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Porosity Assessment of Melt Electrospun PLA

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Abstract: Melt electrospun materials are by far less explored than solution based ones, due to the challenges that come from both temperature and electrical voltage simultaneously. Within this respect, the fibers produced by melt electrospinning are much thicker than 1 micron. This paper focuses on the design of polylactic acid (PLA) microfilament materials melt spun on Spraybase, with previously generated 2D models in three different geometries. The PLA materials have difference in terms of filament densities (distance between the filaments of 0.5, 1 and 2 mm) and filament positions (vertical, vertical/horizontal, diagonal or at the angle less than 90°). The porosity of the materials is determined using microscope images of the samples and by analyzing their pore sizes and total void volume in ImageJ. The porosity is an important parameter that affects the thermal comfort evaluation of materials and it is dependent upon their e.g. thickness, filament diameter, filament distribution or geometry and pore sizes.

Keywords: electrospun; melt; microfilaments; PLA; porosity; 2D models

1 INTRODUCTION

1.1 Melt Electrospinning Direct Writing

Melt electrospinning is the process of microfibers (up to 500 microns) formation with the aid of high voltage power supply that stretches a polymer melt. The production of nanofibers via melt electrospinning is more challenging than in solution electrospinning due to the absence of a solvent that suppresses the bending instabilities and jet thinning [1]. However fine fibers can be formed with careful control of the temperature that is the viscosity and solidification of the filaments, the electrical field, as well as by the increase of the electrical conductivity through targeted additives [2, 3]. The polymer parameters that will also affect the final fiber diameter are not to be omitted. These include: 1) electrical conductivity, 2) molecular weight, 3) tacticity and 4) extensional viscosity [4]. As reported, electrical conductivity is the dominant factor that affects the jet stability that is, a semi-conductive polymer will be ideal for a stable jet formation. Jet instability is present when electrospinning highly conducting materials or the jet can't be initiated due to low stretching forces in case of insulating materials [4, 5]. Stronger stretching forces were generated due to the increased jet electrical charges when sodium oleate was added to the polymer melt [6]. The jet stability also depends upon the polymer molecular weight which is related to its viscosity, modulus and tensile strength. Lower molecular weight will also result in thinner fibers [4, 7]. It is also suggested that more oriented molecular structure that is higher tacticity polymer melts will produce finer fibers [4, 8]. The polymer melt extensional viscosity is directly related to the device set temperature or the polymer melting point. In the usual non-isothermal electrospinning conditions the fiber diameter is restricted of further thinning when the jet flies far away from the spinneret and solidifies due to temperature gradual reduction [9].

The need to control the electrospun structure has emerged a process that combines melt electrospinning and 3D printing. Melt electrospinning direct writing is the process where the melt polymer jet is deposited through an automated translating collection system in order to form highly organized fibrous architecture. These polymer melt jets are drawn into continuous lines according to previously designed geometry and can be laid in the third direction to form a 3D structure [10]. It was reported that the excellent control of the microfibers layout and interspacing can result in the production of aligned, crimped and random fibrous materials as well. Initially the application field was biomedicine for the development of 3D tissue scaffolds [11], but these materials have huge potential due to the controlled porosity and fibers/pores sizes.

In this study melt electrospun materials with three different target geometries were prepared through direct writing electrospinning. The same were evaluated in terms of total porosity and pore size as the dominant factors that will affect i.e. materials thermally insulating performance or in case of chemically protective clothing where the breathability is directly related to the wearer comfort.

2 EXPERIMENTAL PART

2.1 Materials and Methods

The polymer used to produce the melt electrospun materials was polylactic acid (PLA), Luminy L175 with density of 1.24 g/cm^3, purchased from Total Corbion. The electrospun materials were produced on a melt-electrospinning direct writing device Spraybase, Avectas Ltd., Ireland.

The processing parameters were as follows: 1) electrical voltage of 11 kV, 2) temperature of 200 °C, 3) head nozzle to collector distance of 1.2 cm and 4) air pressure of 11 bars. Three groups of materials were produced depending on the filament density and filament position. In the first group, the filaments were positioned vertically with several perpendicular reinforcements, in the second group the filaments were positioned vertically and horizontally at the angle of 90º, while in group three there were additional positions at an angle smaller than 90º, Fig. 1. The filament density concerns the distance among each filament and it was set to 0.5, 1 and 2 mm, except for group three where materials with only 1 and 2 mm filaments distances were produced. Prior melt-electrospinning, 2D models representing the three groups of materials' geometry were designed using the device software, SEL generator.

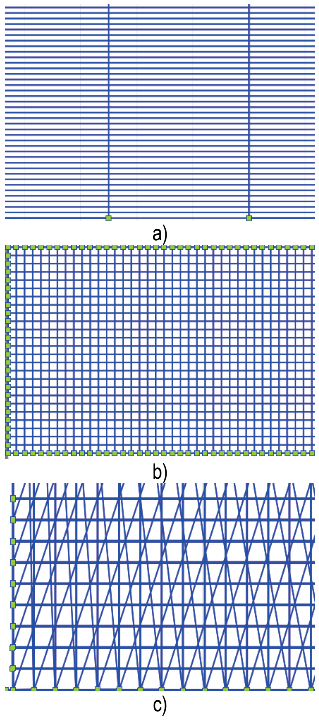

Figure 1 2D models of the melt electrospun materials: a) group 1, b) group 2 and c) group 3.

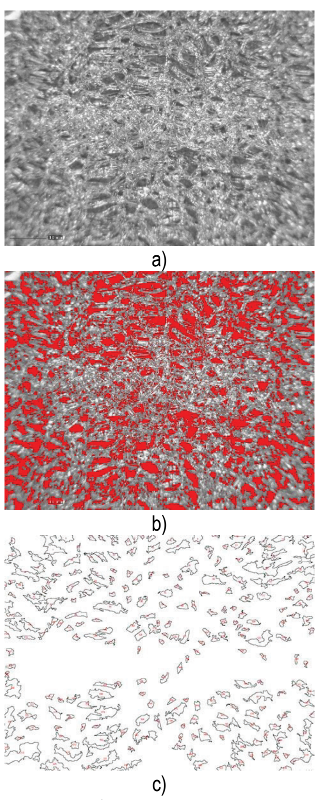

Figure 2 Threshold adjusting of the material's optical image: a) 8-bit image, b) threshold adjusting and c) marked pores to be measured; Sample group 1, filament density of 0.5 mm.

2.2 Evaluation of Melt Electrospun Materials' Porosity

Melt electrospun materials' porosity was evaluated in ImageJ software by analyzing their images taken with DinoLite optical microscopy. The procedure to evaluate the porosity includes several steps: 1) 8-bit image selection, 2) image scale setting, 3) threshold adjustment – red pores setting, 4) cutting off pores connections or filling holes if any, 5) analyze particles, 6) automatic mean pore area measurement and porosity calculation by using the total pores area and the total image area. The samples were analyzed in triplicates. Fig. 2 shows the threshold setting of one of the samples taken images.

3 RESULTS AND DISCUSSION

Fig. 3 shows the optical images of the three groups of electrospun materials. Generally, all samples have curly filaments or are forming continuous loops despite the straight lines of the 2D models. This suggests that during electrospinning the combination of the two dominant parameters that is the high temperature and the high electrical voltage resulted in the melt jet instability, thus the formation of the loops. The regular position (in straight lines) of the looped filaments is easily detected in the samples of group 1 and 2, that is samples with the filament density of 1 and 2 mm, Figs. 3a2, 3a3, 3b2 and 3b3, as well as of 0.5 mm, but only in case of group 2, Fig. 3b1. The regularity of the filament positioning is greater vertically than in the perpendicular direction, where certain deformations of the loops can be observed. Figs. 3b3, 3a1, 3c1 and 3c2, show almost random positioning of the microfilaments, which suggests that the lowest filament density of 0.5 mm, Fig. 3a1, as well as the diagonal positioning of the filaments, Fig. 3c1 and c2, affect their overlaying and loop extensions or deformations.

Fig. 4 shows the total porosity vs. mean pore area of the melt electrospun materials. The given results are in accordance with the images of the samples in Fig. 3. The total calculated porosity of the electrospun materials in group 1 is increasing with the increase of the filament density. This is expected as the increasing distance between the filaments increases the void volume thus, materials' total pore area. The significant increase (the max observed as well) of the total electrospun materials porosity is evident in case of sample 3 - group 1, that is of (64 ± 3) %. This material has the highest pore area of (394 ± 57) μm^2 of all groups as well. The same increasing trend for both porosity and pore area is present in group 2 and 3 with the increase of the two parameters for 22 % (118 μm^2) and 17 % (55 μm^2), respectively.

When comparing the three groups of materials an opposite trend can be seen thus the increasing filament density reduces the porosity/pore area and it is most significant again in case of the 2 mm density. This is due to the deposition of the filaments on top of each other in case of group 2 and 3 when the same are laid perpendicularly and diagonally which eventually results in the closure of surface pores.

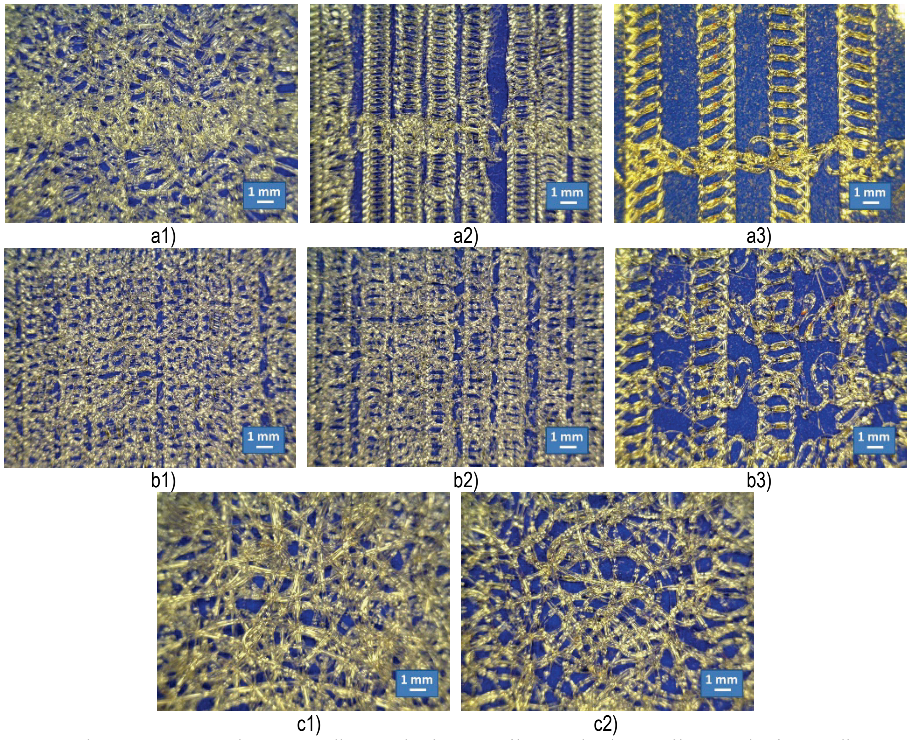

Figure 3 Optical microscopy images of the three groups of samples: a1) group 1 – 0.5 mm, a2) group 1 – 1 mm, a3), group 1 – 2 mm, b1) group 2 – 0.5 mm, b2) group 2 – 1 mm, b3), group 2 – 2 mm, c1) group 3 – 1 mm and c2) group 3 – 2 mm.

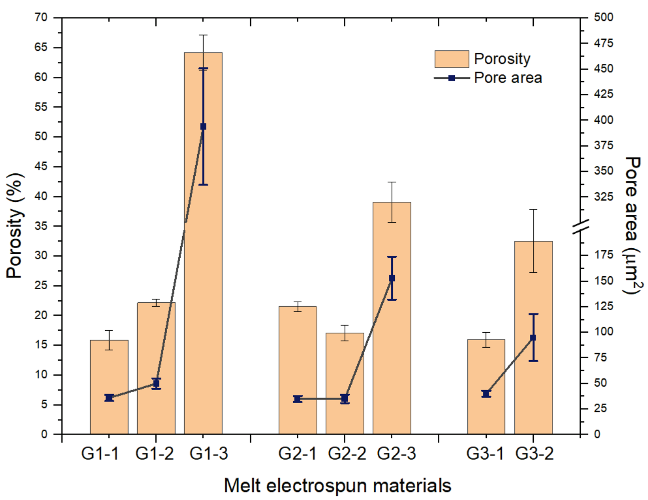

Figure 4 Total porosity vs. mean pore area of the melt electrospun materials.

4 CONCLUSION

In this paper, three groups of materials were prepared via melt electrospinning direct writing having differences in their structure in terms of filament density (filament distances of 0.5, 1 and 2 mm) and position (horizontal, horizontal/vertical and horizontal/vertical/diagonal). The materials' total porosity and mean pore area were evaluated using ImageJ and their optical microscopy images. It was revealed that the higher the filament density was, the greater the total porosity and mean pore area were observed. Significant increase of these parameters was present in case of the samples of all groups with the filament distances of 2 mm, which is due to the greater void area formed during melt electrospinning. The deposition of the second and third layer in case of the materials of group 2 and 3 resulted in the reduction of the two parameters with the less significant effect in case of the 1 mm filament density. By optimizing the porous structure, one can design i.e. breathable and thermally protective clothing.

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