Review
of dissertation thesis
"The Role of Rheological Properties of Polymer Solutions in Needleless Electrostatic Spinning"

by DAO Anh Tuan

The thesis consists of 114 pages including literature references and attachments with experimental data. It is structured into 6 chapters.

Chapter 1 gives a good historical introduction into electrospinning method of production of fine fibers and nanofibers. The principles of both needle and needle-less electrospinning are described. Possible applications of electrospun nanofibers are introduced. The most important part of the chapter is the formulation of the aim of the work, where the reasons for this study are explained. In this section, I would appreciate a little more structured description of main goals; however, the objectives are set clearly in Chapter 2, page 43-44.

Chapter 2 (Theoretical part) is focused on all important aspects necessary to understand electrospinning process. In this chapter, I value most part 2.1 "Rheological properties of macromolecule solutions", which gives a very good theoretical background for subsequent choice of suitable parameters of the polymer solutions to be studied in relation to the electrospinning process. On the other hand, the electrospinning process theory itself is focused mostly on needle electrospinning (part 2.2), but there is just a very limited theoretical background on needle-less electrospinning phenomenon. Author is aware about some publications on this topic (Reference150). Rheological characteristics of PVA solutions are discussed in detail, which is very necessary for the experimental part of the work, as the PVA is the only polymer solution system studied here.

Main effort in Chapter 3 is dedicated to the choice and definitions of independent and dependent parameters for the experimental part of the work, which is the core of the thesis. In this effort, the author is very systematic; he introduced several new useful parameters (values), e.g. Density of cones (D), Life time of jets, Spinning performance per cone, and Non-fibrous area. I consider the latest parameter to be useful for a laboratory study, but I do not see its future application in the industry (non-fibrous area simply must not exist in a real production).

Chapter 4 (Experimental) describes materials and methods used in the experiments. Author used only one polymer solution system (PVA), which is a good model for quite wide range of technological relationships study, however, there is a lot of experience from academia and industry indicated that a more generalized use of such results is limited. In this context, I recommend for the future work to broaden the polymer family used in similar experiments. This could help not only to generate more complete data useful for industrial technology, but also find out what findings are general, and which ones just specific to the concrete polymer.

Author's approach to the experiments is systematic. The results (Chapter 5) are presented clearly, with appropriate comments. The methods and equipment author used are appropriate. Graphs and tables are easy to understand and follow.

Some of the results just verify already known and published relationships, e.g. fiber diameter vs. solution concentration (page 64), but generally, most of the presented data can be used by industrial engineers for better understanding and technological process control. Again, broader verification on other polymer systems (and perhaps also different spinning electrodes) would provide more credibility of the findings.

In Chapter 6, author discusses the results obtained in the experiments and formulates conclusions. Observed effects of polymer molecular weight, solution concentration, "solvent quality", cross-linking agent content, and solution conductivity on dependent process parameters are compared with some data from the literature and with some general relationships indicated in the theoretical part of the work. In several cases, the predicted influence of rheological parameters of the polymer solution on the process was not proved (e.g. Berry number and number of entanglement). The Conclusions (page 81) are formulated logically. The results are qualitatively summarized, which corresponds to mostly empirical character of the work. I would appreciate at least an attempt to formulate a model describing the studied relationships, which could be very helpful for industrial use.

Concluding notes and recommendations:

1. Author collected extensive and very useful amount of systematic experimental data related to the electrospinning process of PVA.
2. Graphical appearance and language of the work is very good (however, one can find several typos).
3. Similar or simultaneous study with other polymer systems and needle-less electrodes would help to find more general relationships between rheological parameters of the polymer solutions and technology process.
4. The study has empirical character; however, author has shown good understanding of the effects he observed. Does the author see some possible ways/approaches which could lead to some mathematical equations (models) describing the studied process?
5. Can author comment his observations and differences between needle and needle less electrospinning? (Especially in relation to the rheological parameters of the solution).
6. Author has published 8 papers, one in a journal, the rest at well attended international conferences. I consider his publication activities so far to be sufficient prove of his independent scientific ability.
7. The importance of the work for the nanofiber industry is very high. The thesis solved just a part of what the industry would need; however, this is a good start and inspiration for eventual continuation of the research in this direction.

I recommend the thesis for the defense
by the Committee for doctoral dissertations
of the Faculty of Textiles of the Technical University of Liberec.

Liberec, December 16, 2010

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Subject: The opponent report on the dissertation work by ***Ing. Dao Anh Tuan***

"The role of rheological properties of polymeric solutions in needless electrostatic spinning".

The dissertation consists of 114 pages (23 annex pages and CD of data files of a little utilization) and 153 references. The text is written clearly and the author shows a good overview of the concept of the current state of solution problematic, which in the recent years acquired a considerable amount of theoretical work and moreover experimental results revealing the leading position of the university (TUL).

The work is written in English (which gives it the necessary internationalist character, which I do welcome in general), is suitably designed and straightforward readable though the text is somehow demandable to be fully understood in details. At the work I am missing a Czech and English written summary as well as discussion needed on the definition of dissertant personal opinion for the processes optimization, including estimates of the prospects for further development. Combining annotation with the list of symbols, abbreviations and figures is somehow inconvenient as such a listing is usually reserved at the ending position.

At review beginning I have to admit that I am not an expert in the entire field of textiles but I found some resemblance with my experience in the study of freeze-in (quenching) of layers of various materials on the moving surfaces (e.g., of a rotating drum) either forming infinite thin ribbons or separated drops of various shaping. Theoretical basis of material micro- and nano-disintegration is thus factually analogous.

However, in addition to the lack of discussion I would like to note some observing that the literature sometimes shows a difference in the behavior of agglomerating particles controlled by their dimensionality, where for the (apparent) radius $r<10\mu m$ can be used the standard Brownian description, because their speed change turn out to be proportional to their decreasing size while for a yet lower dimensionality $r<0.1\mu m$, where the particle motion become related to the shear stress in the matrix liquid, the Smoluchovsky scheme (Physik. Zeitschr., 1916) appears to be preferable. Both cases can be described in terms of either theory, i.e., within classical and the fractal dimensional diffusion, regarding the fractality of the particles themselves and their "collecting" tendency to mutually agglomerate, particularly with regard to self-similarity of their surfaces. How you could explain it in terms of your polymer "entanglement"?

Let me present some further remarks and inquiries.

What is a factual (easy understandable) meaning of the dimensionless number of electrospinning (Γ) and what is the role of inherent curvatures - when the curvatures (K_1 and K_2) get dissimilar and what it would mean?

What course of viscosity would exhibit a fluid polymer bland (mixture of particles in matrix liquid) assuming two dissimilar (small and large) sizes with enough differentiated dimensions?

The formation of Taylor cones and associated theories should be explained in more details referring to the cone generally observed in a hydrodynamic spray processes from which a jet of charged particles emanates above a certain threshold (voltage). It follows from electrical stability (Rayleigh, Phil. Mag., 1882), electrical discharging (Zaleny, Phys. Rev., 1914) and instability, (Tylor, Math. Phys., 1964) – curiously it appeared in the same time within the theory of dendrite growth by Mullin and Sekerka (J.Appl.Phys., 1964 – could there be any connectivity between thermal and electrical gradients?).

Despite a numerous citations there are many other sources, for example and for further interest

J. F. Mora, "*The Fluid Dynamics of Taylor Cones*" Fluid Mechanics 39 (2007) 217;

J. M. López-Herrera etal "*Coaxial jets generated from electrified Taylor cones: scaling laws*" J. Aerosol Science 34 (2003) 535-552

F. Grossmann, disertace „*Gilbert-Taylor cones and multi-phase electrospinning*" Philipps-Universitat Marburg, 2009 archiv.ub.uni-marburg.de/diss/z2009/0693/pdf/dfg.pdf

J. C. Creasey, etal "*Exploding Taylor cones: electrohydraulic discharge*" arXiv:1010.3316v1 [physics.flu-dyn], Cornell University

E. A. Demekhin etal "*On the existence of Taylor cones in high-frequency alternating electric fields*" Doklady Physics 51 (2006) 64-66

A. Barrero, etal, „*Low and high Reynolds number flows inside Taylor cones*" Phys. Rev. E 58, (1998) 7309–7314

G. Larsen, etal, „*Use of coaxial gas Jackets to stabilize Taylor cones of tile solutions and to induce particle-to-fiber transitions*" Advanced Materials 16 (2004) 69,

Within the preparation methods of thin metallic layers and/or consequently disintegrated grains, an important role is played by the worth of cylinder surface, particularly the roughness of the rotating face. Would it have any meaning to artificially facade the surface of the revolving cylinder for better fibers nanospinning?

What an additional role could be played by additional assuming the dielectric properties of polymeric macromolecules?

Curious character is the self-organization of electrospinned jets (Lukas etal, J.Appl.Phys. 2008). It may be related to the early idea of Maupertuis (Oevres de Maupertuis, Paris 1768) as applied to recent repetitive systems by Mareš etal (J. Chem. Phys., 2004) connecting particle mass, speed and distance (self-organized wave-length) by an universal constant (h). How could be electrospinning incorporated in this schema assuming the crucialily of surface tension and capillarity?

Within the dissertation there is no acute handling of thermal/temperature gradients, would it be possible to account them in the case of the evolved ΔH during the solvent evaporation and/or melt solidification?

In conclusion I am satisfied with the presented text and its scientific and expert contents ranking the dissertation in the standard average of comparable presentations within similar material specializations.

The work meets the requirements for a doctoral thesis specifiled both by the Ministry of Education, Sport and Young (MSMT) and the Technical University in Liberec, and therefore recommending the work for an appropriate support and positive defense realization as well as the dissertant to be granted by a PhD degree.

Best regards,

Yours

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