Electrospinning and structure of bicomponent polycaprolactone/gelatine nanofibers obtained using alternative solvent system

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Introduction

Incorporating non - toxic solvents to advanced methods of bio-compatible materials fabrication seems to be desirable from the tissue engineering perspective. Advantages of this trend may arise not only from toxicity issues but also from different, potentially favourable interactions of alternative solvent systems with processed materials. In this study bicomponent polycaprolactone/gelatine nanofibers were successfully formed for the first time by electrospinning using a novel polymer – solvent system consisting of acetic acid and formic acid which are alternative to the commonly used toxic solvents like fluorinated alcohols. The effect of electrospinning conditions on morphology and structure of nanofibers was investigated.

Experimental

Polycaprolactone (PCL) (M_n = 80,000 g/mol), gelatine (Gt) from porcine skin Type A (Gel Strength ~ 300g Bloom) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Sigma-Aldrich Co. Acetic acid (AA, glacial pure 99,5%) and formic acid (FA, pure 98-100%) were purchased from Chempur and Avantor PM Poland respectively. The mixture of AA/FA with a ratio 90/10 w/w was used as an alternative solvent system.
Structure of solutions was investigated using Pluta polarizing-interference microscope (Biolar PI) produced by Polish Optical Works (PZO). Electrical conductivity of solvents and solutions was measured using Elmetron CC-401 conductometer while viscosity - by rotational viscometer Brookfield HADV-III Ultra with cone/plate configuration. Crystallinity of PCL was analysed using differential scanning calorimetry (DSC) - Perkin-Elmer Pyris-1. Wide angle X-ray scattering (WAXS) measurements were performed using Bruker D8 Discover diffractometer. The electrospinning equipment was operated in horizontal mode. It consisted of single syringe pump (New Era Pump Systems, NE-1000 model), collector and high voltage generator, connected with positive terminal to a stainless steel needle (0,34 mm inner diameter) and grounded to the collector (steel plate). Distance between needle and collector was fixed at 15cm, flow rate of solution at 600 µl/h while changing applied voltage. For electrospinning process 15% w/w and 5% w/w solutions were prepared, for alternative solvent system and for HFIP, respectively.

Results and discussion

Optical investigations of PCL/Gt blends clearly show the emulsion nature when using AA or mixture of AA/FA as solvent. This fact may be related to the lack or very limited miscibility of PCL and Gt [1] together with relatively weak interactions with both acids,

resulting in separation of both polymers. Addition of a polymer to a solvent, either AA/FA or HFIP, leads to changes of electrical conductivity, decreasing it with addition of nonpolar PCL while increasing with addition of Gt, which is highly polar, containing amino and carboxyl groups which are susceptible to ionization. It is evident that irrespective of the solvent used, viscosity decreases with increasing content of Gt. Nevertheless, for AA/FA solutions at the applied 15% w/w of polymer, addition of Gt brings more considerable and consistent decrease in viscosity compared to HFIP 5% w/w solutions.
Despite the emulsion character of the system, SEM images of fibers do not indicate any inhomogenity along fibers and the electrospinning process is stable. On the other hand, the internal inhomogenity along the fibers spun from AA/FA system can be deduced using optical microscope with crossed polarizers. Addition of Gt at any content leads to reduction of mean fiber diameter, which is particularly evident for HFIP system and fiber diameter distributions can be treated as unimodal contrary to bimodal distributions for pure PCL nonwovens.
WAXS investigations show that Gt remains amorphous, indicating random coil conformation in the applied solvents systems, while PCL crystallinity of fibers spun using AA/FA solvent system is in general higher than for fibers spun using HFIP. On the other hand, DSC data do not indicate any differences in temperatures of melting of PCL crystals for both solvent systems.

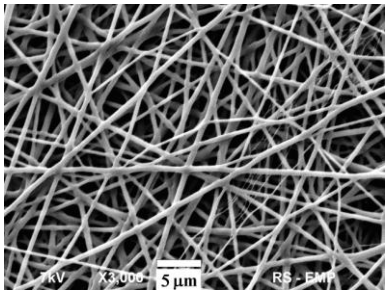

Fig.1 Bicomponent PCL/Gt fibers electrospun using AA/FA solvent system

Conclusions

It is possible to obtain PCL/Gt fibers using AA/FA mixture with morphology similar to that for fibers spun from HFIP solutions. The mixture of PCL and Gt either in AA or AA/FA solvents shows emulsive structure. This kind of structure does not affect morphology of fibers. Further investigations of these materials and its structure towards biomedical applications are intended.

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References

[1] Kołbuk D., Sajkiewicz P., Denis P., Choińska E., Investigations of polycaprolactone/gelatin blends in terms of their miscibility, Bulletin of The Polish Academy of Sciences: Technical Sciences, 61, 3, 629-632, 2013