Solvent System for Steady State Electrospinning of Polyamide 6.6

Sander De Vrieze, Philippe Westbroek, Tamara Van Camp, Karen De Clerck

Department of Textiles, Ghent University, Technologiepark 907, 9052 Gent, Belgium

ABSTRACT: A mixture of formic acid/acetic acid makes it possible to electrospin polyamide 6.6 in steady state conditions. Steady state conditions are essential in nozzle electrospinning to generate a stable process which fabricates reproducible material, permitting industrial upscaling. This study shows that only a limited mixture range of formic acid/acetic acid allows electrospinning of polyamide 6.6 in steady state.

Furthermore, the weight concentration in solution; the tip to collector distance and the flow rate have been changed to control the average diameter of the nanofibres. The average diameter increases by increasing weight concentration in solution, increasing volume fraction of acetic acid in the mixture, increasing tip to collector distance and increasing flow rate. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 837–842, 2010

Key words: nanofibres; electrospinning; steady state

INTRODUCTION

Electrospinning is an interesting process, capable of producing fibres with diameters typically one to two orders of magnitude lower than extrusion and conventional solution-spun fibres.[1] The fibres are spun from a variety of polymer/solvent systems. In addition, the ability to produce highly porous nanofibrous membranes with structural integrity is also an attractive feature of electrospinning.

The concept of electrospinning was invented and patented around 1930.[2] However, the past 15 years, electrospinning experienced a renewed interest, both through academic research as well as in industry. Electrospun materials offer opportunities for medical applications, such as blood vessels,[3] filtration applications,[4] or protective clothing.[5]

A key parameter for successful nozzle electrospinning is the steady state condition. Electrospinning reaches steady state when the amount of polymer that is transported through the needle per time unit equals the amount of polymer that is deposited as nanofibres on the collector per time unit. The second condition for steady state is a continuously stable Taylor cone as a function of time.

Most of the research in electrospinning is performed with a nozzle system. This research is focused on the ability to electrospin a specific polymer solution into a nanofibrous structure. It is, however, commonly performed without giving any indication about the stability or reproducibility of the process. For nozzle electrospinning to become an industrially relevant process, steady state electrospinning is an absolute prerequisite. When electrospinning is in steady state, frequent nozzle set up problems (clogging, droplets, and beads) can be avoided. This allows a long-term stability of the electrospinning, as is needed for industrial upscaled processes.

At present experimental knowledge on steady state electrospinning does not exist. There is, however, some theoretical knowledge of steady state electrospinning.[6] More attention was given to "stable electrospinning," with stable electrospinning being described as electrospinning with a stable jet. This is, however, not the same as steady state electrospinning as the latter also requires a stability in time of the Taylor cone and the resulting nanofibres. For stable electrospinning it is possible to collect reproducible nanofibres, but only for a limited time, before problems like clogging and droplets occur. Moreover, the present knowledge on stable electrospinning is mostly based on a general theoretical modeling.[6–8] Although this is sometimes very relevant and promising, it often does not allow yet accurate predictions for a specific polymer solvent system.

Polyamide 6.6 has already been successfully electrospun in numerous studies.[4,9–14] In most of the research on electrospinning,[4,9–11] formic acid is used as a solvent. In[12,13] m-cresol and HFIP are used as

Correspondence to: S. De Vrieze (sander.devrieze@Ugent.be).

solvents. These very toxic and expensive solvents are, however, rarely used in other studies. In[14] a study on different solvents for electrospinning of polyamide can be found. Sulphuric acid, ethanol, and acetic acid were used as solvents in mixtures with m-cresol and formic acid. However, no in depth study on the stability of the electrospinning can be found in.[14]

The present article focuses on steady state electrospinning of polyamide 6.6, with the steady state being a prerequisite for an industrial relevant nozzle electrospinning. For this purpose a solvent mixture of formic acid and acetic acid is to be used. A broader study on the different process parameters is performed, resulting in the knowledge of the steady state interval and the average diameter of the nanofibres.

EXPERIMENTAL SECTION

Materials

Polyamide 6.6 (PA 6.6, Mw: 3.05×10^4 g mol^{-1}) was supplied from Sigma Aldrich and used as received. Solvents chosen for this research were 98 wt % formic acid and 99.88 wt % acetic acid (Sigma-Aldrich). The solutions for electrospinning were prepared by dissolving PA 6.6 pellets in various formic acid/acetic acid solvent mixtures. The solutions were slightly stirred with a magnetic stir bar for at least 3 h at room temperature.

Equipment

Electrospinning

The nozzle electrospinning setup used is shown in Figure 1. The setup comprises an infusion pump (KD Scientific Syringe Pump Series 100) and a high voltage source (Glassman High Voltage Series EH). A grounded aluminum foil was used as collector. The experiments were conducted at room temperature ($\pm$293 K) and room humidity ($\pm$45 %RH). An 18-G Terumo mixing needle was used to perform the experiments. The needle was directly charged (DC+) from the high voltage source.

SEM analysis

The morphology of the electrospun nanofibres was examined using a scanning electron microscope (Jeol Quanta 200 F FE-SEM) at an accelerating voltage of 20 kV. Prior to SEM analysis, the sample was coated with gold using a sputter coater (Balzers Union SKD 030). The average diameter was determined by taking 50 measurements for one set of parameters.
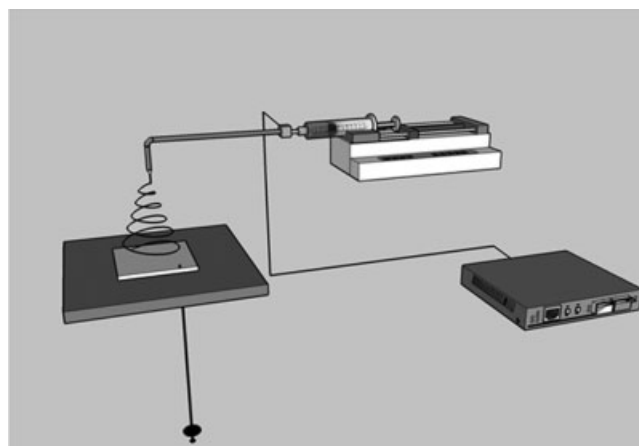
Figure 1 Schematic drawing of the electrospinning setup.

METHOD

The definition of steady state electrospinning as given in the introduction comprises two conditions. The first condition is that in time all the polymer that is spun from the nozzle and collected at the target is converted into nanofibres, including the absence of beads or drops in the structure. This is verified with SEM in this article. The second condition is the stability of the Taylor cone, which needs to be verified visually or with a camera as a function of time. A visual analysis was done till 60 min of continuous electrospinning for the optimal spinning parameter values. The experiments reported in this article all showed steady state for the full duration of the 60 min of the experiments, except for the first start-up minute.

RESULTS AND DISCUSSION

Steady state electrospinning of polyamide 6.6

The optimal steady state parameter values are summarized in Table I for electrospinning PA 6.6 nanofibres from a formic acid/acetic acid solution. In Table I, the applied voltage and the tip-to-collector distance (TCD) are constant at 30 kV and 6 cm, respectively, while the ratio of formic to acetic acid, polymer content (in weight percent) and polymer solution feeding rate are varied in order to obtain a steady state process.

Table I shows that only for a limited combination of process condition (wt % PA 6.6 and volume fraction formic acid/acetic acid) steady state could be established. In the grey and the black region not one combination of the electrospinning parameters could be obtained that resulted in steady state electrospinning of these PA 6.6 mixtures.

As to obtain a solution that can be electrospun in steady state a minimum weight percentage of 10 wt %

TABLE I
Steady State Electrospinning Parameters for the Pa 6.6 Solutions (TCD: 6 cm, Applied Voltage: 30 kV)

wt %	100/0	75/25	66/33	60/40	55/45	50/50	45/55	40/60	33/66	25/75	0/100
					Volume fraction formic acid/acetic acid						
10						3 mL h^{-1}	4 mL h^{-1}	5 mL h^{-1}			
11					3 mL h^{-1}	4 mL h^{-1}	5 mL h^{-1}				
12				2.5 mL h^{-1}	4 mL h^{-1}	5 mL h^{-1}					
13			2.5 mL h^{-1}	3.5 mL h^{-1}	5 mL h^{-1}	6 mL h^{-1}					
14			3 mL h^{-1}	5 mL h^{-1}	6 mL h^{-1}	7.5 mL h^{-1}					
15			3.5 mL h^{-1}	6 mL h^{-1}	7.5 mL h^{-1}						
16			4.5 mL h^{-1}	6.5 mL h^{-1}	8.5 mL h^{-1}						
17			5 mL h^{-1}	7.5 mL h^{-1}							
18			6 mL h^{-1}								
19											
20											

Light grey shading indicates no steady state possible.
Dark grey shading indicates PA 6.6 pellets do not dissolve completely.
The values given in mL h^{-1} indicates ideal flow rate for the above conditions.

PA 6.6 is needed. When a lower wt % is used, only unstable Taylor cones are observed at all the different process parameters. The higher the acetic acid content in the solvent mixture, the lower the solubility of PA 6.6. The black region represents those solvent mixtures where PA 6.6 did not dissolve or dissolves only partially.

The grey region represents solutions with a high percentage of formic acid. These solutions can be electrospun, but not under steady state condition. The Taylor cone will be unstable or droplets will be ejected from the needle. The main reason may be found in the relatively high dielectrical constant of formic acid (57.2 ε_0 at 298 K[15]). Such a high dielectrical constant indicates that formic acid has a high polarity, so when brought into an electrical field it will rearrange its orientation as a function of the intensity and the direction of the electrical field lines.[16] The rearrangement of the orientation of formic acid is position dependent during electrospinning because at each position the electrical field intensity and the formic acid concentration are different. This may explain instabilities which prevent the system from obtaining a steady state condition.

Increasing the fraction of acetic acid shows a clear improvement. From a minimum fraction of 33 vol % a steady state can be obtained when using the right concentration. Possibly, the much lower dielectrical constant of acetic acid (6.6 ε_0 at 298 K[15]) can explain this effect. The presence of acetic acid can reduce the interactions between formic acid and PA 6.6. This can result in new interactions between formic and acetic acid and acetic acid and PA 6.6. On average, the complete system would carry much less polarity, which results in a stability in time. Therefore steady state conditions can be obtained.

The region in Table I stating flow rates of the polymer solution represents the combination of pa-

rameters that result in a steady state condition. The interest is now focused on this specific region where steady state electrospinning is possible. With increasing concentration of PA 6.6 and with increasing acetic acid fraction (Table I), the ideal polymer solution flow rate that results in steady state is higher. This means that one can obtain a much higher production in steady state at the border points.

The ideal solution flow rates increases from 3 to 7.5 mL h^{-1} when looking at the 50/50 solvent mixture between 10 and 14 wt % of PA 6.6. The only difference is actually the amount of polyamide in solution. The explanation of the different ideal flow rate lies in the solvent mixture. In the 14 wt % PA 6.6 solution, much more formic acid will be needed to solve the amide functions. The surrounding solvent mixture contains a higher amount of acetic acid and this gives the solvent mixture a lower dielectric constant. This results in a higher ideal steady state flow for the 14 wt % solution. Also as the wt % in solution is increasing, the limit of solubility is nearer. During electrospinning the solvent is evaporated. When the solubility limit is reached, the fibres solidify. This happens faster for the solutions with 14 wt % of PA 6.6, which allows the flow rate to be higher.

The same effect can be noticed in Table I on the horizontal line. It is to be noted that for a certain wt % of PA 6.6 in solution, e.g. 14 wt % with an increasing acetic acid content in the solvent mixture, a higher ideal flow rate can be obtained. The higher flow rates can be explained by the decrease of the formic acid fraction. As already pointed out, formic acid has a much higher dielectrical constant than acetic acid. The resulting change in interactions is the main cause in the change of the ideal steady state flow rates.
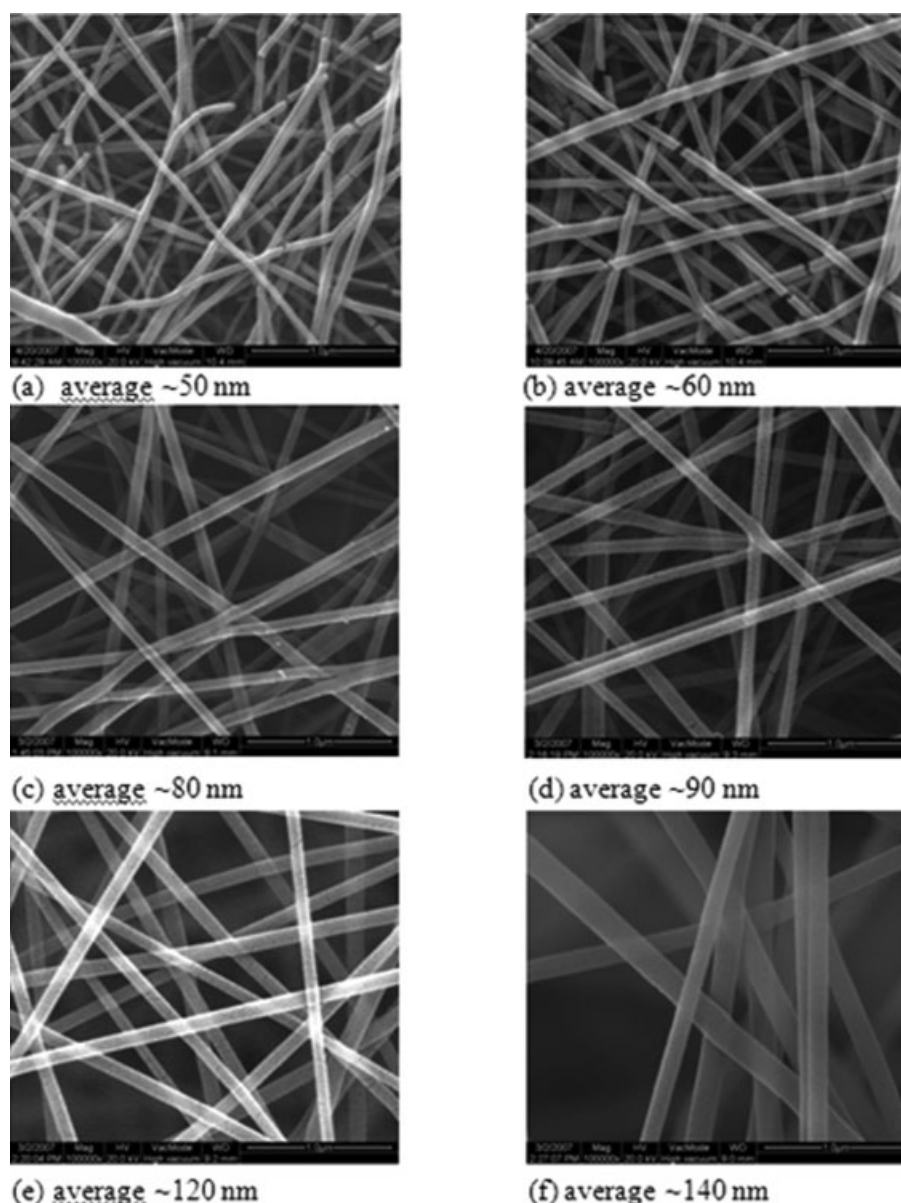
Figure 2 SEM images of PA 6.6 spun out of a 50/50 [vol/vol %] mixture.

Table I illustrates the specific combination of two process parameters: a TCD of 6 cm and an applied voltage of 30 kV. It must be specified that if either of these process parameters changes, the flow rate that results in steady state also changes. For all the solution mixtures that can be spun under steady state conditions, similar findings occur: if the applied voltage is lower, the flow rate that results into steady state will also be lower. If the TCD is higher and the applied voltage stays the same, the flow rate that results in steady state will be lower. Specific case studies follow in section 2.

It is thus shown that formic acid/acetic acid is a suitable solvent mixture for electrospinning PA 6.6 nanofibres under steady state conditions. Having set up the optimal electrospinning parameters to obtain steady state, Table I, the next section will concentrate on the effect of these parameters on the diameter of the obtained nanofibres.

Diameters of pa 6.6 nanofibres

The PA 6.6 nanofibres are shown in SEM pictures in Figure 2. As in this part the isolated influence of the weight concentration on the diameter was looked at, all other parameter values were kept constant. Therefore, no steady state condition could be obtained for the results in Figure 2. It is, however, important to stress that although the production parameter in Figure 2 are not suitable for future

TABLE II
Average Diameter (nm) of PA 6.6 Nanofibres as a Function of PA 6.6 Concentration and Solvent Mixture at a TCD = 6 cm, a Flow Rate = 2 mL h^{-1} and Applied Voltage Adopted to Obtain Steady State

wt %	Volume fraction formic acid/acetic acid		
	60/40	55/45	50/50
10	–	–	65 ± 12
11	–	–	74 ± 15
12	65 ± 15	70 ± 12	88 ± 24
13	78 ± 14	83 ± 13	104 ± 12
14	124 ± 21	136 ± 32	143 ± 29
15	150 ± 36	157 ± 26	–
16	222 ± 60	209 ± 22	–

upscaling, they did allow stable electrospinning (during a limited time) of nanofibres suitable for characterisation as needed here.

For increasing concentration of PA 6.6 in 50/50 formic acid/acetic acid solution the fibres become thicker, Figure 2. For 9 and 10 wt % breaking of the fibres is observed due to a disrupted solidification process. Fang et al. mentioned that when the solvent evaporates too quickly, the solidification process results in the formation of brittle PHVB fibers.[16] In our case, the PA 6.6 solutions have a low viscosity at low concentrations. More splitting occurs during electrospinning, resulting in finer fibres. The finer fibres are more sensitive to deformation or cleavage due to their fineness. Moreover, due to the lower viscosity, the fibre formation is probably only completed very close to the collector plate. This makes the nanofibres again more sensitive to deformations.

In the literature[4] similar findings as in Figure 2 occur when the initial polymer concentration increases, a much higher average diameter is obtained. When looking at the 50/50 mixture, the diameter more than doubles from 10 to 14 wt %. This cannot be solely explained by the increase in wt% in solution.

When the jet is ejected from the Taylor cone, the solvent starts to evaporate. This means that in the case of PA 6.6 the formic acid and acetic acid are removed out of the liquid fraction. Because the vapour pressure of formic acid is higher than the one of acetic acid,[17] formic acid evaporates faster. When the wt % of PA 6.6 is higher, more formic acid is needed to keep the polyamide dissolved. At a certain moment during electrospinning, the jet will reach a critical amount of formic acid that remains in the liquid phase to keep the polyamide dissolved. This will occur in the higher wt % solutions much faster. This results in a faster precipitation of the PA 6.6 and in thicker nanofibres. The polyamide in the lower wt % is kept longer in dissolved form, resulting in a longer time of stretching and/or splaying of

the system and thinner nanofibres. The common explanation for the above results is that the thickness of the nanofibres is dependent on the viscosity of the spinning dope.[18]

To further investigate this, Table II gives some more data for other formic acid/acetic acid mixtures. This time steady state condition was reached by adjusting the applied voltage. Otherwise, no stable nanofibres could be spun for the full range.

Table II shows two separate effects. The first effect is that for the three solvent mixtures a confirmation of the weight concentration effect can be seen. The second effect is that the average diameter is dependent on the ratio formic acid/acetic acid. The average diameter increases with a decreasing amount of formic acid. This effect is less strong then a change in weight concentration, but it can also be explained with the solubility of the polyamide. Because the formic acid content in the 60/40 mixture is higher, the polyamide chains are longer dissolved during electrospinning. A longer stretching can occur, resulting in thinner fibres.

Finally, this agrees with the effect of the dielectric constant of the solvent on the resulting average diameter as described in[19] for PEO fibres with various solvents. In[19] a decrease in average diameter is also described for solvents with a higher dielectric constant. In our case, solutions with a higher content of formic acid have a higher dielectric constant because of the high dielectric constant of formic acid.

Besides the parameters discussed above also other electrospinning processing parameters have an influence on the steady state and the final diameter of the nanofibres. Two main processing parameters are studied: the TCD (tip to collecor distance) and the applied flow rate in electrospinning. These are studied with polymer solutions of 14 wt % PA 6.6 and 50/50 (vol/vol %) formic acid/acetic acid. This solution was chosen as it was most suitable for possible future upscaling. Similar as the results reported in Table II, and in contrast to Figure 2, the applied voltage was changed to obtain steady state, as otherwise no reproducible nanofibres could be produced.

TABLE III
Average Diameter (nm) of PA 6.6 Nanofibres Made From Different Solvent Mixtures and Different TCD's (Solution Concentration: 14 Wt %. Flow Rate: 2 mL h^{-1}, Applied Voltage: Steady State)

TCD (cm)	Volume fraction formic acid/ acetic acid			Electrical field
	60/40	55/45	50/50	
6	124 ± 21	136 ± 32	143 ± 29	3.33 (kV/cm)
7	102 ± 15	124 ± 17	148 ± 20	3.28 (kV/cm)
8	94 ± 14	114 ± 19	115 ± 21	3.25 (kV/cm)
9	91 ± 10	112 ± 23	112 ± 21	3.17 (kV/cm)

TABLE IV
Average Diameter (nm) of PA 6.6 Nanofibres Made From
a 50/50 (vol/vol %) Mixture With 14 Wt % PA 6.6 With
Different Flow Rates (TCD: 6 cm, Applied Voltage:
Steady State)

Flow rate (ml h^{-1})	Average diameter (nm)	Applied voltage (kV)
2	143 ± 29	20
3	131 ± 23	21.5
4	138 ± 31	23
5	128 ± 27	25
6	126 ± 32	26.5
7	118 ± 28	28

The TCD is varied between 6 and 9 cm and the results are shown in Table III. TCD's higher then 9 cm were not considered because very high voltages must be applied for obtaining steady state conditions. For TCD's lower then 6 cm the deposited nanofibres sometimes "rises" from the collector surface, probably due to the fact that the tip of the nozzle is very close to the collector. This effect is disadvantageous and because of the irreproducible character of the effect the TCDs below 6 cm are not further considered. In general, if the TCD increases, the average diameter of the nanofibres decreases. This was also seen in other electrospinning experiments.[20] This is attributed to the change in the electrical field behaviour when changing the TCD. This changes the bending/splitting behaviour of the fibrous jet.

Another remark that must be made with Table III is that the same effect of the solvent mixture takes place. The higher the volume fraction of formic acid, the lower the average diameter.

Another important parameter is the flow rate of the electrospinning process. The flow rate can be varied from 2–7 mL h^{-1} for the (50/50) formic/acetic acid mixture, Table IV. A higher flow rate requires a higher voltage to keep the electrospinning into steady state. The higher voltage here is again needed to obtain the necessary material to obtain the experimental data. It can be seen that the average diameter of the nanofibres decreases with increasing steady state flow rate.

There are actually two opposing mechanisms. When the flow rate is increased, a higher volume of solution is drawn from the needle tip per time unit. This should results in much thicker nanofibres with increasing flow rate. However, an increase in the flow rate implies an increase in applied voltage to maintain the steady state. That increase in voltage results in a change of the electrical field, which is opposing the effect of thicker fibres through effects of bending and splitting. The reason that a decrease of the average nanofibre diameter is observed indicates that the increase in applied voltage determines much more the final average diameter compared with the influence of the increasing flow rate.

CONCLUSIONS

Steady state conditions are important for nozzle electrospinning. They permit electrospinning to become a continuous process. It is possible to electrospin PA 6.6 in steady state with the mixture formic acid/acetic acid. This is, however, limited to mixtures between 66/33 and 40/60 (v/v%) of these chemicals.

The resulting average diameters of the PA 6.6 nanofibres can be controlled with different parameters. Change of the concentration of polymer and the mixture range can change the average diameter of the nanofibres between 65 and 222 nm. An increase in flow rate decreases the average diameter from 143 to 118 nm. An increase in TCD decreases the average fibre diameter to about 80% for different solvent mixtures. All the samples have a very low standard deviation of the average diameter.

Steady state electrospinning gives the possibility for nozzle electrospinning to obtain stable, reproducible material, allowing potential for industrial upscaling of the process.

References

 1. Pedicini, A.; Farris, R. J. Polymer 2003, 44, 6857.
 2. Formhals, A. "Process and apparatus for preparing artificial threads". U.S. Pat. 1,975,504, (1934).
 3. Sell, S. A.; Bowlin, G. L. J Mater Chem 2008, 18, 260.
 4. Li, L.; Frey, M. W., et al. J Eng Fibers Fabrics 2006, 1, 1.
 5. Lee, S.; Obendorf, S. K. Text Res J 2007, 77, 696.
 6. Spivak, A. F.; Dzenis, Y. A., et al. Mech Res Commun 2000, 27, 37.
 7. Spivak, A. F.; Dzenis, Y. A. Electrostatics 1999, 163, 175.
 8. Helgeson, M. E.; Grammatikos, K. N., et al. Polymer 2008, 49, 2924.
 9. Jeong, J. S.; Jeon, S. Y., et al. Diamond Relat Mater 2006, 15, 1839.
10. Dersch, R.; Liu, T. Q., et al. J Polym Sci Part A: Polym Chem 2003, 41, 545.
11. Tan, K.; Obendorf, S. K. J Membr Sci 2007, 305, 287.
12. Han, X. J.; Huang, Z. M., et al. High Perform Polym 2007, 19, 147.
13. Carrizales, C.; Pelfrey, S., et al. Polym Adv Technol 2008, 19, 124.
14. Supaphol, P.; Mit-Uppatham, C., et al. Macromol Mater Eng 2005, 290, 933.
15. John, D.; Lange's Handbook of Chemistry and Physics, 15th edition; 1998 Publisher: McGraw-Hill.
16. Fang, Z. X.; Zhang, L., et al. Acta Polym Sin 2004, 8, 500.
17. Lide, D. CRC Handbook of Chemistry and Physics, 84th ed.; 2003.
18. Kim, K. W.; Lee, K. H., et al. Fibers Polym 2004, 5, 122.
19. Son, W. K.; Youk, J. H., et al. Polymer 2004, 45, 2959.
20. Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. J Appl Phys 2000, 87, 4531.