Study on Behaviour of Polymer Solutions in Electrospinning Technology

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Electrospinning has become during the last few years a promising method for obtaining long and continuous fibers, with nanometer diameters, from a great variety of polymers. The applications range from performant filtering mediums or membranes, to driving sensors or systems, to medical textiles and medicines controlled-delivery to molecular photonics. This work presents polymer solutions with different concentrations of polyetherimide (PEI) in the range 8-14%, ratio 1:1 of dimethylacetamide – tetrahydrofuran (DMA/THF), which were studied taking in consideration the physical characteristics (superficial tension, conductivity and viscosity). These characteristics were analyzed in correlation with electrospinning technology and morphological and structural properties of obtained fibers.

Keywords: electrospinning, nanofibers, polyetherimide, dimethylacetamide/tetrahydrofuran

The electrospinning process, in its simplest form consisted of a pipette (spinneret) to hold the polymer solution, two electrodes and a voltage supply in the kV range [1-5]. Under a high voltage applied to a polymer liquid (solution or melt) charges accumulate on the surface of a droplet of the polymer liquid located at the tip of the pipette, (fig. 1).

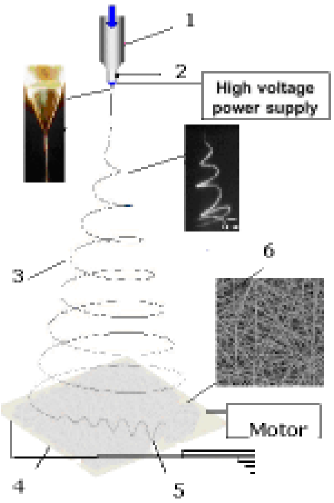

Fig. 1. Diagram of the electrospinning principle from polymeric solution: 1. syringe with polymer solution, 2. pendant drop, 3. envelope cone, 4. collector device, 5. secondary bending instability, 6. fiber mesh

With increasing the voltage the Coulombic repulsion forces destabilize the partially-hemispherical shape of the droplet and a cone-like shape (i.e., Taylor's cone) is formed. At a critical voltage the repulsive force within the charged solution is larger than its surface tension and a jet is erupting from the tip of the pipette. The jet is electrically charged and the charge causes the fibers to bend in such a way that every time the polymer fiber loops, its diameter is reduced. The fiber is collected as a web of fibers (nonwoven mesh) on the surface of a grounded target (collector).

The Taylor cone (fig. 2) is formed in the moment when the electrostatic charge of the polymeric drip equilibrates the surface pressure so that the free surface of the drop takes the form of a cone with an approximately 49.3° angle [2-9].

The voltage increases with every phase up to the moment when equilibrium between the surface stress and the electrostatic force is being obtained (phase 3 in figure 2). As the electrical charge exceeds the surface stress, the fluid is split into small drops. Under the action of straining due to the field of electrostatic forces there appears a dynamics of the deformation of the polymer cone. Subsequently, after the polymeric filament has come out of the cone area in an approximately linear form under the action of the field, the filament is subject to some complex bending stresses, period in which the electrostatic forces stress and thin the jet at especially high ratios [9-12].

Bending instabilities appear which determine the tortuous movement of the jet between the tip of the capillary and the target connected to the mass. These instabilities determine the thinning of the jet under the straining exerted by the electric field, thus the nanofibers

a. phase 1 b. phase 2 c. phase 3

Fig. 2. Forming phases of the Taylor cone [2]

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being formed. The diameter of the jet decreases with 4–5 orders of magnitude due to the high speeds of elongation. The adjustment of the fluid flow and the magnitude of the electric field control the spinning rate. If electrospinning takes place from solutions, then evaporation of the solvent takes place during the movement of the jet to the collector, a fact which determines the solidification of the nanofibers [4-12].

Important features of the polymer solution are on one hand a suitable vapour pressure of the solvent such that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range. It has been shown that high volatility of the solvent leads in general to thicker fibers by faster evaporation and earlier fiber solidification. On the other hand the viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor too small to allow the polymer solution to drain freely from the pipette. Several studies show that an increase in the concentration of the polymer solution, which is related to both viscosity and surface tension, leads to an increase in fiber diameter and reduced bead formation [13, 14].

From device point of view, the applied voltage should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette. Also, the distance between the pipette and grounded surface should not be too small to create sparks between the electrodes but large enough for the solvent to evaporate in time for the fibers to form [15-18]. It was shown that thinner fibers are formed by increasing the voltage and the distance between the pipette and the collector [19-22]. Many other parameters have been studied however, their exact effect on the electrospinning process has yet to be fully understood.

This work presents polymer solutions with different concentrations of polyetherimide (PEI) in the range 8-14%, ratio 1:1 of dimethylacetamide – tetrahydrofuran (DMA/THF) which have been characterized from the visco dynamic and rheological properties point of view.

Experimental part

Materials

Polyetherimide (abbreviated PEI and commercial name ULTEM) is synthesized through nucleophilic substitution of disodium salt of bisphenol A at aromatic nucleus 1,3-bis(4-nitroftalimido)benzene [22]. The chemical reactions are presented in figure 3. The polymerization takes place at temperatures between 80 and 130°C in polar solvents (methyl pyrrolidone and dimethylacetate).

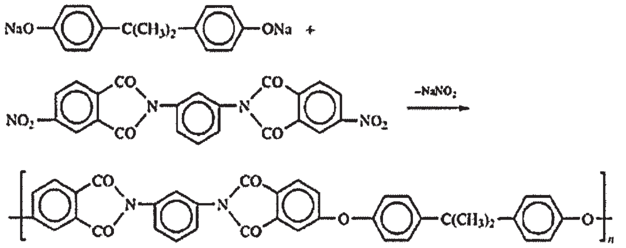

Fig. 3. Chemical reactions for obtaining polyetherimide [2]

Polyetherimide is an amorphous thermoplastic with very good physical and electrical insulation properties, having the following characteristics: molecular weight M_w = 39000g/mol; high long-term heat resistance exhibiting a glass transition temperature (Tg) of 217°C; tensile strength up to 200°C; tensile strength 105MPa; elongation 60%; compressive strength 150MPa; hardness Rockwell 109; Poisson raport 0.36; dielectric stiffness 27kV/mm; dielectric constant 3.15; surface resistivity is higher than 13Ω; specify weight 1.27N/m^2; contraction coefficient 0.007; water absorption 0.25 - 1.25%.

Dimethylacetamide (DMA) is the organic compound which is commonly used as a polar solvent in organic chemistry. DMA is miscible with most solvents, although it is poorly soluble in aliphatic hydrocarbons [23]. DMA used in these experiments has the following characteristics: molar mass 87.12g mol^{-1}, density 0.94g/cm^3, specific gravity 0.94, boiling point 164-166°C, melting point -20°C.

Tetrahydrofuran is a colorless, water-miscible organic liquid with low viscosity at standard temperature and pressure [23]. THF used in our experiments has the following characteristics: molar mass 72.11g/mol; density 0.8892 g/cm^3, viscosity 0.48cP at 25°C; solubility - miscible in water; melting point -108°C; vapor density (Air = 1) 2.5; evaporation rate 8.0.

Preparation and Characterization of the Blend Solutions

Preparation of polymer solution

To be used in our experiments, PEI was dried during 2 h at 100°C inside a vacuum owen. Then it was added into the mixture of solvents DMA/THF proportion rate 1:1, PEI having concentrations between 8-14%. The polymer solutions were prepared by dissolving the PEI in pure solvents or solvent mixtures under intensive stirring at elevated temperature (up to 50°C) for 24 h. There were obtained polymer solutions with different PEI concentrations.

Characterization of the Blend Solutions

For PEI solutions with concentrations between 8 and 14%, rate DMA/THF 1:1, main characteristics were determined because they have direct influence on electrospinning process and fibers morphology, respectively: superficial tension, conductivity and viscosity.

Superficial tension at the polymer solution – air interface is the result of interaction between molecules from the free surface and those placed inside the fluid. The outside molecules are attracted to the fluid inside that is why appears a tense pellicle formed by molecules. The superficial tension of a polymer solution determines the limits (upper and lower) of the electrospinning process capability field when all other variables are maintained constant. By reducing superficial tension there are avoided the hidroelectrodinamic instability phenomena for delivered jets which will eliminate the drops formation on the collector surface [8, 9, 23-28]. Despite that, a lower value of a solvent superficial tension is not always optimum for allowing the electrospinning process for the solution. The determination of the surface tension of the PEI/DMA/THF polymer solutions was done by using the plate method on the Krüss K9 equipment. This method involves placing the plate in the polymer solution in two stages: firstly, the plate is half introduced in the solution; secondly, the plate is raised so its end will touch only the upper level of the solution.

Conductivity of solution is another characteristic that influences electrospinning. A high value determines:

- decreasing the Rayleigh instability and increasing the “whipping” instability [8, 9];
- increasing the possibility of jet separation and solidification which allows the obtaining of fine fibers with good uniformity and less defects [23, 27-34].

A very low conductivity value determines an insufficient jet elongation [35-37]. There are methods of increasing polymer solutions conductivity through pH modification or salin effect (electrolytic), through salt adding [37-39]. The polymer solutions conductivity has been practically determined with the Eurotech Chromoservis 510 conductometer.

The rheological characteristics of polymer solution.

Polymer nature and characteristics influence the rheological behaviour of the polymer solution through: molecular mass, shape and arrangement of macromolecules, and polymer-solvent interactions. The high volume of polymer solution macromolecules depends on: polymer structural parameters (chain length, elasticity, polymer-solvent interactions), associations/ rejections which appear between macromolecules, solution concentration, molecular mass, temperature and deformation velocity. The following terms can be defined: shear stress, shear strain, shear velocity and shear rate (fig. 4).

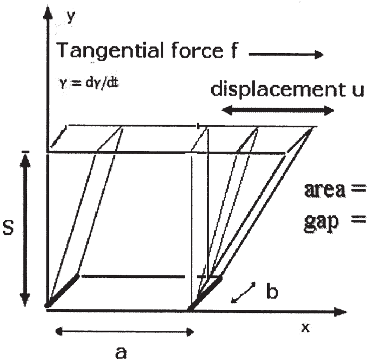

Fig. 4. Shear Rheometry

Shear stress τ(Pa) is computed as a ratio between force F(N) that actions upon the surface A(m^2), $\tau = F/A$ or $\tau = Fta/A$(Pa). *Shear strain* is computed as $\gamma = u/S$, where *u* is the length of horizontal movement and S is height of retangle. *Shear rate* is $\gamma^* = dY/dt = dv/Y$ (s^{-1}) [23].

Polymer solution viscosity measures the flowing resistance of the fluid and it is controlled through the value of polymer concentration [40-47]. *Shear viscosity* (flow resistance of a sample*)* $\eta = \tau/\gamma^*$ and depends on: shear rate, physico-chemical structure of the sample, time, pressure, and temperature. Viscosity value greatly influences electrospinning of polymer solution, this means the diameter and the morphology of electrospinned nanofibers [48-50]. A high value of viscosity shows a high polymer concentration that allows the obtaining fibers with high fineness, but a value greater than a certain limit stops the jets formation because the drops dry before the jets initiation [51, 52]. A too low value of viscosity determines the phenomena called electrospraying that means the formation of polymer drops (like beads).

Table 1

CHARACTERISTICS OF PEI SOLUTIONS 8-14%

Sample	Zero shear viscosity (Pas)	Conductivity (mS/cm)	Surface tension (mN/m)
P8	0.032	1.24	30.8
P10	0.048	1.20	31.0
P12	0.191	1.18	30.3
P14	0.281	1.17	31.2

Viscosity of solutions PEI and (DMA/THF) polymeric solution has been measured by using the Gemnini Rotational 2 Rheometer with two functions of this equipment: *viscometry* (determines zero shear viscosity of solutions, behaviour of viscosity under shearing) and *oscillation* (gives the value of complex modulus, viscous modulus, elastic modulus).

Tests made in the oscillation shearing conditions describe the tested material internal structure and allow the determination of limits for the viscoelasticity domain; by using these tests there can be computed:

a. Complex modulus G* (gives the stiffness of a sample);

b. Storage modulus G'(signify elastic storage of energy);

c. Loss modulus G" (signify viscous dissipation - loss);

d. Phase shift, δ (ratio of elastic/viscous between 0° to 90°C).

These oscillation tests can be achieved as scanning tests of amplitude or frequency.

Results and discussions

The measured values of superficial tension, conductivities, viscosities for polymer solutions are shown in table 1 where P8... P14 represents the samples of polymer solutions with concentrations between 8 and 14% PEI [5, 23].

The structural and technological design of fibers from PEI 8-14% with 1:1 ratio DMA/THF requires the rheological characteristics determination for processed polymer solutions. Figure 5 puts in evidence the influence of shear velocity on polymer solutions viscosity. It is shown that solutions with 8%, 10% and 12% PEI concentrations have a newtonian behaviour, and the solution with 14% PEI concentration has an almost pseudoplastic behaviour.

The correlation between shear stress and shear velocity shows that polymer solutions with 8-14% PEI and ratio 1:1 DMA/THF have an ideal viscous behaviour, their diagram being linear (fig. 6).

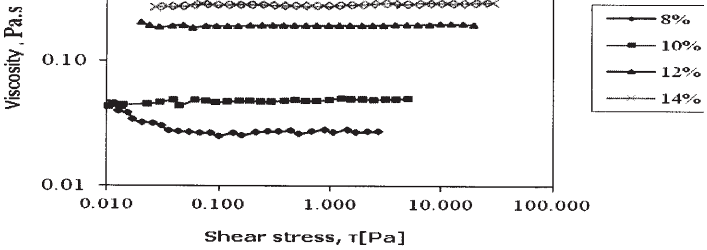

Fig. 5. The correlation between viscosity and shear for polymer solutions with 8-14% PEI and DMA/THF 1:1

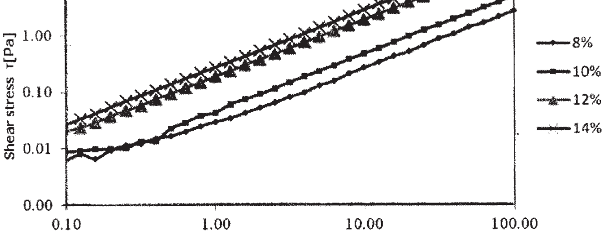

Fig. 6. The correlation between shear stress and shear velocity for solutions with 8-14% PEI and ratio 1:1 DMA/THF

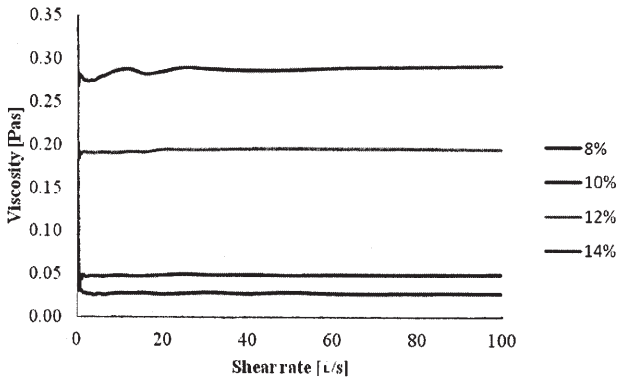

Fig. 7. The dependence of polymer solutions viscosity vs. shear rate

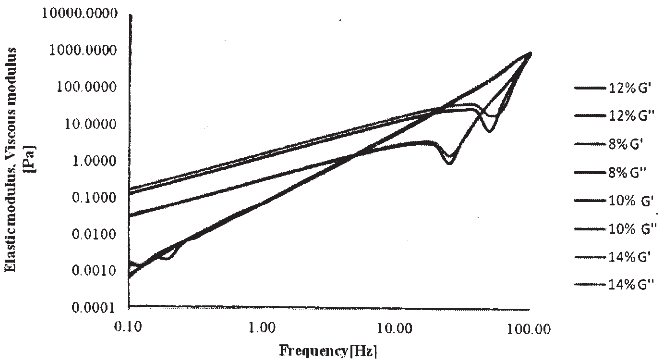

Fig. 8. The dependence of elastic modulus, viscous modulus vs. frequency

Table 2

SCANNING TESTS FOR SOLUTIONS WITH 8-14% PEI AND 1:1 RATIO DMA/THF

Characteristics		Polymer concentration (%)			
		8	10	12	14
Amplitude scanning G'= G"	τ, (Pa)	0.05	0.09	0.09	0.11
	G' = G", (Pa)	1.58	1.64	23.13	34.47
Frequency scanning G'= G"	f, (Hz)	5.01	5.01	19.95	19.95
	G' = G", (Pa)	1.58	1.65	23.13	29.53

Amplitude scanning allows the determination of limits for viscous-elastic domain. Between these limits the sample can be reversible deformed but outside these limits the sample loses its predominant solid character. Elastic modulus G' is specific for gel state. If this modulus has upper values than plastic modulus G" the energy necessary for material deformation is stored and can be later used for bringing the material to the initial shape after the stress removal.

Frequency scanning tests are used for determination of bonds types from the material inside and their intensity. These tests allow the calculation of elastic modulus, plasticity modulus and complex viscosity (material viscosity depending on oscillation frequency). Also long term behaviour (at low frequencies) or short term behaviour (at high frequencies) can be determined. Amplitude scanning can be accomplished taking into consideration shear stress or applied deformation, but into both cases frequency is maintained constant. The shear rate dependent on the solution's viscosity was determined. The results are shown in figure 7.

Figure 8 shows the dependence of elastic modulus, viscous modulus vs. frequency.

For polymer solutions with 8-14% PEI and 1:1 ratio DMA/THF there were determined the values of intersection points between accumulation and loss modulus and viscosity vs. shear frequency. The shear stress value (deformation) for this phenomenon – going from liquid state (predominantly viscous) to gel state (predominantly plastic) – increases directly proportional with polymer concentration in the polymer solution. The same phenomenon can be noticed in the case of frequency scanning tests (table 2).

Figure 9 shows the correlation between viscosity and frequency for polymer solutions with 8-14% PEI and DMA/THF 1:1.

The viscosity of polymer solutions with 12% and 14% PEI puts them into newtonian materials category with a viscosity which is not influenced by shear velocity or shear frequency. Polymer solutions with 8% and 10% PEI have an expanding behaviour.

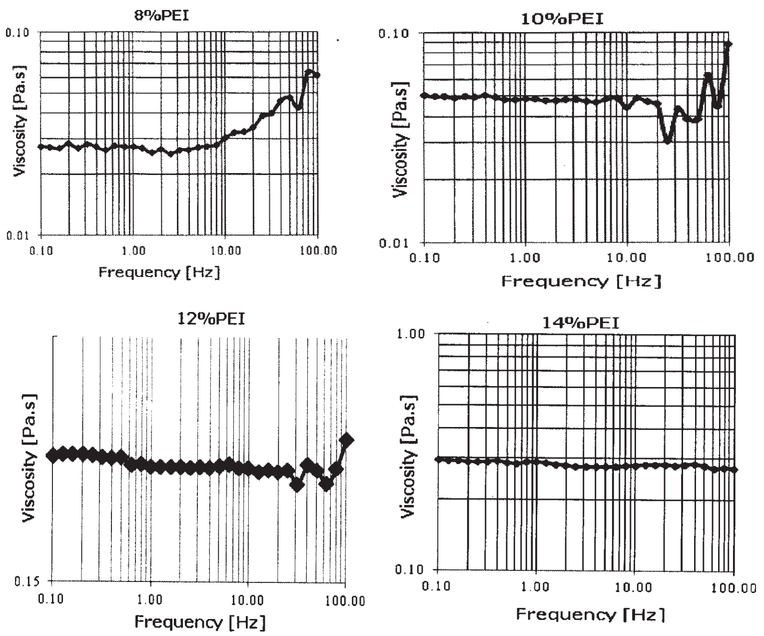

Fig. 9. The correlation between viscosity and frequency for solutions with 8-14% PEI

Conclusions

There were studied superficial tension, conductivity, viscosity, rheological characteristics of polymer solutions, and depending on their values it will be selected the optimum value for polymer solution concentration that will be processed by electrospinning equipment for obtaining nanofibers. The experiments allow us to formulate the following conclusions:

- the increasing of PEI concentration in polymer solutions is directly proportional with solutions viscosity;
- the increasing of PEI concentration in polymer solutions leads to the decrease of conductivity for these solutions;
- the increasing of PEI concentration in polymer solutions does not influence the values of surface tension;
- the studied polymer solutions have an ideal viscous behaviour which allows the processing through electrospinning, in the conditions of a stable static process.

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