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Komarek, Michal, Martinova, Lenka and Lin, Tong 2009, Formation of multiple taylor cones on the free liquid surface during melt-electrospinning, in *AUTEX 2009 : World Textile Conference*, Ege University, Izmir, Turkey, pp. 1-7.

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FORMATION OF MULTIPLE TAYLOR CONES ON THE FREE LIQUID SURFACE DURING MELT-ELECTROSPINNING

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ABSTRACT

In this work, we have studied needleless melt-electrospinning process to define the influences of material properties and operating parameters on self-organization of Taylor cones from free surface of polymer melts and the resultant fiber diameter and morphology. The formation of multiple Taylor cones from a free fluid surface allows production of numerous fibers at the same time, thus significantly increasing the productivity. This principle was developed and patented by researchers of the Department of Nonwovens at Technical University of Liberec [1], and has been utilized by the Elmarco Co. to develop nanofiber production units (Nanospider™).

During the experiment, a needleless melt-electrospinning apparatus, designed by the Department of Nonwovens, was used. Polymers of different properties were selected as materials, and they were electrospun from the molten state. Parameters such as viscosity and surface tension at different temperatures were measured to define the spinning ability. Influence of ionic additives, e.g. surfactants, on the behavior of polymer melts in the electrostatic field was also examined.

KEYWORDS: Melt-electrospinning, needleless, process parameters, multiple jets, mathematical interpretation.

1. INTRODUCTION TO THE THEORY

For better understanding and prediction of the melt-electrospinning, a theoretical approach was used to analyze the self-organized jets from free liquid surface [2], which allows estimating critical parameters existing in the electrospinning process, such as critical field intensity, dimensionless electrospinning number, critical wavelength and relaxation time. Theory is based on analysis of dispersion law introduced by Landau and Lifshitz [3,4] which simplifies the Euler equation to the form:

$$\nabla \left(\rho \frac{\partial \Phi}{\partial t} + p \right) = 0. \quad (1)$$

Where ρ is the fluid density, Φ is the scalar velocity potential and p is the pressure on the liquid surface consisting of components of hydrostatic pressure p_h , capillary pressure p_c and electrostatic pressure p_e . Electrostatic pressure is proportional to the square of the field strength on the liquid surface, i.e., $p_e = \frac{1}{2} \epsilon E^2$, where ϵ is the permittivity of the ambient gas. The dispersion law for ω^2 is derived as:

$$\omega^2 = (\rho g + \gamma k^2 - \epsilon E_0^2 k) \frac{k}{\rho} \quad (2)$$

Where k is the wave number, g is the gravitational acceleration, E_0 is the field strength and γ is the liquid surface tension.

For dielectric liquids, such as polymer melts, the permittivity in the equation (2) has to be replaced by the relation:

$$\epsilon = \epsilon_0 \frac{(\epsilon_r - 1)}{\epsilon_r (\epsilon_r + 1)} \quad (3)$$

Where ϵ_0 stands for the permittivity of the vacuum and ϵ_r represents relative permittivity of the dielectric liquid. ϵ , going to the equation (2), is the permittivity responsible for decrease of the value of the electrostatic pressure in the case of non-conductive dielectric liquids.

When analyzing the dispersion law, it is important to understand that the positive values of ω^2 are signaling the stability of the natural waves on the liquid surface, so called “running waves”. These waves are characterized by the constant amplitudes and different wave numbers. In that state no Taylor cones are formed. However for the field strengths higher than a critical value (E_c), the ω^2 becomes negative and the wave number k become the function of applied field strength. The minimal value of k is when $k_c = \epsilon E_0^2 / 2\gamma$. At the critical field strength, the surface waves become unstable. The wave amplitude starts to rapidly increase and jets are thus formed. E_c can be expressed as:

$$E_c = \sqrt[4]{4\gamma\rho g / \epsilon^2} \quad (4)$$

In ideal case jets are distributed equidistantly because of the equilibrium of the charge on individual jets. Average distance between jets depends on the intensity of electrostatic field and material parameters with relation:

$$\lambda = 12\pi\gamma / [2\epsilon E^2 + \sqrt{(2\epsilon E^2)^2 - 12\gamma\rho g}] \quad (5)$$

Time needed for self organization of the electric charges on the surface of liquid and creation of the jets after switching on the external electrostatic field is derived as:

$$T = \frac{3}{2K(K\Gamma - 1)} \quad (6)$$

Where K is dimensionless wave number and Γ is so called “electrospinning number” (for definition see [2]).

2. EXPERIMENTAL PART

2.1 Materials

Isotactic polypropylene (PP) with MFR200 and polycaprolactone (PCL) from Aldrich with M_n 10000 were used as received. Surface tension and rheological properties were measured experimentally, permittivity of the polypropylene was measured as a function of temperature and the permittivity of PCL was taken from the literature [ref]. A cationic surfactant dodecyl tri methyl ammonium bromide (DTAB) was added to PP to increase electrospinning ability. The chemical structure of PP, PCL and DTAB are given in Figure 1.

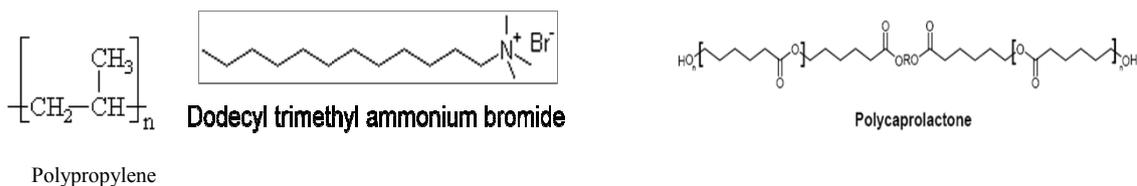


Figure 1. Structures of polypropylene, DTAB and polycaprolactone

2.2 Measuring methods

2.2.1 Surface tension

Several methods for measuring the surface tension of polymer melts have been described in the literature (e.g. maximal bubble pressure method, pending or sessile droplet shape analysis). In this work we used a modified Wilhelmy method to characterize surface properties of polymer melts. The standard setup consists of a digital balance to measure force acting on measuring element, a platinum plate of known dimensions and fluid container. Measured force is expressed with respect to perimeter of the plate in contact with measured liquid. In the modified Wilhelmy method, we used a glass fiber to replace the Pt plate. .



Figure 2. Measuring method for characterization of the surface tension of polymer melts.

2.2.2 Rheology

Although the theory introduced in section 1 assumes that the liquid has no viscosity (because of simplifications needed for expressing the equations of jets formation), it is well known that the rheological properties affect significantly the stretching of the polymer jet in the stable and unstable region of the jet path. In this work we used a Gemini HR nano® rotation/vibration rheometer with parallel plate or cone-plate measuring setup to characterize the flow properties of electrospun polymer melts.



Figure 3. Rotation/vibration rheometer for characterization of flow properties of polymer melts.

2.2.3 Real intensity of the electrostatic field

The real intensity of electrostatic field was calculated for given geometry of emitting electrode and collector, and critical electrostatic potential between electrodes using modeling software ANSYS 10.0.

2.3 Melt electrospinning

Melt electrospinning was performed on a needleless melt electrospinning device designed at the Department of Nonwovens TUL, which allows to control the temperature of polymer melt, the spinning distance between and collector and the applied voltage (Fig. 4). The Taylor cones on the electrospinning device are formed on the free surface of polymer melt and the characteristic inter jet distance (wavelength) is influenced by the parameters of electrospun polymer and intensity of electric field at the point of jet formation.

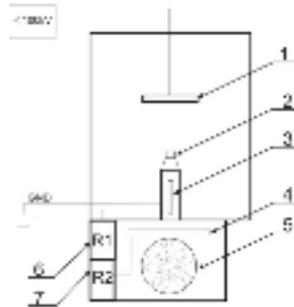


Figure 4. Description of melt-electrospinning apparatus:

1 – Metal plate collector, 2 - Heated electrode, 3 – Cartridge heater, 4 - Heating of the air, 5 – Ventilation blower, 6 – Temperature regulator of heated electrode, 7 – Temperature regulator of air heating.

3. RESULTS AND DISCUSSION

3.1 Surface tension

The modified Wilhelmy method is a versatile technique to measure indirectly either the surface (wetting) tension of polymer melts or the contact angle at the solid-polymer melt interface. The advantages of the modification are that the density of polymer melt is not needed to calculate the surface tension. Since the thermal extensibility of glass is much smaller than that of platinum, the errors from the changes of measuring element dimensions due to high temperatures are negligible.

The surface tension of PP was measured to be 22.1 ± 0.3 mN/m at 230°C , and the value for PCL at electrospinning processing temperature 180°C was 34.2 ± 0.4 mN/m.

3.2. Rheology properties

Although the theory introduced in section 1 is not viscosity related, the viscosity of polymer melt does affect significantly the fiber stretching. The viscosity of polymer was measured to understand how this property influences the electrospinning ability.

Dependency of viscosity on the shear rate measured for PCL at 180°C and PP at 230°C is shown in Fig 5. Both polymer showed almost perfect Newtonian behavior (in the range approximately 1 to 100 1/s), which is unusual for polymer melts. This behavior can be dedicated for relatively low molecular weight of the polymers and associated low entanglements among the polymer chains in the melt state.

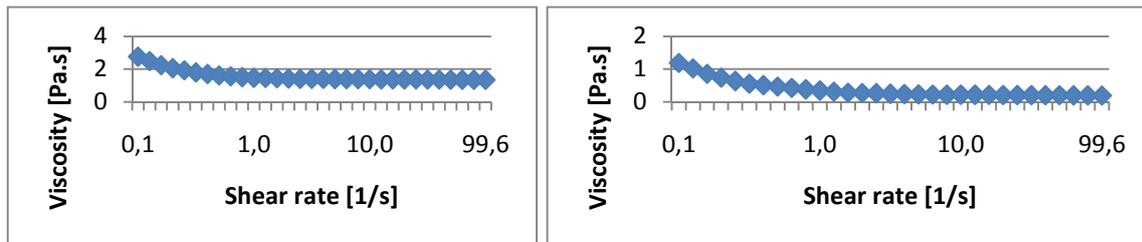


Figure 5. Shear rate dependence of viscosity for PCL at 180°C and PP at 230°C .

3.3 Melt-electrospinning

It was shown that both polycaprolactone and polypropylene can be melt-electrospun into nanofibers. Generally PCL formed better quality fibers with respect to mean fiber diameter and uniformity (see Fig. 7). However bead defects were observed in the majority of prepared samples. Attempts to improve quality of polypropylene fibers by addition of surfactant additive is described in subsection 3.5.

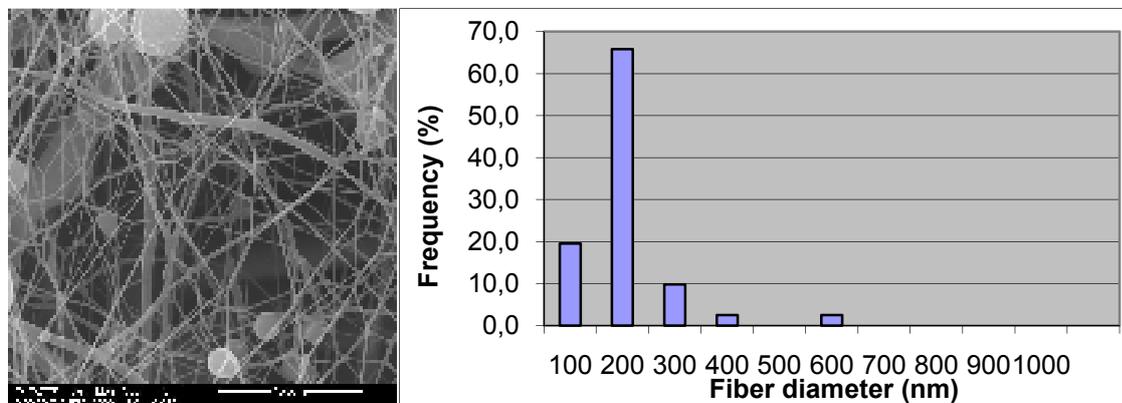


Figure 7. SEM and Distribution of fiber diameters for PCL melt-electrospun nanofibers

In accordance with the theoretical presumptions it was demonstrated experimentally that the critical intensity of electrostatic field depended on the surface tension of the liquid, thus liquids with higher surface tension require higher field intensity for formation of jets. With further increasing of the electrostatic field intensity the characteristic inter-jet distance decreases as more jets are produced. This phenomenon is depicted in Fig. 8 and it is valid for both polar and non-polar polymers.

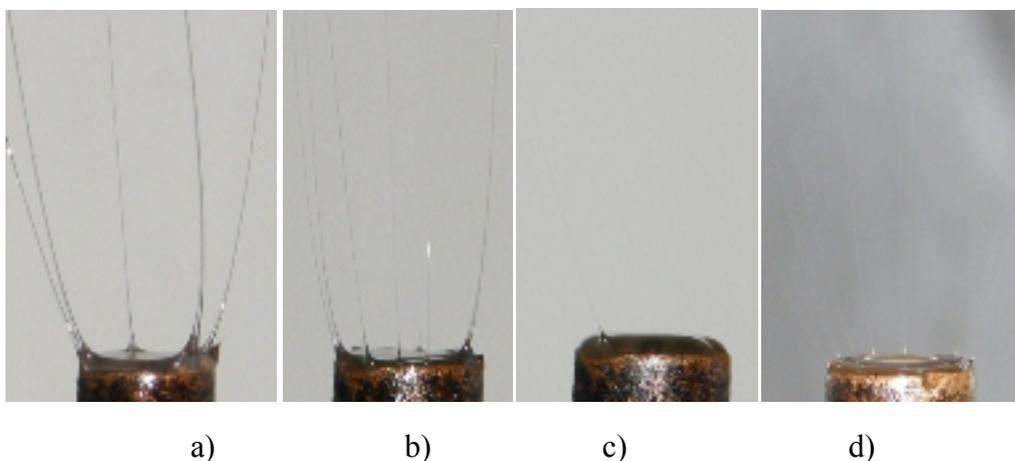


Figure 8. Comparison of different modes of surface melt-electrospinning,

a) PP 2,1 kV/cm, b) PP 2,91 kV/cm, c) single jet of PCL at $E_c = 2,18$ kV/cm, d) multiple jets from PCL at 2,47 kV/cm.

Equations (4), (5) and (6) from chapter 1 calculated for polypropylene show values $E_c = 1,66 \cdot 10^6 \text{ Vm}^{-1}$, $\lambda_c = 2,54 \cdot 10^{-2} \text{ m}$ and $T = 0,21$, which is in good agreement with experimental observations as the experimental $E_c = 1,69 \cdot 10^6 \text{ Vm}^{-1}$ and experimental $\lambda_c = 1,57 \cdot 10^{-2} \text{ m}$.

3.4 Effect of surfactant

It was shown that the addition of DTAB to polypropylene for melt-electrospinning resulted in a considerable decrease in fiber diameter, from tens of microns to submicrons, and the DTAB concentration affected both fiber diameter and morphology. An optimum of concentration of DTAB can be found with respect to the mean diameter of fibres. Further increasing of the DTAB concentration led to formation of beads (see Fig.9).

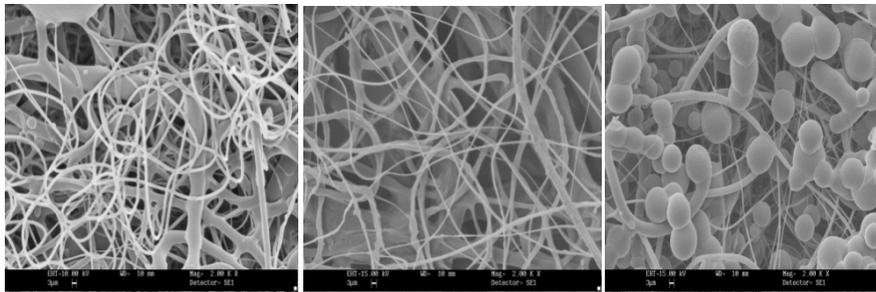


Figure 9. SEM of polypropylene fibers melt-electrospun with (DTAB). (The DTAB concentration was 1, 2 and 3% w/w, respectively, from the left)

4. CONCLUSION

In this work, both polar (PCL) and non-polar (PP) polymers were successfully melt electrospun to form nanofiber nonwoven layers. It was shown that for both polymers the critical intensity of the electrostatic field E_c depended on the surface tension of the molten polymer at given temperature, and further increasing of the electrostatic field intensity led to decrease of the inter-jet distance, thus increasing the number of the jets. It was found that fiber diameter and morphology were affected by an ionic surfactant and its concentration.

5. REFERENCES

1. Jirsák O., Sanetník F., Lukáš D., Kotek V., Martinová L., Chaloupek J., *CZ Patent*, 294274 (B6), WO 2005024101 (2005), A Method of nanofibers production from polymer solution using electrostatic spinning and a device for carrying out the method
2. Lukas D., Sarkar A., Pokorny P. “*Self-organization of jets in electrospinning from free liquid surface: A generalized approach*”, *J. Appl. Phys.* 103, 084309 (2008); DOI:10.1063/1.2907967
3. L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, 2nd ed. Butterworth-Heinemann, Oxford, 1984.
4. L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, 2nd ed., Butterworth-Heinemann, Oxford, 1987.

ACKNOWLEDGEMENT:

This work was supported by MSMT 1M 0554 of Czech Republic, Australian Research Council (ARC, DP0985364, LP0776751) and Deakin University under centre research grant scheme. Author would like to thank Prof. Xungai Wang² for his kind support to the experimental works.