

# Biodegradable micro- and nanofibers prepared from polyesteramides based on $\epsilon$ -caprolactone and $\epsilon$ -caprolactam

Daniela Lubasova, Lenka Martinova, Lenka Malinova and Jiri Brozek

**Abstract**—The formation of novel high aspect ratio nano- and micro-fibers from polyesteramides based on  $\epsilon$ -caprolactone (CLO) and  $\epsilon$ -caprolactam (CLA) is reported in this study. It was proved, that copolyesters CLA/CLO with different content of CLO units or different molecular weight of final copolyester are materials suitable for preparation of fiber layers by meltblown technology and solution-electrospinning (technology Nanospider™).

**Keywords**— $\epsilon$ -caprolactone,  $\epsilon$ -caprolactam, nanofibers, electrospinning

## I. INTRODUCTION

IN the last three decades, the attention in the area of polymer synthesis focused on the theme of biodegradable copolymers [1]. The main reason is an increasing pollution of the environment with polymeric waste, especially products with short lifetime. About one-third of the world production of synthetic polymers is used for disposal products. They mainly represent the application of plastics in wrapping industry. A valuable contribution to the protection of the environment would be at least a partial replacement of the classic non-biodegradable polymers with those that are prone to degradation by active biological system. For that reason, a number of biologically degradable materials based on the use of lactic acid [2],  $\epsilon$ -caprolactone [3] and aliphatic dicarboxylic acids and diols [4], [5] have been developed.

Copolymer based on a certain monomer with some amount of another, functional co-monomer may have specific characteristics, which predetermined this copolymer as raw material for products with required properties. Copolymerization can improve many properties, including biodegradability. A polyamide 6 is one of the most significant synthetic fibers forming polymer. Incorporating other structure unit into the polyamide backbone enables to prepare a large variety of materials having diverse physico/chemical

and mechanical properties. One of the interesting, biodegradable copolymer can be obtained by incorporating an ester unit derived from  $\epsilon$ -caprolactone (CLO) into polyamide. These polyesteramides (PEA's) can be prepared by anionic [6] or hydrolytic polymerization [7,8] of CLO and  $\epsilon$ -caprolactam (CLA).

As it was described in numerous studies, polyamide has already been successfully spun into micro- or nanofibers. Accordingly, the processing of biodegradable copolymer as CLA/CLO is going to be challenge. Polymer fibers with diameters in the micron range can be produced by conventional fiber melt-spinning technology as is meltblown. In the contrast, a solution-electrospinning is an interesting process for producing of fibers with average diameters in the range below 1000 nm. In this process, continuous fibers are drawn from a polymer solution by high electrostatic forces and deposited on a grounded metal collector screen [9]. The unique Nanospider™ technology (needle-free high voltage, free liquid surface electrospinning process) enables industrial scale nanofiber production without nozzles, needles or spinnerets [10].

## II. MATERIALS AND METHOD

### A. Materials

A set of PEA's based on CLO and CLA was synthesized with various molar ratio of CLO units (from 20 to 80 mol.%). PEA's derived from the cyclic monomers  $\epsilon$ -caprolactam and  $\epsilon$ -caprolactone have been synthesized by the anionic polymerization [11].  $\epsilon$ -Caprolactam magnesium bromide was employed as unique initiator giving high yield of copolymer across the whole range of monomer concentrations at 150 °C. Owing to a variation of the content of CLA and CLO component in polyesteramide backbone a large variety of materials having diverse physico-chemical and mechanical properties have been prepared. PEA's have been prepared at the Institute of Chemical Technology in Prague and characterized by viscometry measurements, see Table 1.

Daniela Lubasova is with the Technical University of Liberec, The Institute for Nanomaterials, Advanced Technology and Innovation, Liberec, Czech Republic (corresponding author's phone: 00420 485 353 575, e-mail: daniela.lubasova@tul.cz).

Lenka Martinova is with the Technical University of Liberec, The Institute for Nanomaterials, Advanced Technology and Innovation, Liberec, Czech Republic (e-mail: lenka.martinova@tul.cz).

Lenka Malinova is with the Institute of Chemical Technology, Prague, Czech Republic (e-mail: lenka.malinova@vscht.cz).

TABLE I  
 VISCOSITY OF USED PEA'S

Specimen	Reduced viscosity $\eta_{red}$ [cm <sup>3</sup> /g]
CLA/CLO (80/20)	290
CLA/CLO (60/40)	260
CLA/CLO (40/60)	200
CLA/CLO (20/80)	170

**B. Solution-electrospinning**

The minimum equipment requirements for demonstration of simple electrospinning in the laboratory setup are as follows: (i) a viscous polymer solution, (ii) an electrode (hollow tubular or solid) that is maintained in contact with the polymer solution, (iii) a high-voltage DC generator connected to the electrode, (iv) a grounded or oppositely charged surface to collect the nanofibers. A schematic representation of the equipment generally used in laboratory solution-electrospinning is depicted in Fig. 1.

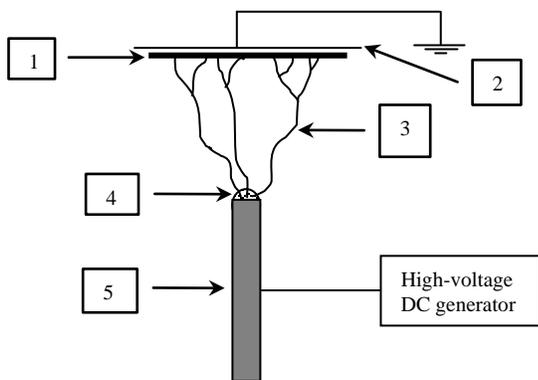


Fig. 1 Schematic of a simple electrospinning experiment; 1 - nanofiber sheet, 2 - electrode grounding shield, 3 - direction of nanofiber formation, 4 - a viscous polymer solution, 5 - a positive electrode

**C. Meltblown technology**

Meltblown (MB) is a process for producing fibrous webs or articles directly from molten polymers using high-velocity air or another appropriate force to attenuate the filaments (Fig. 2). MB microfibers generally have diameters in the range from 2 to 4  $\mu\text{m}$ , although they may be as small as 1  $\mu\text{m}$  and as large as 10 to 15  $\mu\text{m}$ . Compared to solution-electrospinning the MB is characterized by higher technological and energetic demands on the viscosity of the polymer melt and on the volume of hot air, on the other hand MB eliminates problems associated with the usage of the polymer solvents, alternatively problems with their toxicity and flammability.

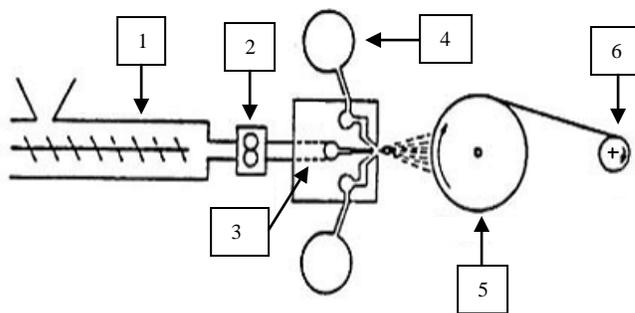


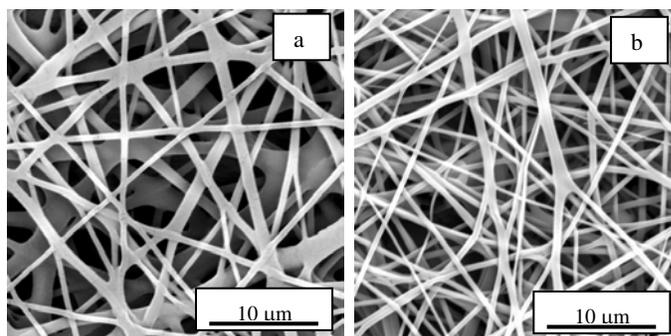
Fig. 2 Process of MB technology; 1 - extruder, 2 - gear pump, 3 - die, 4 - hot air, 5- collector, 6 - winder

**III. EXPERIMENTAL RESULTS AND DISCUSSION**

**A. Electrospinning of PEA's from the solution**

Electrospun solutions were prepared from PEA's with (i) different molecular weight and (ii) various molar ratio of CLO units (20-60 mol%). All tested PEA's were dissolved in solvent system consist of formic/acetic acid (vol. ratio 2/1). The concentration of the PEA's solutions was kept at 10%wt in all cases. The effects of various molecular weights and various molar ratios of CLO units on the electrospinning process and resulted fibers were studied by taken scanning electron microscopy images (SEM). Electro-spinning of CLA/CLO polymer solutions was carried out at voltage of 30 kV, a distance of electrodes 10 cm, air temperature 20°C and air humidity 47%.

Nanofiber layers prepared from all PEA's was successfully electrospun (Fig. 3-5). The molecular weight and the distribution of molecular weight have influenced by the electrospinning process because the solvent's evaporation rate and solutions viscosity can strongly interfere in the electrospinning process. The smallest diameters of fibers were obtained through the electrospinning of specimen CLA/CLO with a ratio of 80/20 and the molecular weight of 12 000 g/mol, followed by specimen with molecular weight of 44 000 g/mol, while specimen with higher molecular weight of 60 000 g/mol produced the largest fibers. Therefore, as a rule, as the molecular weight increased, the nanofibers average diameters also increased. The same character of electrospinning process was observed by fiber-forming of polymer CLA/CLO with a ratio of 60/40.



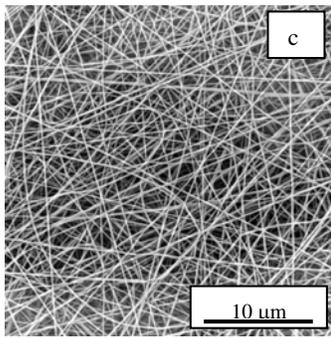


Fig. 3 SEM images of nanofiber layers prepared from polymer CLA/CLO with ratio of 80/20 and molecular weight: (a) 60.000 g/mol, (b) 44.000 g/mol and (c) 12.000 g/mol

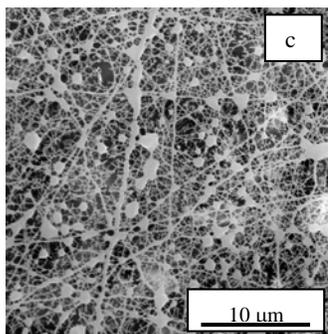
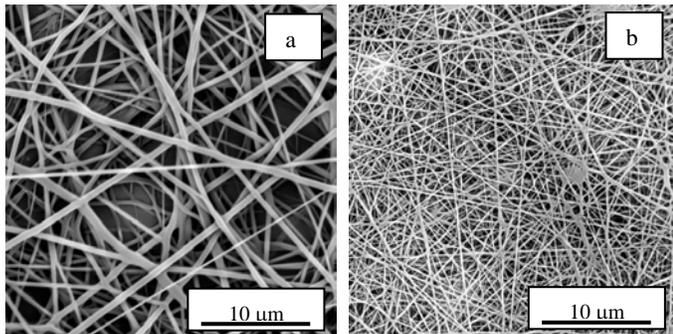
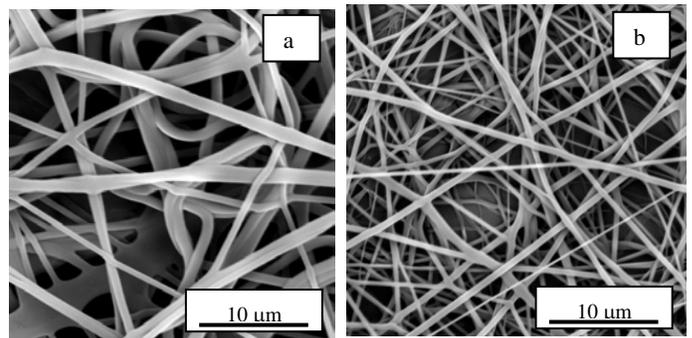


Fig. 4 SEM images of nanofiber layers prepared from polymer CLA/CLO with ratio of 60/40 and molecular weight: (a) 40.000 g/mol, (b) 11.000 g/mol and (c) 10.000 g/mol

The morphology of nanofibers also changed when the content of CLO units in PEA's increased. Fig. 5 clearly shows that the copolymer CLA/CLO with a ratio of 80/20 provided fibers with partly ribbon shape and with a higher diameter and partly cylindrical shapes with a small diameter. Very fine fibers are spun from copolymer CLA/CLO with a ratio of 60/40. Further, average size and distribution increased with increasing content of CLO units (CLA/CLO with a ratio of 40/60 and 20/80). These nanofibers had more point-bonded junction. Aggregation of nanofibers is evident for copolymer PEA with 80 mol.% CLO units. It can be explained by lower polarity of PEA's in comparison to copolymer PEA with 20 mol.% CLO units and lower crystallinity of the copolymer. The solvent is binding in an amorphous phase of nanofibers being formed and thus preventing their fixation.

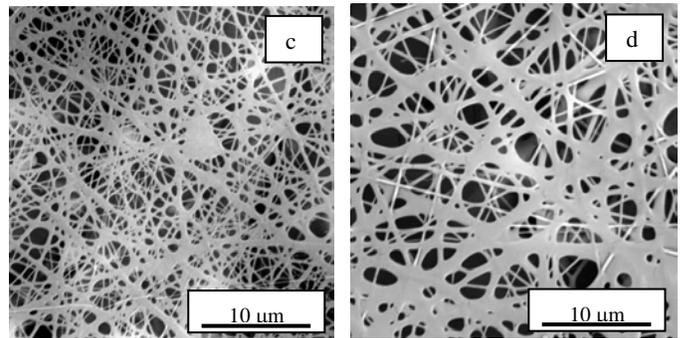


Fig. 5 SEM images of nanofiber layers prepared from polymer CLA/CLO with different content of CLO units: (a) 20mol.%, (b) 40mol.%, (c) 60mol.% and (d) 80mol.%

### B. Spinning of PEA's by meltblown technology

Copolymers CLA/CLO with a ratio of 80/20 and 60/40 were dried overnight in the lab oven at 50 °C. The copolymers were extruded and spun on the Desktop unit for MB from J and M Laboratories. It was necessary to meet the requirements of melting temperature 179°C and 121°C for CLA/CLO with a ratio of 80/20 and 60/40, respectively. The MB extrusion profiles are given in Table 2. Three different jet-collector distances were used: 17 cm, 30 cm and 50 cm.

TABLE II  
MB EXTRUSION PROFILE AND AIR TEMPERATURE PARAMETERS

Conditions	CLA/CLO 80/20	CLA/CLO 60/40
Air Temperature	260°C	205°C
Extruder 1 Temperature	177°C	121°C
Extruder 2 Temperature	205°C	160°C
Extruder 3 Temperature	205°C	182°C
Die Temperature	238°C	216°C
Air Pressure	2 Bars	2,5 Bars
Polymer Throughput	0,022g/hole/min	0,022g/hole/min
Number of Holes	60	60

Dynamic viscosity ( $\eta$ ) of applied polymer is influenced by a polymer molecular weight. Also a structure of meltblown layers depends on a melt viscosity of the PEA's. The used copolymer CLA/CLO 60/40 was characterized by  $\eta \sim 60$  and 33 Pa.s at a temperature of 220°C and 240°C, respectively. The second copolymer CLA/CLO 80/20 was characterized by

$\eta \sim 190$  and  $91$  Pa.s at a temperature of  $220^{\circ}\text{C}$  and  $240^{\circ}\text{C}$ , respectively. The meltblown layers from both copolymers did not contain any defects. PEA's were suitable for fabrication of microfiber layers by MB technology as it can be seen from SEM (Fig. 6). Resulting microfibers were partly cylindrical shape with relatively broad distribution diameters in the range of microns.

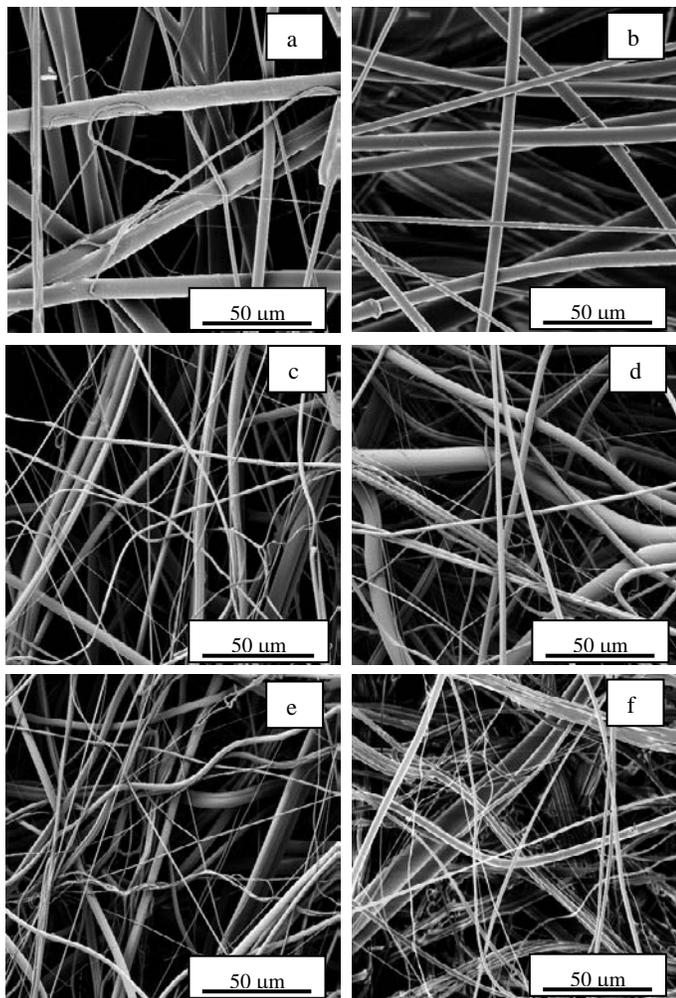


Fig. 6 SEM micrographs of meltblown layers prepared from (i) copolymer CLA/CLO 60/40 and (ii) copolymer CLA/CLO 80/20 with jet-collector distance (a)+(c) 17 cm, (b)+(d) 30 cm and (e)+(f) 50cm

#### IV. CONCLUSION

In this study, a series of CLA/CLO copolymers have been prepared by the anionic polymerization of CLA and CLO and used for fabrication of micro- and nano-fibers layers by meltblown technology or electrospinning process (technology Nanospider<sup>TM</sup>). It was proved that all prepared PEA's are processable by both used technologies. Nanofiber layers from PEA's were electrospun from the solvent system consist of formic/acetic acid (vol. ratio 2/1). Effect of different molecular weight and content of CLO units in PEA's was found out very important during the electrospinning

process. Also the effect of reduced viscosity of copolymers was confirmed as significant in MB technology.

The micro- and nanofiber layers prepared from biodegradable CLA/CLO are promising for an application in both medical and technical areas, e.g. as a disposal filters. These layers will be tested as carriers of a fungal microorganism in the bioremediation of water contaminated with the organic pollutants.

#### ACKNOWLEDGMENT

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