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PRODUCTION OF POLYMERIC NANOCOMPOSITE POWDER FOR TISSUE ENGINEERING APPLICATION

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Abstract. The use of composite materials are increasing in industries and it has been shown that the use of nanocomposites in the field of Tissue Engineering can increase compatibility between cells and polymer matrix material, as well as promote tissue regeneration and inhibit the formation of fibroses. In this work, we report on the production of poly(vinyl alcohol) (PVA) nanocomposite, with nanocellulose or carbon nanotube (CNT), aiming at its use as a biomaterial in scaffolds. The composite powders were produced by spray drying. Their morphologies were verified with a scanning electron microscope and their crystallinity analysed by X-ray diffractometry. The particles obtained by this method are not rigid, although the shapes are spherical-like. Despite the powder could be obtained, it appears that the polymer undergoes degradation, probably due to the high temperature used for its preparation.

Keywords: *nanocomposites, carbon nanotubes, nanocellulose, spray drying, scaffolds.*

1. INTRODUCTION

In tissue engineering, new and functional tissues are manufactured from living cells that are associated with matrices known as scaffolds. In these scaffolds the highly porous microstructure is fundamental for the survival, proliferation and migration of cells in vitro, which must withstand tensions and loads after implantation (do Nascimento and Lombelo, 2016). The scaffolds, besides the adequate geometry necessary to fit the implantation spaces, have to provide sufficient mechanical support as the growing tissue replaces the gradually degrading scaffold matrix. Therefore, the scaffold should be designed with a degradation and resorption rate such that the strength of the scaffold is kept until the tissue engineered implant is fully accommodated by the host tissue and can assume its structural role (Hutmacher, 2001; Wiria *et al*., 2007). Besides that, a 3D environment that simulates a more realistically a natural tissue, with controlled pore sizes and interconnectivity, is desirable.

Conventional methods to fabricate scaffolds, like solvent casting-particle leaching process, freeze drying, phase separation, electrospinning and melt molding, among others (Puppi *et al.*, 2010), present some drawbacks that involves from use of organic solvents, or incomplete solvent removal, to insufficient interconnectivity of pores within the matrix or a non-porous surface, which does not favor cells growth. Other inconvenience is the difficulty to fabricate 3D structures with controlled geometry and pore sizes that fit the patients need.

One technique that was recently introduced in tissue engineering is the selective laser sintering (SLS). In this technique, a laser scan a powder bed inducing partial fusion of the powder particles, which merge to originate a complex 3D piece. With this technique, highly porous scaffolds, with irregular shapes and structures containing channels with complete pore interconnectivity, can be achieved. In case of polymers, it is solvent free and does not require any extra binding system, thus minimizing the risk of material contamination. However, some limitations of SLS are the fact that the material must be in powder form and is limited to the processing of thermally stable polymers (Leong *et al*. 2003; Yeong *et al*., 2004).

At first any material in powder form can be sintered, however, the set of polymeric materials that can be processed by sintering is still quite restricted. The material must possess characteristics of easy processability and biodegradability at controlled rates, besides guarantee the mechanical integrity to keep the spaces required, as well as rough surfaces and hydrophilic characteristics, two important factors that determine cell adhesion and proliferation.

To explore the advantages of laser sintering of polymeric materials, it is necessary to find biomaterials in powder form that can be processed by laser sintering without compromising the chemical and physical stability of the material. Among the most studied synthetic polymeric materials that shows biocompatibility and biodegradability is poly(vinyl alcohol) (PVA), which have been used largely in hydrogel form in tissue engineering. Some of the advantages presented by this polymer include their biocompatible, non-toxic, non-carcinogenic and bioadhesive characteristics, added to its high water solubility, chemical resistance and easy processabillity. Because of these characteristics, the use of PVA to simulate natural tissues that can be readily accepted into the body is possible (Baker *et al.*, 2012; Hassan and Peppas, 2000).

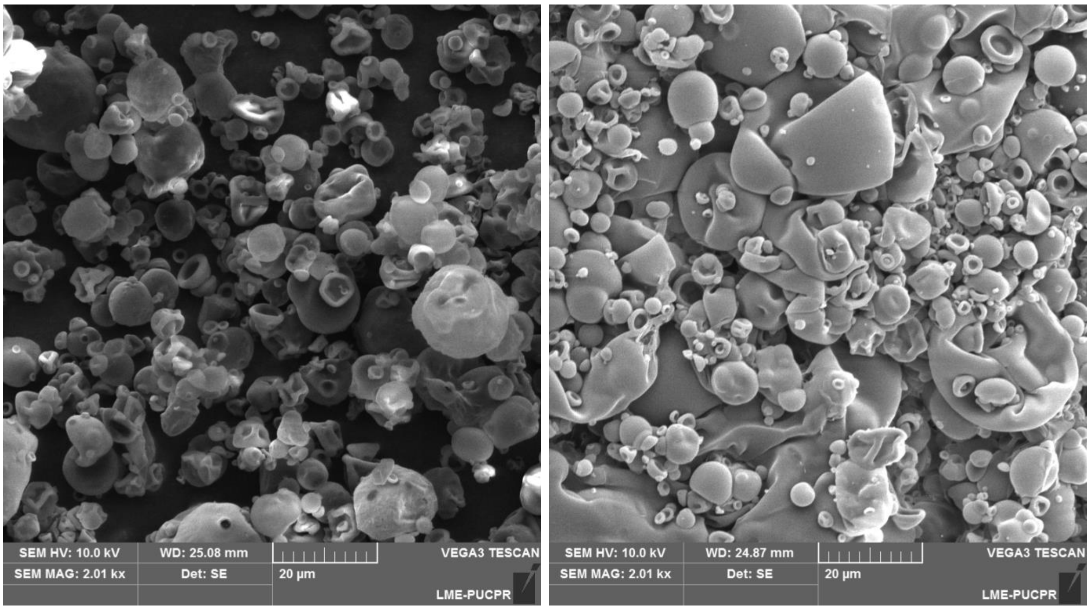
Therefore, the aim of this work is to produce nanocomposite powder based on poly(vinyl alcohol) (PVA), a polymer that is being already studied for tissue engineering applications, as in its pristine (Shuai *et al.*, 2015) form as in composites (Li *et al*., 2013), and presents adequate characteristics for use in SL technology (Wiria *et al*., 2008; Shuai *et al*., 2014 and Eosoly *et al*., 2010).

2. METHODOLOGY

Both composite materials were prepared using a PVA (P.S. Vetec) solution as base that was prepared by dissolving the PVA in distilled water. As the mixture tends to turn a hydrated gel, to reach the desired viscosity and degree of mixing, it was necessary to heat the solution which was kept at 60 C while stirring. The best concentration value was experimentally determined to be 20 mg/mL, which led to a 2% solid fraction dispersed in the solution. After that, 10 wt% of nanocellulose relative to PVA was added. In the case of carbon nanotube (MWCNT, Nanocyl) composites, due to CNT low solubility, the carbon nanotubes were previously sonicated with sodium dodecyl sulfate surfactant (SDS, Sigma). The composite solutions of nanocellulose and NTC-SDS dispersed in the PVA matrix were then taken to the Spray Dryer (ELETTRONICA VENETA, MSD/EV) for powder production. The operational parameters used in the spray dryer, that allowed powder preparation and collection, were 200 ºC temperature at drying chamber, 105 ºC in the exhaustion chamber and a 1 L/h flow. The nanocellulose was prepared from Eucalyptus cellulose pulp by mechanical defibrillation in a Masuko Sangyo Co. Super Masscolloider, MKCA6-3. The crystallinity of the samples were analysed using a Shimadzu XRD-7000 Diffractometer, CuKα radiation, in thin film mode, with scan parameters of 2°/min in the range 4-60° (2θ). Scanning electron microscopy was performed in a Tescan VEGA3 LMU, for which the samples were gold coated. Differential scanning calorimetry was performed in a Netzsch DSC 404 Pegasus®, in the temperature range of 20 to 210 ºC in steps of 10 °C/min.

3. RESULTS AND DISCUSSION

The macroscopic aspect of the materials as removed from the spray dryer, not shown, was quite different. While the composite with nanocellulose resembled cornstarch the composite with carbon CNT presented a more fibrous characteristic. The microscopic morphology however, for both materials, resembles pierced balls, Fig. 1, instead of the expected solid particles.



(a) (b)

Figure 1 – SEM microscopy of PVA/nanocellulose (a) and PVA/CNT (b) composites produced by Spray Drying.

For use in laser sintering it would be interesting to have a more homogeneous particle size distribution, but as can be observed directly in figure 1, the control of particles sizes cannot be achieved, at least not with the parameters used.

It is important to note that the higher the crystallinity, the higher are the density, stiffness, dimensional stability, chemical resistance, abrasion resistance, melting temperature (T_m) and glass transition temperature (T_g) of the polymer (Canevarolo, 2013). Hence, it is desired that the material, after processing, maintain its crystalline characteristics. The crystalline characteristic of the materials, for both composites, with nanocellulose and with CNT, are shown in figures 2 and 3, respectively. Comparison between the diffractograms of PVA and PVA/nanocellulose evidences the partial suppression of the first peak, at 2θ = 11.2°, and a strong reduction of intensity of the peak positioned at 9.5°, indicating the loss of crystallinity of the polymer matrix.

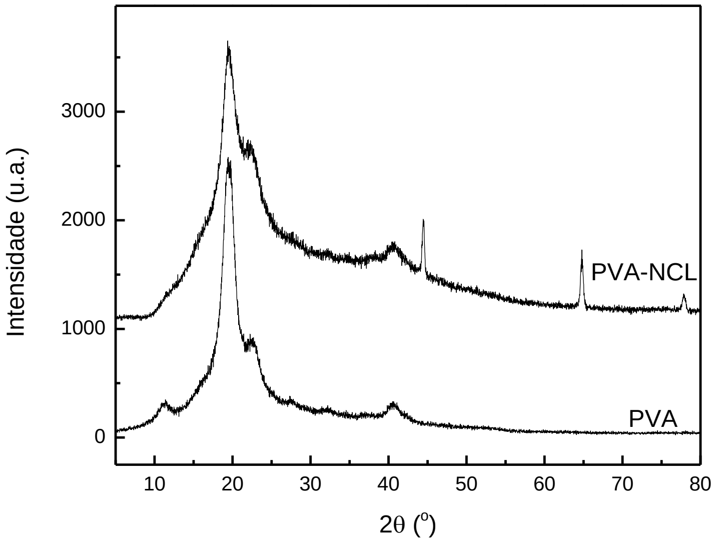


Figure 2. X–ray diffractograms of PVA/nanocellulose composite and the PVA powder.

This is also the case for the composite with CNT. However, in the PVA/nanocellulose diffractogram, figure 2, one observes that new peaks, at positions 44.5°, 64.8° and 77.8° have arisen. At a first glance, it would appear that these peaks are a result of a crystalline rearrangement induced by the nanocellulose insertion in the polymeric matrix. However, the same peaks, at the same positions, are evident in the PVA/CNT diffractogram, figure 3.

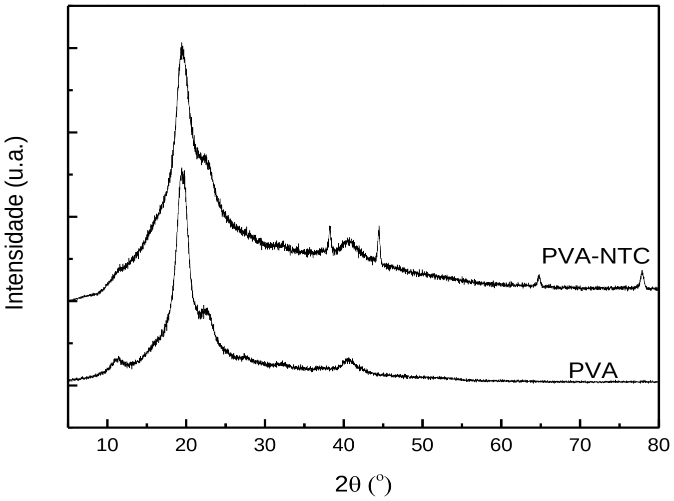


Figure 3. X–ray diffractograms of PVA/CNT composite and the PVA powder.

Since the mass fraction of nanocellulose, or of CNT, used to prepare the composites is much smaller than that of the polymer, one would expect that the crystalline characteristics of the composites would be entirely dominated by the polymer. Hence, the emerging of new peaks also would be a reflex of polymer matrix crystalline changes that could be a result of the interaction between the polymer and the nanomaterials incorporated. However, no peaks associated to the diffractogarm of the pure nanomaterials used matched the new peaks. In that case, these new peaks indicate the formation of PVA sub-products, resultant of polymer degradation during processing in the spray drying. This is confirmed by the observation of the same peaks in the diffractogram of the PVA powder, prepared by spray drying under the same conditions. This degradation was not expected since the melting temperature of PVA varies from 190 °C to 230 °C (Roohani *et al.*, 2008), however there are reports that shows that PVA undergoes degradation prior reaching the melting temperature (Hodgkinson and Taylor, 2000; Marten, 2002).

Differential scanning calorimetry (DSC) measurements, were performed in both samples, in an attempt to understand the XRD results. In Figure 4, the thermograms of pure PVA, nanocellulose, PVA-nanocellulose composite prepared from solution and PVA-nanocellulose composite prepared by spray drying, are shown, and are indicated by numbers from 1 to 4, respectively.

For pure PVA, curve 1, 2 endothermic peaks are observed, one broad peak at, approximately, 98 ^{o}C and the second at, approximately, 190 ^{o}C. The first peak is usually related to water evaporation, since PVA is highly hygroscopic, being the second peak associated with the melting transition. The thermogram of nanocellulose, curve 2, shows only one broad peak. From curve 3 in Fig. 4, the thermogram for composite prepared from solution, one observes that the thermal profile of the composite it is very similar to the pure PVA thermogram, what indicates that addition of nanocellulose to the PVA does not change its thermal properties. However, from curve 4 in Fig. 4, which is the thermogram for the PVA/nanocellulose prepared via spray drying, it becomes clear that the thermal characteristics of the composite were lost. According to Hodgkinson and Taylor (2000), this degradation would occur at the temperature of 150 ^{o} C with water release and conjugated double bonds formation.

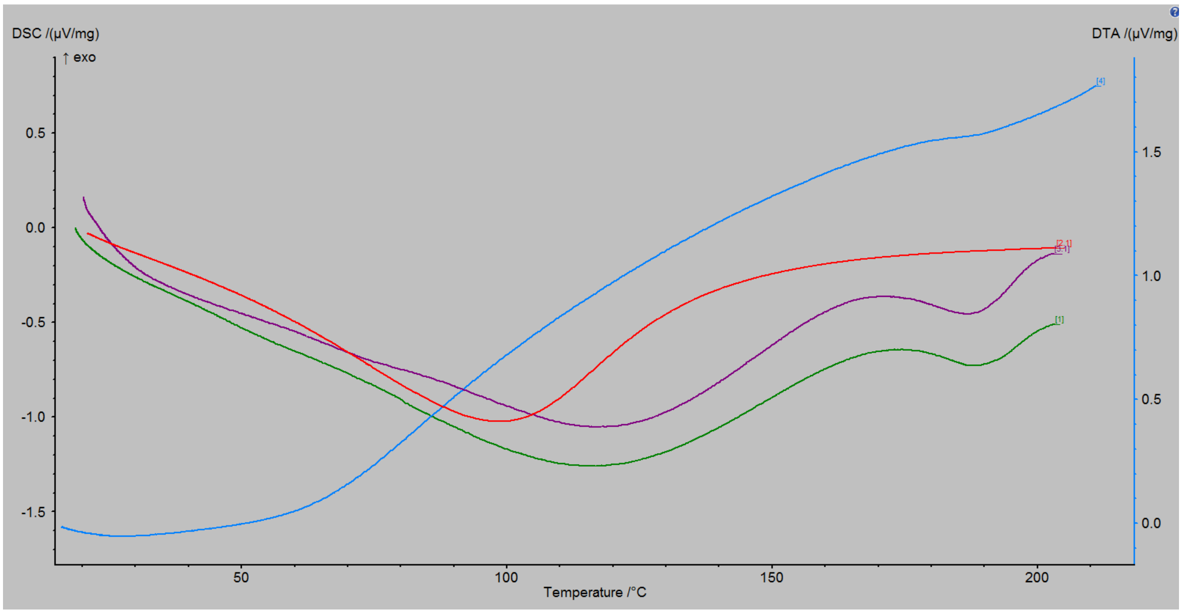


Figure 4. DSC thermograms of pure PVA powder (green), nanocellulose (red), PVA/nanocellulose composite prepared from solution drying at room temperature (purple) and PVA/nanocellulose composite prepared by spray drying (blue).

A different behaviour is observed for the PVA/CNT composite, Fig. 5. Comparing the pure PVA thermogram, curve 3-Fig.5, and the thermogram of the PVA/CNT composite prepared by letting the solution to dry at room temperature, it is possible to observe that the PVA thermal property is supressed by addition of small fractions of CNT (~0.5 wt.%) to the polymer, since the characteristic peak associated to the melting transition disappears. This is an unexpected result that needs further investigation.

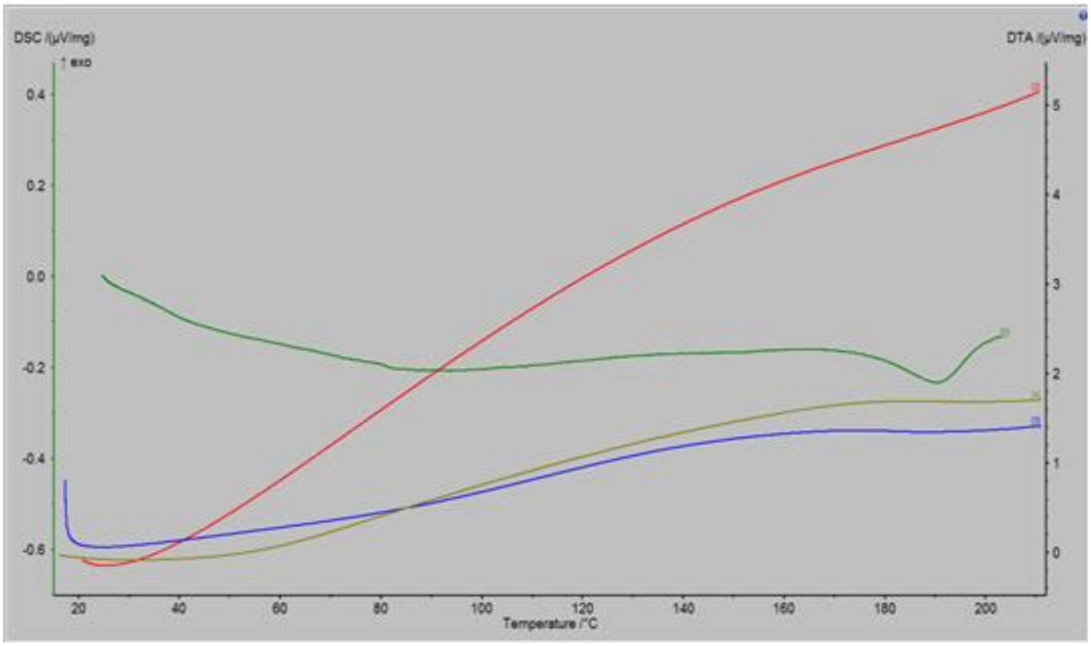


Figure 5. DSC thermograms of pure PVA powder (green), CNT (red), PVA/CNT composite prepared from solution drying at room temperature (blue) and PVA/NTC composite prepared by spray drying (yellow).

The thermogram for the composite prepared by spray drying, curve 4 in Fig. 5, shows basically the same profile observed for the nanocellulose composite, loss of thermal characteristics. The difference is that it cannot be attributed only to the process, since the suppression of the composite thermal properties was induced by CNT-surfactant mixing.

4. CONCLUSION

In this work it has been shown that PVA nanocomposite powders can be obtained by use of the spray drying technique. However, synthesis parameters have to be adjusted and optimized in order not to alter the physical properties of the materials, and to allow size and density control.

5. ACKNOWLEDGEMENTS

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