Study Concerning the Processability of Polyetherimide (PEI) Solution for Obtaining Nanofibers

LILIANA ROZEMARIE MANEA[1,2]*, ION SANDU[2,3]*

[1] “Gheorghe Asachi” Technical University Iasi, Faculty of Textile and Leather Engineering and Industrial Management, 29 Dimitrie Mangeron Blvd., 700050, Iasi, Romania

[2] Romanian Inventors Forum, Str. Sf.P.Movila 3, L11, III/3, 700089, Iasi, Romania

[3] ”Alexandru Ioan Cuza” University of Iasi, ARHEOINVEST Interdisciplinary Platform, 11 Carol I Blvd., Corp G demisol, 700506, Iasi, Romania

Electrospinning came into prominence during the last years as a promising procedure to obtain fibers sized under 1µm from a wide variety of polymers. The electrospinning process, technology and equipment are relatively complex, yet efficient, able to produce continuous, exceptionally long fibers, with controlled orientation. Nowadays, the electrospinning technology is the only one able to lead to the formation of continuous filaments, with diameters of some nanometers. The present paper contains a study related to the processability of polyetherimide solution with a concentration of 12%, using as solvents a mixture of dimethylacetamide/tetrahydrofuran 1:1 ratio. Adjusting the flow rate, the distance between needles and collector and the voltage, 100 technological experiments were carried out. The main destination of these nanofibers is filtering surfaces. All fibers were studied by Scanning Electron Microscope method for analyzing the consistency of fibers disposal, the fibers diameter uniformity, and the presence of defects on fibers.

Keywords: electrospinning, nanofibers, polyetherimide, SEM, defects, filter

There are numerous technologies to produce nanofibers, among which the electrospinning is considered to be the most efficient, offering also the most numerous implementations in various applications [1-7].

The polymeric compounds are solid materials so that they need to be brought into liquid state for electrospinning (extrusion) processing. This can be done either by melting the synthetic thermoplastic polymers or by dissolving the polymers, which are soluble in various solvents and non-thermoplastic. If none of these methods can be applied, the polymeric compounds must be chemically treated in order to obtain their soluble derivatives. There are four conventional spinning methods: wet, dry, from melt and from gel. In the case of electrospinning, solution and melt procedures can be applied.

To form an electrically charged jet of polymeric solution or melt, a high-voltage is used; an electrode is placed in the solution/melt, another is attached to the collector [8-12]. The electric field is applied to the capillary tube which contains the polymeric fluid, kept by its own surface tension. When the intensity of the electric field increases, the semi-spherical surface of the fluid from the tip of the capillary is elongated, forming a cone known as the Taylor cone. By increasing the intensity of the electric field, a critical value is reached and the electrostatic repulsion force exceeds the surface tension; in this moment, the electrically charged fluid jet is ejected from the tip of the Taylor cone [13-20]. The jet starts a twisting process (during which the solvent is evaporated, or solidified respectively in the case of the melt spinning) leaving behind an electrically charged polymeric nanofiber which is deposited randomly on the collector.

By using the classic melt spinning technology, one can obtain the thinnest fibers with diameters ranging around the minimum value of 0.5microns, two orders greater than the spider silk. The disadvantages of this procedure arise from the following:

- the difficulties that appear while keeping the polymer melt for a sufficient time in the electrospinning area;
- the necessity to recover the solvent and its ecological implications.

An overview of the electrospinning process shows a huge diversity of the technologies for obtaining the nanofibers, and the typologies of structures created through electrospinning. Table 1 shows this diversity [21-30].

The electrospinning process is influenced by a series of technological, structural, environmental parameters [31-35].Among these parameters, the present work investigates the effect of the applied voltage, flow rate and distance between electrodes on the processability of PEI solution in DMAc/tetrahydrofuran 1:1 mixture, obtained through electrospinning technology from solution on equipment with uniaxial delivery, multijet, with needle, with normal atmosphere processing. Obtaining nanofibers from polimeric solutions of polyetherimide is novelty in the field of electrospinning, as very few articles in current literature are tangential to this topic [36-42].

Experimental part

Materials

The materials used in the experiments were the polymer PEI (polyetherimide) with molecular mass M_w = 39000g/mol, and as solvents DMAC/THF (1:1 mixture ratio). PEI has the following favorable characteristics: excellent stability of physical and mechanical properties at high temperatures, due to its high glass transition temperature (217°C); controllable stiffness and resistance up to 200°C; excellent resistance to hydrolysis; lack of physiological activity; very good resistance to high energy radiation (gamma, X-rays and UV); good electrical and dielectric insulation; good chemical and thermal stability; resistance to environment factors [15, 43-47]. Dimethylacetamide used in experiments has the following characteristics:

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* email: manearozemarie@yahoo.com, +40-721-334034
sandu_i03@yahoo.com, +40-744-431709

Table 1
CLASSIFICATION CRITERIA OF ELECTROSPINNING TECHNOLOGIES

	Criterion	Classification
1.	Electrospinning procedure:	
	- electrospinning from solution	a. capillary method (for conductive polymer solutions)
		b. charge injection method (two electrodes sunk into a non-conductive fluid)
	- electrospinning from melt;	
2.	Feeding type:	
	- electrospinning with mono-axial feeding;	
	- electrospinning with coaxial feeding (co-electrospinning);	
3.	Deposition procedure:	
	- monolayer electrospinning	
	- multi-layer electrospinning to produce stratified architectures with hierarchically ordered layers	
	- mixed electrospinning (utilization of different syringes for simultaneous deposition of different polymer solutions on the collecting surface)	
4.	Type of delivery mechanism (pulverization type):	
	- electrospinning with single jet delivery	
	- electrospinning with multi-jet delivery	setting up several syringes on the same support of the feeding pump
		two delivery mechanisms and one collector- delivery of two different polymer solutions resulted from two different delivery mechanisms, equally spaced from the collector, with generation of different electric voltages;
5.	Existence of delivery needles:	
	- electrospinning with needle;	
	- electrospinning without needle – this type of electrospinning eliminates the shortcomings related to syringe needle clogging;	
	• air jacketing	
	• gas jacket (two capillary tubes and saturated gas)	
6.	Polarity generated by the high voltage source: - electrospinning with positive polarity; - electrospinning with negative polarity;	
7.	Processing medium: - electrospinning in normal atmosphere; - electrospinning in inert atmosphere;	
8.	Destination – electrospinning to obtain polymer, ceramic or composite nanolayers for biomedical applications (medical dressings, tissue engineering, artificial organs, drugs, textile carriers for drugs etc.); industrial biotechnologies (filters, protection), aero-spatial applications, chemical finishing treatments, information storage devices, practical applications (insecticides, pesticides, cosmetics), protection clothes, electronics and nanosensors.	
9	Structure of the obtained nanofibers: mono-components, bi-components with different arrangements (shell core, side-by-side, pie-wedge, island in the sea etc.);	
10	Spatial shape of the obtained nanofibers – electrospinning to obtain flat, twiggy, twisted, spiral, tubular (3D) nanofibers; spatial (3D) electrospinning to produce nanofibers: a. fiber in tube, hollow structure; b. Architectures of MPE (extracellular proteic matrices) type; c. deposits resulted through centrifugal electrospinning (centrifugal electrospinning, continuous deposits which disrupt from rod, therefore electrospinning without needle); d. hierarchical structures; d. honeycomb structures;	
11	Existence of morphological zones and formations- electrospinning to obtain porous or smooth nanofibers, interior structure within the porous fiber interior through the polymers blends etc.	
12	Nanofibers disposal type on the collector: - ordered disposals (uniaxial or axial disposal); - random deposits; - differentiated, cross-linked deposits etc.	

viscosity 1.956×10^{-3} Pa·s, molar mass 87.12g·mol^{-1}, density 1.156g/mL, melting point 20°C, boiling point 164°C, and the tetrahydrofuran characteristics are: viscosity 0.461×10^{-3} Pa·s, molar mass 72.11g·mol^{-1}, density 1g/mL, melting point 108°C, boiling point 66°C [15, 48-56].

Preparation and characterization of the blend solutions

The polymer solution was made following this procedure [13-15, 43-45, 57-59]:

- the polymer is dried in standard atmosphere (Nuve EV018) at 100°C for 120 min;
- the polymer is dissolved in the solvents blend under magnetic stirring (stirrer Heidolph–MRHei Standard), dissolution time 24h at 50°C.

Next, the polymer solution characteristics, with direct influence on processing and characteristics of electrospun fibers, have been determined, namely: conductivity, viscosity, surface tension and rheological characteristics. Using an Eurotech Chromoservis 510 conductometer a conductivity of the solution equal to 1.18mS/cm was found. The viscosity of polymeric solutions was determined by using the Gemini Rotational 2 Rheometer, and the mean value for zero shear viscosity was of 0.191Pa·s. The surface tension was determined with the Krüss K9 device using the plate method. The average value of the surface tension for the polymer solution of PEI 12% with DMAC/THF (1:1 blend ratio) is 30.3mN/m. The density of the polymer solution was equal to 1300kg/m^3. Rheological characteristics of the polymer solution have been defined by the following terms: shear rate (s^{-1}), shear stress (Pa), viscosity (Pa·s), frequency (Hz), elastic modulus (Pa), viscous modulus (Pa), complex modulus (Pa) [13-15, 43-45, 57-59]. The interdependences between the studied characteristics of the polymer solution are plotted in Figures 1, 2 and 3.

The measurements of the 12%PEI solution in the 1:1 DMA/THF blend show a Newtonian behavior, with a viscosity which is not influenced by the shear rate or frequency. This ideal viscous behaviour of the 12%PEI polymer solution allows the processing through electrospinning in conditions of a stable static process.

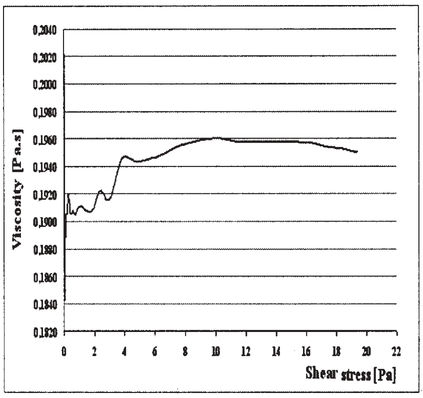

Fig. 1. Shear rate effect on the viscosity of 12 % PEI solution in DMAC/THF

Nanofibers electrospinning equipment

The electrospinning equipment used in these experiments was designed and constructed by our team [48, 49] and it is characterized by a permanent control of the electrospinning process.

In relation with the criteria shown in table 1, this original electrospinning equipment uses a needle (criterion 5), a polymer solution (criterion 1); it has monoaxial feeding (criterion 2), creates a monolayer and a multijet (criteria 3 and 4), and works in normal atmosphere (criterion 7). The equipment has been designed to obtain nanofiber structures that will be later functionalized through electrospraying in order to be used in producing filtering surfaces.

In all the experiment a three-nozzle delivery mechanism and a rotation drum type collecting mechanism have been used. The displacement speed of the nozzle support along the OX direction was automatically set from the command and control mechanism at the value 300mm/s, where the inter-nozzle distance was constant (2.5cm). The displacement of the nozzle support along the OY direction was of 100mm, while it was modified along the OZ direction within the interval 45-130mm, according to the experimental plan. Plastic syringes with diameter of 10mm and volume of 3mL were used during the experiments. The syringes were attached to the capillary tube through a transparent plastic tube; the inner diameter of the needle was 0.2mm.

A metallic smooth rotation drum collector was used to increase the orientation degree of the obtained fibers by increasing the rate of solvent evaporation [2, 23, 27]. It is known that the porosity of the collector influences the density of electrospun nanofibers. A perfect smooth surface determines a high density of fibers because of high evaporation speed of the residual solvents remained on the fiber surface.

The rotation speed of the collecting drum was maintained constant (v = 1000 rpm) during the experiments. The flow rate of the polymer solution Q, mL/min was varied in the range 0.05 - 0.15mL/min, the selected five values being typed directly on the feeding pump display (0.05mL/min, 0.075mL/min, 0.1L/min, 0.15mL/min and 0.2mL/min). The distance D, mm, between needles and collector was varied within the interval 45-130mm, and the individual values were 45mm, 70mm, 100mm, 120mm and 130mm. The voltage U, kV, ranged between 15-35kV (15kV, 20kV, 25kV, 30kV, 35kV), and the electric field strength was maintained within the interval 1.25kV/cm - 7.78kV/cm.

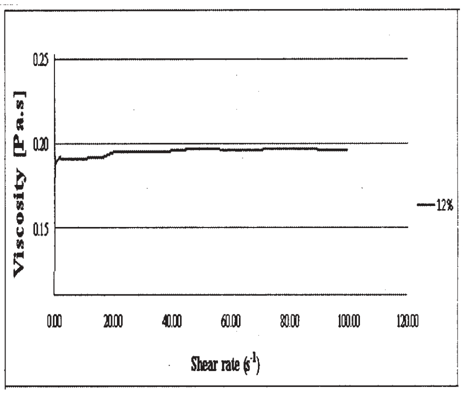

Fig. 2. Shear rate effect on the viscosity of 12 % PEI solution in DMAC/THF

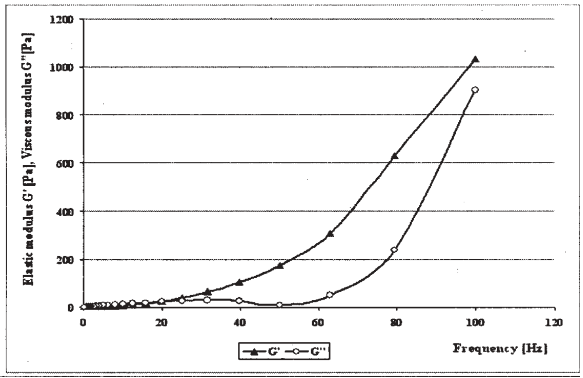

Fig. 3. Frequency effect on viscous modulus and elastic modulus for 12 % PEI solution in DMAC/THF

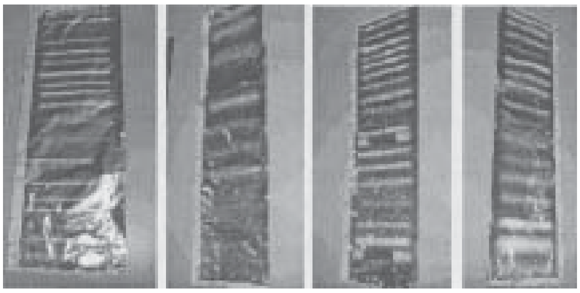

Fig.4. Configuration of 12% PEI/DMA/THF nanofiber on dark paper

According to the experimental plan, at the same level of flow rate Q, the applied voltage U was varied at the five values mentioned above. Also at the same level of U, five values for the distance D have been adopted (total number of technological variants = 100). The technological parameters settings were inputted directly from the command and control unit of the equipment.

All experiments were carried out in specific atmospheric conditions: temperature 20 ± 2°C, relative humidity U = 40% and normal atmospheric pressure. Relative humidity influences the value of fibers diameter, their size, the distribution and shape of their pores. The processing temperature controls the evaporation speed of the solvents, which means it has a great influence upon fibers morphology [2, 23, 27]. These levels for the atmospheric conditions have been chosen considering the destination of the fibers (filtering surfaces) and knowing how these parameters influence fibers characteristics [2, 23].

A wide range of nanofibers was obtained by changing the technological parameters. Figure 4 presents, as an example, a series of determinations sets from the accomplished experiments.

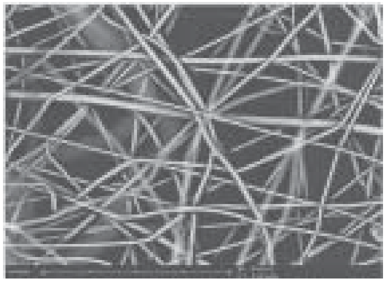

Fig. 5. SEM image of fibers from 12 % PEI solution in DMAC/THF (1:1 ratio), obtained on electrospinning equipment with Q = 0.075mL/min, U = 15kV, D = 45mm

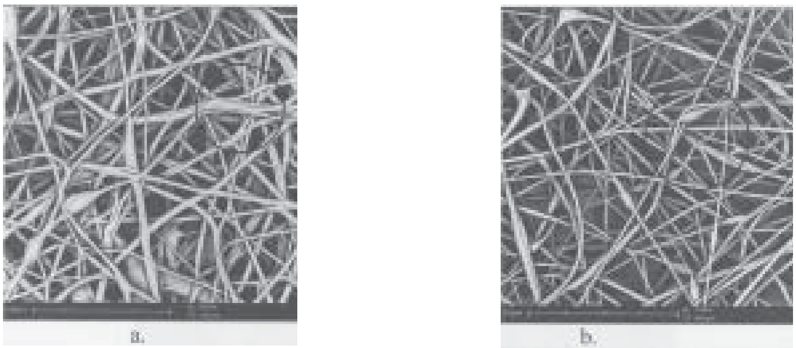

Fig. 6. SEM images for fibers with defects from 12 % PEI solution in DMAC/THF (1:1 ratio), processed on electrospinning equipment at flow rate Q = 0.2mL/min: a.fibers with drops (U = 15kV and D = 100mm); b. linked fibers (U = 15kV and D = 130mm);

Investigation methods

The experimental plan was created in order to study the processability of the PEI polymer solutions. Scanning electron microscopy was used to study the nanofibers obtained through electrospinning (a Phenom G2 pro Desktop SEM was employed) [15].To obtain clear sharp scanning electron microscope images, a Tesla SCD equipment was used to gold plate the fibrous surfaces [15]. Nis-Elements and Lucia software were used to determine the fiber diameter. Over 100 measurements were made at each technological variant and the average fiber diameter (d, nm) was calculated [15].

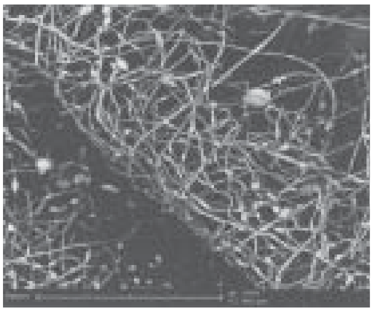

Fig. 7. SEM images for fibers with defects from 12 % PEI solution in DMAC/THF (1:1 ratio), processed on electrospinning equipment at flow rate Q = 0.2mL/min, linked fibers and with drops (U = 35 kV and D = 130mm)

Results and discussions

This study is focused on two aspects the processability of the 12% PEI solution in a mixture of dimethylacetamide/ tetrahydrofuran (DMAC/THF), 1:1 ratio. The diameter of electrospun nanofibers is a very important characteristic because of their technical applications. The main properties of the polymer solution (concentration, electrical conductivity) together with the technological and constructive parameters considered in this study are determinant factors influencing the diameter size and its uniformity.

The average fiber diameter, nm, and standard deviation, nm, were calculated. For each technological variant from the experimental plan, sets of 100 values x_i (determined with Lucia software) were statistically tested using Microsoft Excel application. Fibers with good diameter uniformity (CV less than 20%) and a high uniformity of their disposal on rotating collector were obtained at experimental variants with low voltage (U) and large distance between electrodes (D). The explanation is that a larger distance between the needle and the collecting surface allows the electrostatic field to become more homogenous at low intensity; so the jet is continuous and fibers are more uniform in diameter (fig. 5).

For the analyzed polymer solution it was not possible to produce coherently nanofibers at the flow rate Q = 0.2mL/ min. The resulted fibers had various types of defects (drops or random polymer films on the surface of the layer, linked fibers or fibers with drops, etc.) as shown in figures 6 and 7.

It can be stated that electrospinning of 12% PEI solution in a mixture of dimethylacetamide/ tetrahydrofuran (DMAC/ THF), 1:1 ratio, at a flow rate over the limit of 0.15mL/min is not adequate for obtaining high uniformity fibers.

Rare defects were present when working with other experimental variants too. Their appearance was determined by some correlation problems in the adopted experimental plan (for example, the distance between electrodes vs. voltage). At low distances D (mm), there isn’t enough time for solvent evaporation, and that is why drops are formed on the collecting surface. The deficiency that occurs most often and which is difficult to remove is called beading [2, 23, 60-68]. It appears especially when voltage is low, because the flow rate can be hardly controlled in this case, or when the voltage values overpass a certain limit of processability. At the same time, at low voltage (15kV) the fiber consistency is very poor, so that very few fibers have been collected.

Fibers with defects were obtained when the electrospinning experiments were conducted at high voltage (35kV). The phenomenon can be explained by the fact that raising up voltage beyond a certain limit, the jet instability raised too and drops were formed on fibers.

It was noticed during experiments that the intensity of the created electric field was not enough to form fibers if the distance between needle and collector was set over 120mm and the voltage was lower than (15kV). Fibers defects were present at voltages of 25 and 30kV, no matter the value of the flow rate. For obtaining good fibers diameter uniformity when having a distance D over 120mm it is necessary to apply high voltages (over 20kV).

Conclusions

The present study reveals that a good processability of 12% PEI solution in DMAC/THF mixture (1:1 ratio) depends on the applied voltage, because a low value can determine the appearance of fibers with drops, due to the effect of voltage on the shape of drops formed at the needle tip. By growing the voltage it is seen a decrease of electrospun fibers diameter and of their length as a result of a better elongation of the jet formed by the polymer solution.

The analysis of electrospinning of the 12%PEI solution in DMAC/THF (1:1 ratio) using a computerized equipment, by following an experimental plan, shows that the best results in terms of fibers morphology and uniformity are obtained for U = 20-25kV (maximum 30kV), with a distance between needle and collector D = 70 - 100mm (maximum 120mm). If these limits are exceeded, the fibers diameter becomes irregular and many fibers defects occur. For the above mentioned range, it is considered to obtain a good processability and the stability of electrospinning process (it achieves the minimum energy). Within these intervals, the fibers layers are consistent, the uniformity of the fiber diameter is good and there are only few fiber defects.

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