Milda Adomavičienė,
***Anne Schwarz,**
Sigitas Stanys

Kaunas University of Technology, Faculty of Design and Technologies, Department of Textile Technology,
Studentu Str. 56, LT-51424, Kaunas, Lithuania,
e-mail: milda.adomaviciene@ktu.lt

*** Ghent University, Department of Textiles**
Technologiepark 9
9052 Gent (Zwijnaarde), Belgium
e-mail: Anne.Schwarz@UGent.be

Influence of Liquid Nature on Wetting Behaviour of an Inclined Fibre

Abstract
In a previous publication [3] it was shown that the inclination angle of a fibre being immersed and druwn out from a liquid reservoir (glycerol) influences the development of liquid instability, and consequently the formation of droplets on the fibre. In this paper, further investigation is presented, in which the phenomenon was explored by using another test liquid – polyvinylalcohol (PVA). Here, we verify that the behaviour of liquids on a fibre is influenced by its inclination angle. Furthermore, the results show that the behaviour of a PVA film on an inclined fibre differs from the behaviour of a glycerol film, despite the fact that test conditions were the same.

Key words: *liquid film instability, Rayleigh wavelength, mother-daughter droplet, fibre wetting, wetting behaviour.*

Introduction

This article addresses our previous publication [3], in whichthe instability of a glycerol film on a motionless polyamide 6 fibre after extracting it at varying inclination angles from a liquid reservoir was investigated. It was demonstrated that the inclination angle of the fibre can be described as one of the parameters of the liquid-fibre system that influence the development of liquid film instability.

However, further research was needed to evaluate the influence of the inclination angle on liquid film instability. Thus, we decided to investigate the system using the same fibre, but with another test liquid, in this case (PVA). This polymer is widely applied in the textile sector, for instance fibres are spun from it the using electrospinning technique [1, 2]. Especially in electrospinning, what has to be dealt with is spinning jet instability after the liquid jet emanates from the spinning nozzle (see Figure 1.a). The same happens with a liquid film, which is formed around a cylindrical body, e.g. fibre (see Figure 1.b and 1.c).

The parameters that influence the behaviour of the fibre-liquid system were discussed in [3].

Experimental

As in [3], a polyamide 6 monofilament with a diameter of 200 μm was used for the experimental investigations. The test liquid was 16 % PVA solution.

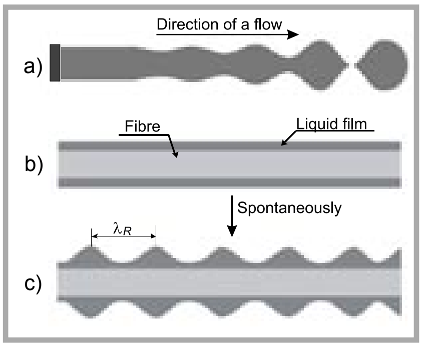

Figure 1. *a) The formation of the instability of the jet [2]. b) and c) The formation of liquid film instability [3].*

To observe the formation of liquid film instability , the experimental set-up used was identical to the previous experiments [3]: the polyamide fibre was unwound from the yarn supply unit, passed through a liquid reservoir containing the test liquid, guided by an inclination angle adjusting system and wound onto a rotating cylinder. Using a stereo microscope, it was possible to capture the fibre-liquid system in the range of 1-2 seconds after it passed out of the liquid reservoir. The speed at which the filament was drawn was 0.003 m/s in order to result in a uniform thin annular film, and to obtain comparable results.

After the fibre was uniformly coated by liquid, the winding unit was stopped and the process of breaking the liquid film into an array of droplets was recorded from a side view. Twenty recordings for each inclination angle were done from a side view with nineteen different inclination angles ranging from 0° to 90° (at an interval of 5°). Liquid was exchanged every 120 minutes in order to prevent changes in viscosity.

Still images were captured from video recordings. Particular images were chosen according to their development stage of instability and interpreted using am image analysis system. Analysis software allowed quantification of the parameters of the liquid-fibre system.

Results and discussion

Instability development of PVA film was observed and the initial film thickness as well as wavelength between neighbouring droplets was measured. Furthermore, characterising the parameters of droplet profile, namely the contact angle, radius of droplet curvature and droplet height were measured. Contact angles and Rayleigh wavelength were also calculated using correspondent equations.

Having captured the moment when the liquid film surrounding the monofilament was still unperturbed, it was possible to measure the initial thickness of the liquid film. Mean values of the initial film thicknesses measured for each inclination angle are specified in the following Table 1.

Starting from an inclination angle of 0°, the initial film thickness increases. The inclination angles of 45° and 90° should be highlighted as the ones that differ quite remarkably from the main tendency. For better visualisation the

Table 1. *Mean values of initial thickness of PVA film. Coefficients of variation range from 6.3 % to 15.41 %.*

Inclination angle, °	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**
Mean value, μm	43 ± 7	50 ± 4	49 ± 7	49 ± 4	51 ± 16	51 ± 12	55 ± 5	50 ± 10	62 ± 9	38 ± 8
Inclination angle, °	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
Mean value, μm	38 ± 8	57 ± 10	58 ± 16	56 ± 8	59 ± 11	60 ± 6	65 ± 15	66 ± 16	75 ± 16	108 ± 12

mean values of each inclination angle are presented in Figure 2.

The linear trendline shows that the initial film thickness increases with increasing inclination angle. In the previous research a critical inclination angle of 50° was identified. In this research the critical angle is 45°, where the initial film thickness (38 μm) is the lowest. Another angle - of 90° - also differs from the main tendency. In this case the initial film thickness is much greater than the others (the same tendency was observed in the previous research [3]).

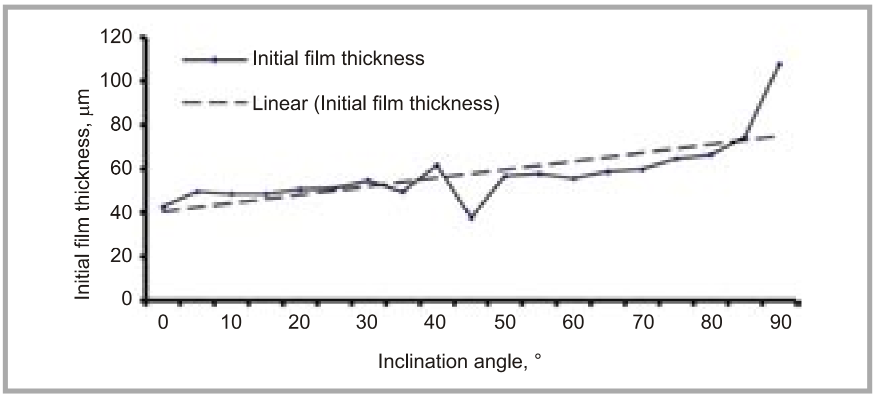

Figure 2. *Initial PVA film thickness.*

As the constant withdrawal rate was ascertained, a conclusion can be made that the initial film thickness is influenced by the inclination angle of the fibre. Further, it might be that the distribution of secondary forces or the chain length of the polymers changes (which influences the viscosity), which conversely influences the initial film thickness [4, 5].

Comparison. Experimentally, it was found that the initial film thickness is significantly greater for PVA than for glycerol; the difference in thickness ranges from 14 μm at 45° up to 71 μm at 90°. This experimental result is in good accordance with theory [4,5]. The initial film thickness depends, among others, on the surface tension of liquid, which, as we measured, is lower for PVA (44.57 mN/m) than for glycerol (63.75 mN/m). As a general rule it can be said the lower the surface tension, the higher the initial film thickness.

Comparing the results presented in [3] and Figure 1.b and 1.c, it should be noted that the slope of the linear trendline is slightly steeper for the initial thickness of PVA films. One reason for this difference might be the different origins of PVA (polymer) and glycerol (trivalent alcohol). This difference may mean that the inclination angle has a greater influence on the initial film thickness of PVA than that of glycerol.

Break-down mechanism. Independently of the inclination angle, it can be observed that the break-down of PVA film proceeds in steps, which are presented in Figure 3. First, in (1), the film covering the fibre is unperturbed. Later the film starts to show small waves (2). The amplitude of the waves increases with time (in (3) and (4)) until the film ruptures (5) and an array of droplets is formed. The droplets are still connected by a thin annular film, seen in (6). Once the droplets are formed, they stay in place and do not move along the fibre.

The reasons for these happenings are the Laplace and the disjoining pressures acting in the liquid film, which were discussed in [3]. Sufficiently far away from the fibre-liquid interface, the disjoining pressure can be neglected, and the solely acting Laplace pressure causes the liquid film at the liquid-air interface to undulate. Finally, droplets are formed that are connected to each other by a thin film in which the disjoining pressure can not be ignored. Hence, the thin film is stable.

Comparison. The glycerol film breaks down into droplets at a much faster rate than a PVA film. One reason for this difference might be the initial film thickness: as a PVA film is generally thicker than a glycerol film, more time is needed for a PVA film to break down. This might be justified with the smaller Laplace pressure acting in a thicker film. Probably, the break-down time is also influenced by the viscosity of the liquid, as PVA is more viscous. The shorter break-down time of glycerol may be partially attributed to its higher surface tension.

It is worth mentioning that the formation of droplets of both PVA and glycerol starts in the part of the fibre-liquid system that was extracted from the liquid reservoir earlier and then proceeds downwards. This confirms the theory of Rayleigh instability, which states that the amplitude of the surface wave increases exponentially with time.

Wavelength. in Table 2 mean values of the distance between neighbouring droplets for the different inclination angles are given. They are calculated from at least 20 measurements for each angle.

The distances between neighbouring droplets were examined immediately after their formation. These measure-

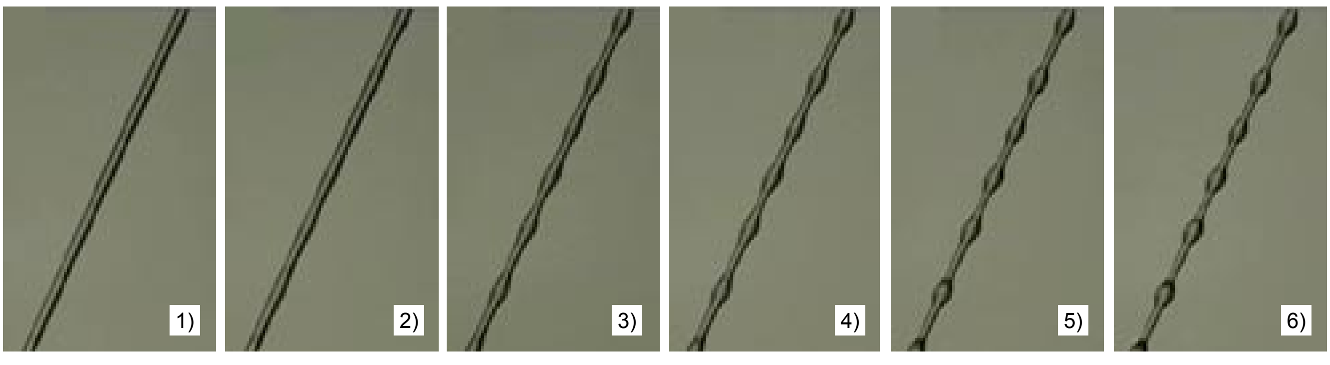

Figure 3. *Development of PVA film instability on polyamide fibre inclined at 70°: pictures (1) – (6) were taken every 0.5 sec.*

Table 2. *Mean values of measured wavelengths of neighbouring PVA droplets residing on fibre. Coefficients of variation varied in the limits of 6.51-18.75 %.*

Inclination angle, °	0	5	10	15	20	25	30	35	40	45
Mean value, μm	1170 ± 162	1803 ± 117	1818 ± 242	1668 ± 225	1673 ± 239	1690 ± 276	1466 ± 275	1559 ± 234	1879 ± 271	1611 ± 232
Inclination angle, °	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
Mean value, μm	1611 ± 232	1974 ± 260	1577 ± 254	1474 ± 189	1642 ± 227	1613 ± 227	1805 ± 219	2083 ± 293	1987 ± 290	2300 ± 354

Table 3. *Calculated values of wavelengths between neighbouring PVA droplets according to Rayleigh´s equation.*

Inclination angle, °	0	5	10	15	20	25	30	35	40	45
Mean value, μm	1278	1400	1400	1466	1389	1368	1400	1371	1446	1228
Inclination angle, °	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
Mean value, μm	1228	1543	1620	1375	1411	1333	1490	1510	1662	1836

ments provide the basis for subsequent calculations.

To examine if the wavelength shows the same tendency when it is calculated, the investigation was confined to Rayleigh´s formula (equation (4) in [3]). In Table 3 the calculated values are presented.

Average values are increase with rising inclination angle, from 1278 μm at 0° to 1836 μm at 90°. According to Rayleigh´s formula, the wavelength is dependant on the initial thickness of the liquid film. Therefore, as the initial film thickness increases, the wavelength is also expected to increase. This, in turn, agrees well with the experimental results.

Alternation of calculated values is more continuous than measured ones. This can be explained by the smaller errors for the initial thicknesses of the PVA film compared to the measured wavelength between PVA droplets.

Measured values at almost all inclination angles are greater than the calculated ones. As in his formula Rayleigh disregarded interactions taking place between the solid body and the liquid, the differences might be attributed to strong interactions between the monofilament and PVA.

Comparison: Figure 4 shows the measured and calculated wavelengths between droplets for both PVA and glycerol.

The trendline of PVA measured wavelength shows increasing distances between droplets with an increase in inclination angle. Whereas in the case of distances measured between glycerol droplets the situation is different.

It is evident that Rayleigh´s formula gives a better approximation to the situation for glycerol than for PVA. This difference might be explained with interactions occurring between the atoms and molecule of the monofilament and of the test liquids. Therefore, the interactions between the fibre and PVA are stronger than between the fibre and glycerol.

For both liquids, the slopes of calculated wavelength versus inclination angle show a better continuity compared to the slopes of measured wavelength.

Mother-daughter droplet arrangement. Visually examining the recordings, it can be reported that at certain inclination angles (5°, 50°, 80°, 85° and 90°) sometimes one daughter droplet appears between two mother droplets (Figure 5).

Inclination angles of 5° and 90° are the most preferred angles for the formation of daughter droplets: a daughter droplet appeared between almost all mother-mother droplets.. For inclination angles of 50°, 80° and 85°, it can be stated that the formation of daughter droplets is apparently lower.

It is striking that the formation of droplets only occurs when the distance between two mother droplets is in the range of 1800 to 2300 μm (see Table 2). Seemingly, there is a critical distance between two neighbouring mother droplets for the development of a daughter droplet between them.

Having observed mother-daughter droplet arrangements formed over a time period of more than 120 seconds, it can be said that the mother droplets first increased in volume and later they tended to flatten. For daughter droplets the case was different - they constantly decreased their volume and there was even the poss-ibility of them disappearing with time. In the case of PVA it was impossible to observe it as the viscosity of the polymer started to increase and the process finally stopped. This process is illustrated in Figure 6: in picture (1) the monofilament with surrounding PVA was captured directly after droplet formation. The situation ten seconds later is depicted in picture (2). It was visible even macroscopically that the mother droplets increased in volume, while the daughter droplets between them and above the upper mother droplet, respectively, decreased in volume.

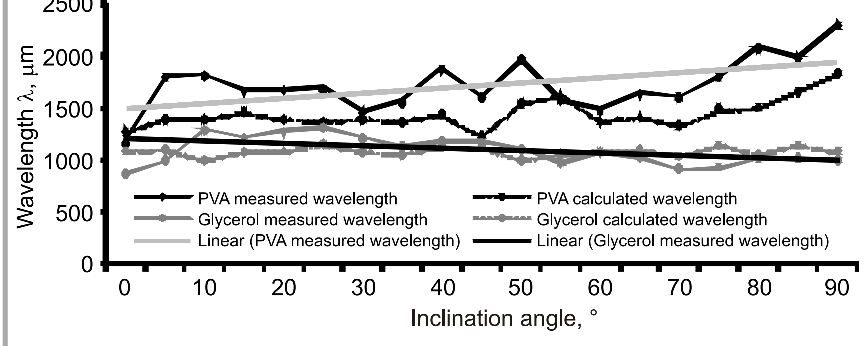

Figure 4. *Comparison of measured and calculated wavelengths between PVA and glycerol droplets.*

Figure 5. *Arrangement of mother and daughter droplets at an inclination angle of 5°.*

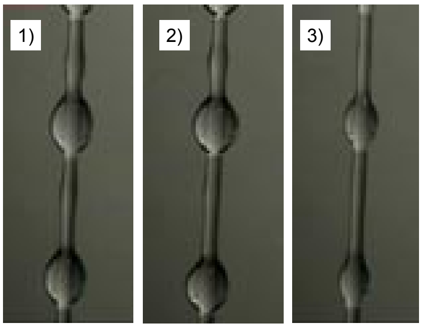

Figure 6. *Representation of droplet flattening as a function of time on the Polyamide filament inclined by 90°.*

This observation is in good accordance with the theoretical background concerning Laplace pressure. According to equation (3) in [3] it is obvious that if we have two fluid droplets of different size, connected by a small channel, the smaller droplet will flow into the bigger one, because the greater the radius of the bubble, the smaller the Laplace pressure will be. The same was found for daughter and mother droplets connected to each other by a macroscopically invisible film. According to Laplace pressure, the internal pressure of the daughter droplet was greater than the internal pressure of the mother droplet, and the daughter drop emptied in the mother drop resulting in a bigger mother droplet.

Observing the same droplets 100 seconds later as in Figure 6 picture (3), it was noticed that the daughter droplets had entirely vanished and the mother droplets had reduced in size. This can be explained with the flow of liquids. Due to gravity, PVA flowed down the fibre.

In the case of glycerol as test liquid, no formation of daughter droplets was observed. The assumption can be made that a critical value for droplet distances lying between 1800 to 2300 µm must be obtained in order that daughter droplets be formed, because, as identified in Figure 6, measured wavelengths between glycerol droplets are significantly smaller than these values.

Radii of curvature. It is evident that the radii of curvature slightly decrease with an increase in inclination angle (see Table 4). This implies that the droplet shape gets slightly rounder and consequently the droplet height should increase to maintain the volume. This investigation is in good accordance with the values of droplet height – their increase was also noticed.

Comparison. In general, the radii of the curvature of PVA and glycerol droplets [3] are approximately the same. The values range from 505 µm to 720 µm for PVA droplets and from 434 µm to 826 µm for glycerol droplets. It was established that the radii decrease more with increasing inclination angle for glycerol than for PVA. It can be said the two test liquids tend to change their droplet profile differently with increasing inclination angle. While glycerol droplets keep their height and reduce their radii of curvature, PVA droplets increase their height and slightly reduce their radii of curvature. Additionally, the internal pressure of glycerol droplets can be assumed to be greater, because the pressure increases with increasing surface tension and decreasing fibre radius, droplet height and radius of curvature.

Contact angle. The results of measured contact angles are presented in Table 5.

Results show that the contact angle rises with the inclination angle. The values that deviate from this tendency can be explained with higher error values. This result is not surprising, as the droplet heights also rise with inclination angle, and the radii of curvature stays approximately the same. Thus, a change in droplet profile is evident with increasing inclination angles.

For the calculation of cos θ, equations derived by Neimark [7] and Bauer and Dietrich [8] (see ref. [3]) were used. cos θ was calculated for each inclination angle using both formulas mentioned above. The results are presented in Table 6.

The results for cos θ calculated using Neimark´s formula are ,in some cases, greater than 1. First, it was assumed that this error value was caused by measurement inaccuracies. However, even approximating a value of 1 for cos θ, which means a contact angle of 0°, is not in accordance with the measured contact angles (Table 6).

Studying the formula, it was found that the case $\cos\theta \le 1$ is only given when $h(b + h)\cdot(2b + h) > R_0h^2$. In 17 out of 20 cases calculated (Table 6) this condition was not given and eventually the case was $h(b + h)\cdot(2b + h) < R_0h^2$.

Consequently, the fraction will be negative and cos θ will be obtained as the sum of 1 and the calculated value of the fraction. Therefore this formula cannot be applied to calculate the apparent contact angle in fibre-liquid systems.

Considering the formula derived by Dietrich and Bauer, which additionally takes into account initial film thickness *e* and measurable quantities: fibre radius *b*, droplet height *h* and radius of curvature R_0, it can be stated that it gives a satisfactory estimate of the apparent contact angle. It can be seen that values obtained

Table 4. *Mean values of radii of curvature of PVA droplets residing on fibre. Coefficients of variation were in the limits of 10.85-15.76 %.*

Inclination angle, °	0	5	10	15	20	25	30	35	40	45
Mean value, µm	642 ± 92	583 ± 79	720 ± 98	659 ± 93	600 ± 93	649 ± 93	505 ± 80	652 ± 100	661 ± 85	670 ± 93
Inclination angle, °	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
Mean value, µm	670 ± 93	701 ± 76	624 ± 93	660 ± 100	688 ± 107	354 ± 80	642 ± 92	625 ± 85	548 ± 81	680 ± 107

Table 5. *Mean values contact angles of PVA droplets residing on fibre. Coefficients of variation were in the limits of 2-17 %.*

Inclination angle, °	0	5	10	15	20	25	30	35	40	45
Mean value, µm	15±3	21±3	15±2	18±2	24±4	23±3	21±3	22±4	25±3	29±4
Inclination angle, °	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
Mean value, µm	29±4	26±3	25±4	19±3	21±3	23±3	23±3	27±4	27±4	32±3

Table 6. *Calculated cos θ and contact angles of PVA droplets with fibre surface.*

Inclination angle, °	cos θ according to Neimark	cos θ according to Bauer and Dietrich	Contact angle, ° according to Bauer and Dietrich
0	1.00	0.96	15.71
5	1.00	0.93	20.89
10	1.05	0.96	16.57
15	1.04	0.94	19.41
20	1.01	0.93	21.84
25	1.05	0.92	23.66
30	0.95	0.92	23.62
35	1.03	0.95	19.03
40	1.05	0.93	20.86
45	1.07	0.93	21.44
50	1.09	0.92	23.39
55	1.02	0.87	29.41
60	1.03	0.95	18.70
65	1.05	0.94	19.09
70	0.97	0.92	23.78
75	1.04	0.92	22.66
80	1.03	0.91	24.23
85	0.98	0.88	28.95
90	1.08	0.89	26.60

by measurement and calculation using this formula correlate quite well.

Comparison: values of contact angles between the surface of monofilament and PVA droplet are greater (for both experiment and calculation) compared to glycerol (see [4]). This can be explained by the greater initial film thickness and droplet height for PVA, because it was identified that the contact angle is dependent on the initial film thickness, droplet height, radius of curvature and fibre radius.

It is evident that an exceptionally good correlation of increase exists for the calculated values for PVA and glycerol.

Conversely, the measured values seem to be dissimilar. The decrease in values of contact angle with increasing inclination angle for the glycerol film might be explained by a flow of glycerol down the fibre caused by gravity.

Conclusions

The results of this sequel demonstrated that the inclination angle of a fibre can surely be described as one of the parameters of the liquid-fibre system that influence the development of liquid film instability. After the investigation of liquid film instability with dependence on the inclination angle of the fibre, as well as a second set of experiments and theoretical calculations, the findings are as follows:

Initial film thickness of liquids of both types' is increases with the increasing inclination angle of the fibre. The observation that the initial film thickness is greater for PVA than for glycerol is in good accordance with theoretical approaches which report that initial film thickness increases with the decreasing surface tension of the liquid.

Break-down mechanism. Visual investigation of the development of droplets on the monofilament leads to the conclusion that the driving forces in this dynamic process are Laplace and disjoining pressures. As droplets of PVA show no tendency to move down the fibre, gravity forces do not play an important role. A similar situation can be noted for glycerol droplets. It was observed that even at high inclination angles, two droplets coalesce by moving towards each other; one droplet moves up the fibre while the other one slides down. Dominance of Laplace pressure over gravity forces is obvious.

Wavelength. Values of calculated and measured wavelength between glycerol droplets correlate exceptionally well, while for PVA, differences in these values are evident. This might be attributed to the fact that Rayleigh´s formula does not account for the occurrence of fibre-liquid interactions, and therefore this formula might not be expected to give an accurate correlation.

Mother-daughter droplets. Daughter droplets appear between two neighbouring mother droplets only when the distance between them (mother-mother droplet) is in the range of 1800 μm and 2300 μm. Thus, for PVA, daughter droplets could only be seen at inclination angles of 5°, 50°, 80°, 85° and 90°. This statement is enhanced by the fact that in the case of glycerol no formation of daughter droplets for any inclination angle could be observed, as the distances between neighbouring droplets was in the range of 868 μm and 1321 μm. Seemingly, a critical value must be reached above which daughter droplet formation occurs. It would be instructive to develop a theoretical model that attempts to explain the experimental results.

Further, in good accordance with the theory of Laplace pressure is the observation that it was simply a matter of time before daughter droplets emptied into mother droplets.

Radii of curvature. Droplet heights are generally smaller for glycerol than for PVA and the radii of curvature are approximately the same; glycerol droplets are apparently smaller in volume. This occurrence is not unexpected, as the initial film thickness is smaller for glycerol. In addition, it is concluded that the internal pressure of glycerol droplets is greater, which is dependant on the former parameters as well as the surface tension of glycerol and the fibre radius.

Contact angle. The formula derived by Neimark, which does not comprise the initial thickness of the liquid film, is not in accordance with the contact angles measured for the fibre-liquid system. Whereas the formula derived by Bauer & Dietrich, which includes the initial thickness of liquid film, represents the apparent contact angle quite satisfactorily.

References

1. *Lukáš D., Košt'áková E., Chaloupek J., Očeretna L., Pociūtė M.; Instability of Liquid Jets // „Strutex" („Structure and Structural Mechanics of Textile Materials"): Proc. of 11th Inter. Conf. pp. 211-218.*
2. *Reinke N. A.; "Electrospraying & Electrospinning", Hauptseminar Angewandte Physik, (SS 2002).*
3. *Pociūtė-Adomavičienė M., Schwarz A., Stanys S.; Fibers and Textiles in Eastern Europe, Vol. 4(2006) No. 3(57) pp. 91-96*
4. *Quéré D., Di Meglio J. M., Brochard -Wyart F.; Science, Vol. 249, pp.1256-1260.*
5. *Ryck A., Quere D.; J. of Fluid Mech., Vol. 311 (1996), pp. 219-237.*
6. *Wagner H.D.; J. of Appl. Physics, Vol. 67, No. 3 (1990), pp.1352-1355.*
7. *Neimark A.V., J. Adhesion Sci. Technol., Vol. 13, No.10, 1999, pp.1137-1154.*
8. *Bauer C., Dietrich S.; Physical Review E, Vol. 62, No. 2, 2000, pp.2428-2438.*

Received 15.11.2007 Reviewed 15.01.2008