being heated in the PEG matrix (see figures 6 and 7). Nevertheless, for the case of PA12 powder it was presented the inconvenient that many of particles coalesced and formed big pellets. Probably and the already spheroidal shape particles of PA12 powder contributed to the mobility of this material in the PEG matrix, facilitating their collision, coalescence and the consequently formation of big pellets, but maybe more important were the poor temperature control and the particles cohesiveness. The desired effect is just to give certain mobility to the molecules in order to promote the reduction of the interfacial area and hence the formation of spheres, but not too much molecules mobility to avoid a very low viscosity, high reduction of interfacial forces, and so coalescence. The ideal condition was probably used in the case of the grinded PBT powder, which did not form any appreciable big particle, in fact, several micrographs of the sample suggest a reduction in the particle size distribution.

It would be interesting to study the kinetic of retraction into spherical shape and coalescence of powders that are potentially suitable for laser melting process, in order to fit the best parameters as the temperature and necessary time to achieve the spherical shape particles without having loss of powder due to formation of big pellets. PEG could be a good polymeric matrix to achieve this goal; it presents the advantages of low melting point, water solubility and broad operation temperature. One first approach could be the theory for coalescence called "film drainage" for totally immobile interface [13, 22], the model considers that when the drop viscosity is much higher

than the matrix viscosity than the interface does not deform under the action of hydrodynamics stresses, nevertheless it also assumes that there is no change in the size of dispersed phase when the shear rate is zero.
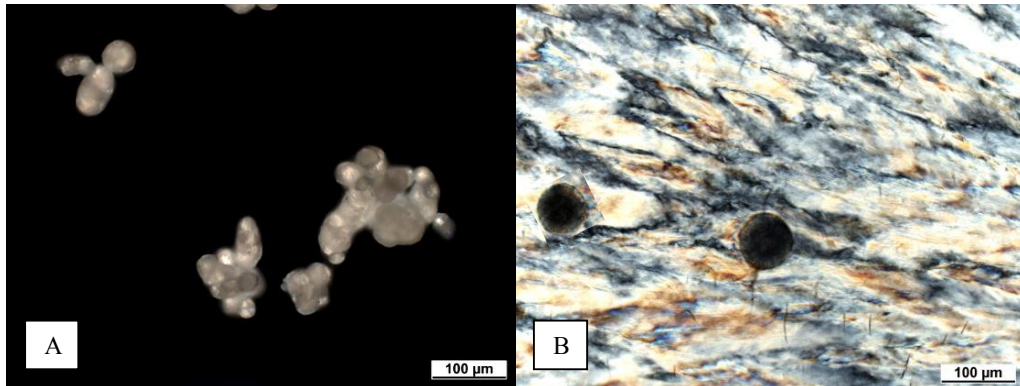

Figure 6. A) EOS powder and B) EOS powder after mixed and heated in PEG matrix.
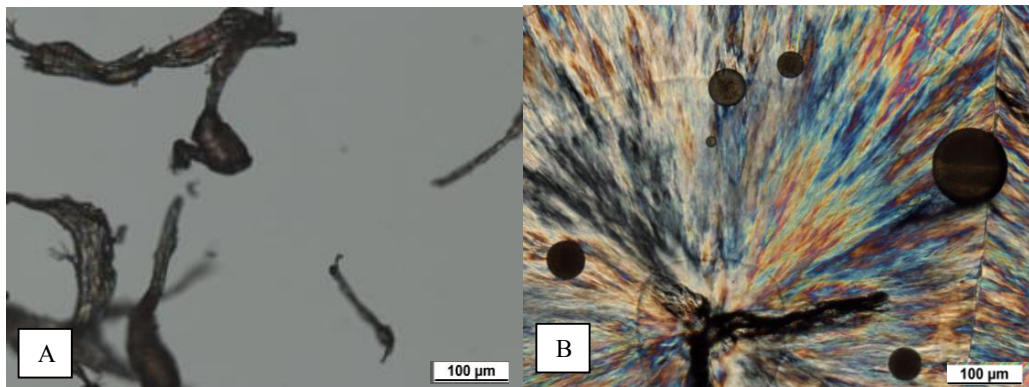

Figure 7. A) PBT powder from cryogenic grinding. B) PBT powder after mixed and heated in PEG matrix.

4. Conclusion

It was investigated the morphology of the blends PA12/PVA and PA12/PEG, as a possible path to generate PA12 powder. PEG and PVA are water soluble which is an environmental advantage regarding to those process that use dangerous solvents to produce polymeric solutions. In the blend of PVA the qualitative analysis showed the formation of lots of very small particles of PA12 (probably in the order of nanometers), there was a total disintegration/deformation of 20% wt composition of PA12. No clear dominant shape particles morphology was found for this blend. In the case of PA12/PEG, spheres was the dominant morphology, with apparently the desired size for laser melting materials, nevertheless this morphology was found in the mixture that flowed out of the machine, and therefore the product yield was low. For PA12/PEG blend the issues to overcome are those associated with the mixing of polymers with high viscosity ratio, specially the high fluidity. The difference of viscosities helps to produce bigger particles and is also associated with the achievement of sphericity. On the other hand, the experiments at laboratory scale (zero shear rate) served to point out the feasibility to modify the shape of irregular particles toward spherical shape, further investigation is necessary to understand the kinetic of irregular morphology retraction and coalescence. The total phase separation and drying of polymeric solution is other important issue that has not been covered in this work.

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