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# Fibres and Textiles (5) 2020 Vlákna a textil (5) 2020

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## Special issue venue the International Conference **NART 2019** *"NANOFIBERS, APPLICATIONA AND RELATED TECHNOLOGIES"* held on September 18-20. 2019 in Liberec, Czech Republic

Organized by: The Institute for Nanomaterials, Advanced Technologies and Innovation at Technical University of Liberec

The Nonwovens Institute at North Carolina State University

#### The University Bayreuth, Bayreuth, Germany

The Selection Committee Members: University of Illinois at Chicago Alexander L. Yarin **Constantine Megaridis** University of Akron Darrell H. Reneker George Chase North Carolina State University Behnam Pourdeyhimi Ruben Carbonell Jan Genzer Saad Khan Peter Fedkiw Eunkyoung Shim **Benoit Maze** Elizabeth Loboa University Bayreuth Andreas Greiner Cornell University, Ithaca, NY, USA Yasser Gowayed Tamer Uyar Technical University of Liberec David Lukas Oldrich Jirsak Miroslav Cernik Stanislav Petrik Mohamed Eldessouki

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John Fitzgerald, Hollingsworth & Vose Company Angelika Mayman, Hollingsworth & Vose Company Tom Birchard, Elmarco Company Jay Forcucci, PGI David Yavorsky, Millipore-Merck Ladislav Mares, Nafigate Corporation Nanofibers, Applications and Related Technologies (NART) 2019 is the fourth in a series of annual conferences that resulted from a sustainable collaboration between leading institutions on both sides of the Atlantic Ocean. The Technical University of Liberec, Czech Republic, is known as the birthplace of Nanospider<sup>®</sup> that generated a new era in industrial technologies for nanofibers. The Nonwovens Institute at the North Carolina State University, NC, USA, established its reputation based on its commitment to industrial application of fine fibers. Both institutions organized the previous three conferences, and expanded the organization committee during 2019 to collaborate with the University Bayreuth, Bayreuth, Germany. The fifth event (NART 2021) will be co-organized and hosted by Istanbul Technical University, Turkey. This expansion shows the promising future of this event and its sustainability to add new scientific communities and grow every year.

Micro- and nanofibers are materials which drive dramatic innovations in many fields. The "Nanofibers, Applications and Related Technologies – NART 2019" conference brought together experts from universities, research institutes and industries that share passion for innovative solutions involving micro- and nanofibers and other related nanomaterials. The scope of the event is broad and caters both academic and industrial interests. The objective of the conference is to accelerate adoption of micro- and nanofibers and related (nano)technologies in a wide range of applications.

NART2019 brought leading international researchers from over 15 countries with a main emphasis on the development and applications of submicron (i.e. nano-/micro-) fibers. The conference program ran 8 sessions and the participants contributed with 30 oral presentations as well as 40 posters. The proceedings of these scientific contributions were peer-reviewed and published by the Technical University of Liberec (ISBN 978-80-7494-512-0). While the Proceedings compiled the extended abstracts of the conference contributions, selected participants were recommended to submit full manuscripts to be reviewed and published by the Journal of Vlakna a Textil.

The conference program covered three themes: *1. Micro and Nanofiber Technology and Trends* (that includes topics focused on: Technology Innovations and Trends; Characterization of Nanofibers; Modeling and Theoretical Considerations; Structure and Morphology of Polymeric; Organic and Inorganic Nanofibers; Surface Modification and Functionalization of Nanofibers); *2. Micro and Nanofibers and Related Materials* (that includes topics focused on: Nanofibers and Functional Nanoparticles; Nanofibers and Other Nanomaterials Synergies; Multi-Nano Applications for nanofibers doped with nanoparticles, nanofibers as nanoparticle carriers, nano-delivery systems for environment and bio-medicine, nano-bio-technologies); and *3. Micro and Nanofibers and other Nanomaterials in Products* (that includes topics focused on: Business Development Trends; Nanofiber Industry Challenges; Nanofiber Cost Benefit Analysis, Return on Investment; Nanofibers and Nanomaterials in: automotive, healthcare / life sciences, energy, environment / water / air, infrastructure).

Finally, we would like to thank all those who contributed to the success of the conference; especially the attendees, organizing committee, staff members, authors, editorial boards as well as reviewers of the papers.

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# THE RELATION BETWEEN VISCOSE FIBERS' CHARACTERISTICS AND THEIR YARN PROPERTIES

#### Abdelhamid R.R. Aboalasaad<sup>1,2</sup> and Mounir Hassan<sup>2,3</sup>

<sup>1</sup>Department of Technologies and Structures, Faculty of Textile Engineering, Technical University of Liberec, Liberec 46117, Czech Republic <sup>2</sup>Department of Textile Engineering, Faculty of Engineering, Mansoura University, Egypt <sup>3</sup>University of Jeddah, Saudi Arabia <u>abd.elhameidrajabramadan.abo.el.asaad@tul.cz; mmhassan@uj.edu.sa</u>

**Abstract:** While cellulosic fibers have the third largest fiber's market-share, the production of viscose (as regenerated cellulosic fibers) was growing globally during the first decade of the 21<sup>st</sup> century with an average annual rate of 7%. Most of these fibers are used for apparel industry and it is necessary to study the performance of these materials in textile yarns. This study reports the results for characterizing two sets of viscose yarns with the same linear density (25 tex) that are produced at two different twist levels (409 and 877 twist/m). Viscose fibers characteristics including cross-section, fineness, orientation, and tenacity were evaluated and correlated to the produced yarns' physical and mechanical properties. Yarn evenness, mass distribution, thin and thick places, yarn hairiness, as well as the tenacity were improved by increasing the twist multiplier. On the other hand, the productivity (kg/h) of these yarns was decreased for that increase in the twist multiplier. These results show the relation between the yarn quality and productivity, where improving the product's qualities might be associated with a decrease in industrial process productivity. Therefore, it is important to carry out similar studies to optimize the processing parameters according to the end use of the produced yarns and their required performance.

Keywords: Viscose fibers characteristics, yarn properties, tenacity, haireness, USTER.

#### 1 INTRODUCTION

Man-made regenerated fibers are defined as fibers created via a chemical change of the natural material [1]. Viscose is a man-made regenerated fiber that is produced from cellulose dissolved pulps and its raw materials such as, wood, cotton or bamboo. Hardwood forests are the main sources nowadays of cellulose used for producing the viscose fibers. Hardwood cellulose is transformed into dissolving wood pulp that is processed into either viscose filament yarns or staple fibers. Wood-based regenerated cellulose fibers are used as alternatives to cotton fibers. The production of viscose (as regenerated cellulosic fibers) was arowina globally, as shown in Figure 1, during the first decade of the 21<sup>st</sup> century with an average annual rate of 7.7% [2, 3].

Considering the relationship between viscose fibers parameters and yarn properties, there were multiple efforts to develop theoretical models to predict the mechanical behavior of twisted short fiber structures. For example, Pan [4] introduces a relationship between the mean fiber volume fraction and the twist level of the yarn and pointed out that the tensile and shear moduli are proportional to the fiber tensile modulus. Fiber volume fraction, fiber length and fiber orientation distribution in the yarn have significant effects on the yarn moduli through these factors [4].



Figure 1 Global consumption of fibers at mills in 2015 [2]

Abbasi and others [5] produced three counts of cotton/polyester blends at different twist factors to study the effect of the twist level on the mechanical and physical characteristics of the low twisted yarns. They found that the yarn manufactured with the higher twist level (230 turns/m) and higher yarn count (50 tex) showed better yarn strength compared to the other twist factors and yarn counts. By increasing the twist level, the coefficient of variation decreased in all yarn counts; this may be due to higher amount of fibers present in yarn cross-section. The irregularity index and yarn hairiness of low twist yarn decreased with the increases of yarn count, moreover it decreased with the increase of twist per meter for the same count [5].

In another study [6], yarn evenness, faults, hairiness and diameter properties were tested using an USTER® Tester 5 for carded and combed yarns. In carded yarns, the increase of twist coefficient increased the evenness, tenacity and elongation values and decreased USTER hairiness and diameter values significantly. In combed yarns, increasing the twist coefficient improved tenacity and elongation and decreased number of thick places, neps, hairiness, and diameter values significantly [6].

The yarn hairiness is formed by protruding fiber portions from the relatively constricted basic body of the yarns. Different methods used for evaluating yarn hairiness were reviewed by Barella and Manich [7]. The hairiness of two-ply yarn decreases as the ply twist increases. The rate of reduction in hairiness with respect to twist is higher for the single-yarn twist than for the ply-yarn twist, particularly for the finer two-ply yarn. Variation in hairiness decreases as the ply twist increases [8].

For the staple yarns the ratio between the fiber tenacity and mean yarn tenacity is an important parameter that affects the yarn strength. The twist level, fiber properties, and fiber orientation are the main characteristics that influence the coefficient of fiber stress utilization. Zubair et al [9] presented a mathematical model, based on the assumptions of small deformation, constant packing density and contraction ratio. He used numerical integration considering real fiber stress-strain relationship and fiber orientation before the process of yarn breakage, when all fibers are mechanically stressed [9]. Neckář [10] also, validated the theoretical models compared with the experimental results. The main goal of this study is to study the relation between viscose fibers' characteristics and their yarn properties.

#### 2 EXPERIMENTAL WORK

#### 2.1 Materials

Two sets of viscose yarns have the same count (25 tex), produced at two different twist levels (409 and 877 twist/m) were used to investigate the relation between viscose fibers' parameters and their yarn physical and mechanical properties.

#### 2.2 Methodology

Viscose fibers were tested for their count, strength (stress-strain curves), and have microscopic images for cross sectional and longitudinal views. Viscose yarns were tested for their count, twist coefficient,

evenness using USTER tester, strength, as well as the microscopic images for the cross-sectional and longitudinal views. Yarns were also scanned through micro computed tomography (CT) scanner.

#### a) Viscose yarn cross-section view

- The preparation of Viscose yarn cross-sectional views passed through the following steps:
- 1. The swelling solution was prepared (glue + special swelling agent) in small plate.
- 2. Thirty samples were taken of each yarn type and dipped one by one in the solution then arranged and fixed them until dried for 1<sup>st</sup> day.
- 3. Samples were treated in the same way during the 2<sup>nd</sup> day, but with the exception of dipping in glue only.
- 4. Samples were treated for their surface during the 3<sup>rd</sup> day using a small painting brush and glue only.
- 5. The wax solution was prepared during the 4<sup>th</sup> day and covered the yarns completely in the middle of metallic molds.
- 6. Samples were placed in freezer for one day, after that the samples were collected.
- 7. The slices of the yarn cross sections were prepared using microtome and the cross-sectional views were collected using optical microscope. Then, the sample images were analyzed using the NIS elements software.
- b) <u>Yarn twist</u>

Twist per meter was measured on yarn twist tester according to standard procedure D1422–99 [9]. Thirty samples from each group of yarn were measured and the mean value of twist was calculated. The measured diameter and yarn twist were used to determine the twist angle (1) according to the following equation [11].

$$\tan \beta_D = \pi D Z \tag{1}$$

where: D is yarn diameter, Z is twist/meter and  $\beta_D$  is maximum twist angle.

#### c) Load-elongation curve of viscose yarns

Load-elongation test of the yarns was performed according to the standard test methods ASTM D2256-02 [12]. Instron 4411 tensile testing machine was used to measure and draw the correlation between the yarn extension and applied load at a constant speed of 200 mm/min.

#### d) <u>Viscose yarns evenness</u>

Yarn evenness, mass distribution, and imperfections (neps, thin and thick places) were measured using USTER tester 4, at the Technical University of Liberec according to the ASTM D1425-96 at standard conditions (temperature: 20±2°C and relative humidity: 65±4%) [13]. The measured sample length was 1000 m, with an extra length of 5 m before each measurement. The machine speed was 400 m/min and five samples from each group were measured, as shown in Figure 2 [14].



Figure 2 USTER tester 4 for yarn evenness

#### e) Viscose fibers fineness and strength

The viscose fibers fineness and strength were measured using VIBRODYN 400 according to the standard test method ISO 5079. For accurate calculations and analysis, one hundred fiber samples were measured as five groups, 20 samples for each. The first step of this test was to measure the fiber fineness (dtex) by hanging one end of the fiber to the optimum pretension Vibro-clips (100 mg for fiber counts ranging between 1.0 to 2.4 dtex), then clamping the other end to measure the fiber fineness. The second step was to measure the fiber strength, as illustrated in Figure 3. Finally, the fiber tenacity (cN/tex) was calculated for each sample.



Figure 3 Testing of fiber fineness and strength using VIBROSKOP and VIBRODYN 400

#### 3 RESULTS AND DISCUSSION

#### 3.1 Viscose fibers fineness and tenacity

The average viscose fiber fineness was measured by VIBROSKOP 400 was 1.45 dtex at significantly high standard deviation 0.30 dtex. Moreover, the average fibers tenacity, tested on VIBRODYN 400, was 37.78 cN/tex with 6.16 cN/tex standard deviation and breaking elongation of 9.29% with 1.74% standard deviation, as listed in Table 1.

No	Titer [dtex]	Force [cN]	Force Elongation [cN] [%]	
1	1.14	5.48	10.90	48.07
2	1.24	5.48	13.60	44.19
3	1.40	4.44	7.40	44.31
4	2.33	8.37	8.60	35.92
5	2.03	8.06	11.10	39.70
6	1.57	4.86	7.20	30.96
7	1.52	5.75	8.90	37.83
8	1.45	5.02	8.40	34.62
9	1.09	4.37	7.70	40.09
10	1.55	5.73	10.20	36.97
11	1.40	5.67	10.90	40.50
12	1.46	5.29	9.90	36.23
13	1.02	5.00	7.70	49.02
14	1.50	5.19	10.60	34.60
15	1.41	3.20	6.40	22.70
16	1.33	4.92	8.60	36.99
17	1.59	6.48	9.70	40.75
18	1.50	5.71	10.90	38.07
19	1.30	4.14	8.90	31.85
20	1.16	5.19	8.20 44.74	
Average	1.45	5.24	9.29	37.78
Std. dev.	0.30	1.19	1.74	6.16

Table 1 Viscose fibers fineness and tenacity

No	Ten/10%	YM1%	YM1%	YM1%
NO	[cN/tex]	[cN/tex]	[cN/dtex]	[g/den]
1	46.64	1067.98	106.80	120.96
2	39.64	1104.84 110.48		125.14
3	0.00	825.00	82.50	93.44
4	0.00	1092.27	109.23	123.71
5	38.55	1064.04	106.40	120.52
6	0.00	1111.46	111.15	125.89
7	0.00	1228.62	122.86	139.16
8	0.00	931.03	93.10	105.45
9	0.00	1362.39	136.24	154.31
10	36.81	746.24	74.62	84.52
11	39.64	932.14	93.21	105.58
12	0.00	948.63	94.86	107.44
13	0.00	2121.57	212.16	240.30
14	33.85	673.33	67.33	76.26
15	0.00	854.61	85.46	96.80
16	0.00	966.17	96.62	109.43
17	0.00	1748.43	174.84	198.03
18	36.97	993.33	99.33	112.51
19	0.00	1184.62	118.46	134.17
20	0.00	1463.79	146.38	165.79
Average	13.60	1121.02	112.10	126.97
Std. dev.	19.15	342.95	34.30	38.84

#### 3.2 Viscose fibers cross-sectional view

The fibers cross-sectional views were prepared by taking the slices using the microtome, and then samples were imaged under the optical microscope. The obtained best images of the 25 tex yarns 409 and 877 twist/m were analyzed using NIS elements software, as shown in Figures 4 and 5 respectively. The average fibers' diameter for 409 Z/m is 12.79  $\mu$ m, whereas for 877 Z/m is 12.30  $\mu$ m. The slightly difference in fibers diameter may be due to the fibers wrapping and compactness obtained by higher twist level.



Figure 4 Viscose fibers cross-sectional view for yarn 25 tex, 409 twist/m



Figure 5 Viscose fibers cross-section for yarn 25 tex, 877 twist/m

#### 3.3 Viscose yarns twist level

The average viscose yarns twist level for the two experimental groups was 409 and 877 twist/m with a standard deviation of 11 and 14 twist/m, respectively, as listed in Table 2.

Table 2 Viscose yarns twist per meter
---------------------------------------

Samples	Sample 1 (409 twist/m)	Sample 2 (877 twist/m)
1	398	862
2	395	883
3	421	879
4	396	887
5	431	855
6	423	850
7	398	879
8	404	864
9	399	852
10	422	898
11	405	891
12	411	873
13	397	885
14	421	879
15	409	886
16	412	883
17	407	864
18	403	885
19	412	889
20	419	897
Average	409	877
Std. dev.	11	14

#### 3.4 Viscose yarns load-elongation curves

There is no significant difference between the average values of viscose yarns load and elongation for both 409 and 877 twist/m, as can be observed from the values in Table 3. The yarn tenacity was calculated as 26.02 and 25.18 cN/tex for the low and high twist, respectively. This slight reduction in the yarn tenacity may be due to exceeding the optimum (critical) twist level [15].

Table	3 Load-elongation	data	of	viscose	yarns	25	tex,
409 an	nd 877 twist/m						

Samples	Sam (409 tv	ple 1 vist/m)	Sample 2 (877 twist/m)		
Code	Load [N]	Elongation [mm]	Load [N]	Elongation [mm]	
1	5.87	35.41	6.46	41.63	
2	5.93	38.56	5.17	33.15	
3	6.54	36.06	5.97	38.96	
4	6.96	39.03	6.94	44.78	
5	6.52	39.4	6.79	41.48	
6	6.6	39.81	5.99	37.7	
7	7.03	38.96	6.67	40.21	
8	6.58	38.13	6.65	42.31	
9	6.65	37.7	6.9	42.3	
10	6.36	36.05	5.41	35.61	
Average	6.50	37.911	6.295	39.813	
Std. dev.	0.38	1.56	0.63	3.51	

#### 3.5 Viscose yarns evenness

The USTER tester 4 statistics for viscose yarns 25 tex (409 and 877 twist/m) are summarized in Tables 4 and 5, respectively. Increasing the twist level improved the yarn regularity and decreased imperfections, hairiness, and yarn diameter. The number of thin places (-40%), thick places (+70%), and neps (+140%) decreased from 13, 23, and 41 to be 5, 1, and 4 /km, respectively. The yarn irregularity (U%, unevenness) decreased from 8.62 to 8.04%. Moreover, the average coefficient of mass variation ( $CV_m$  1m) decreased from 4.87 to 3.74% [16]. These results are consistent with other previous studies [4-5].

# Table 4 USTER 4 statistics for yarn 25 tex, 409 twist/m

Nr	1	Mean CV Q95	Мах	Min
U% [%]	8.62	8.62	8.62	8.62
U inert [%]	1.73	1.73	1.73	1.73
U hi [%]	2.54	2.54	2.54	2.54
CVm [%]	11.37	11.37	11.37	11.37
CVm 1m [%]	4.87	4.87	4.87	4.87
CVm 3m [%]	3.97	3.97	3.97	3.97
CVm 10m [%]	2.78	2.78	2.78	2.78
CVm 50m [%]	1.72	1.72	1.72	1.72
CVm Inert [%]	2.16	2.16	2.16	2.16
CVm Hi [%]	3.17	3.17	3.17	3.17
Thin -30% /km	299.0	299.0	299.0	299.0
Thin -40% /km	13.0	13.0	13.0	13.0
Thin -50% /km	0.0	0.0	0.0	0.0
Thin -60% /km	0.0	0.0	0.0	0.0
Thick +35% /km	53.0	53.0	53.0	53.0
Thick +50% /km	23.0	23.0	23.0	23.0
Thick +70% /km	14.0	14.0	14.0	14.0
Thick +100% /km	9.0	9.0	9.0	9.0
Neps +140% /km	41.0	41.0	41.0	41.0
Neps +200% /km	13.0	13.0	13.0	13.0
Neps +280% /km	7.0	7.0	7.0	7.0
Neps +400% /km	4.0	4.0	4.0	4.0
Н	10.11	10.11	10.11	10.11
sh	1.92	1.92	1.92	1.92
2DØ	0.273	0.273	0.273	0.273
CV2D 8mm [%]	9.40	9.40	9.40	9.40
S2D 8mm [%]	0.030	0.030	0.030	0.030

## Table 5 USTER statistics for yarn 25 tex, 877 twist/m

Nr	1	Mean CV Q95	Max	Min
U% [%]	8.04	8.04	8.04	8.04
U inert [%]	1.07	1.07	1.07	1.07
U hi [%]	1.94	1.94	1.94	1.94
CVm [%]	10.11	10.11	10.11	10.11
CVm 1m [%]	4.87	4.87	4.87	4.87
CVm 3m [%]	3.74	3.74	3.74	3.74
CVm 10m [%]	3.018	3.018	3.018	3.018
CVm 50m [%]	0.95	0.95	0.95	0.95
CVm Inert [%]	1.33	1.33	1.33	1.33
CVm Hi [%]	2.43	2.43	2.43	2.43
Thin -30% /km	174.0	174.0	174.0	174.0
Thin -40% /km	5.0	5.0	5.0	5.0
Thin -50% /km	0.0	0.0	0.0	0.0
Thick +35% /km	11.0	11.0	11.0	11.0
Thick +50% /km	2.0	2.0	2.0	2.0
Thick +70% /km	1.0	1.0	1.0	1.0
Thick +100% /km	0.0	0.0	0.0	0.0
Neps +140% /km	4.0	4.0	4.0	4.0
Neps +200% /km	0.0	0.0	0.0	0.0
Н	5.54	5.54	5.54	5.54
sh	1.17	1.17	1.17	1.17
2DØ	0.205	0.205	0.205	0.205
CV2D 8mm [%]	7.09	7.09	7.09	7.09
S2D 8mm [%]	0.017	0.017	0.017	0.017

#### Table 6 Averages of overall yarn data

Twist level [T/m]	Fiber diameter [µm]	Yarn tenacity [cN/tex]	yarn Irregularity [%]	Thin places (-40%)	Thick places (+70%)	Neps (+140%)	Coef. of mass variation (CV <sub>m</sub> 1m) [%]
409	12.8	26.0	8.62	13	23	41	4.87
877	12.3	25.2	8.04	5	1	4	3.74

#### 4 CONCLUSION

The average viscose fiber fineness was 1.45 dtex, the fibers tenacity was 37.78 cN/tex and breaking elongation was 9.29%. The viscose varn physical properties including fibers' cross-section, diameter and twist have been analyzed for two groups of twist levels. The higher twist multiplier improved the fibers orientation and cohesion forces, which decreased the yarn diameter from 12.79 to 12.30 µm. Moreover, the yarn unevenness, hairiness, thin-, thick-places, at the decreased neps were twist level of 877 twist/m. The coefficient of variation of mass distribution decreased from 4.87 3.74%. to respectively. There are slightly differences between the tenacity and elongation results for both groups that might be due to exceeding the optimum twist level. These results show the trade-off between the varn quality and productivity, where increasing the twist to certain levels might enhance the product qualities, this will also decrease the productivity of the industrial process. Therefore, it is necessary according to optimize these parameters to the required performance and the end use of the produced yarns.

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# THE INFLUENCE OF MICROSTRUCTURE OF 3D PRINTING ON TACTILE PERCEPTION OF HUMANS

#### Zuzana Hrubošová<sup>1</sup>, Stanislav Petrík<sup>1</sup> and Michal Vik<sup>2</sup>

<sup>1</sup>Technical university of Liberec, The Institute for Nanomaterials, Advanced Technology and Innovation, <sup>2</sup>Technical university of Liberec, Department of Material Engineering, Studentská 1402/2,460 01 Liberec 1, Czech Republic <u>zuzana.hrubosova@tul.cz</u>, <u>stanislav.petrik@tul.cz</u>, <u>michal.vik@tul.cz</u>

**Abstract:** Braille script is one of the most important communication tools for visual disable people. This script is a group of six points, systematically composed into Braille cell representing each letter or number in alphabet. It has been used for marking medicine, entrances or exits and other items. The Braille script can be made from different materials, usually paper or metal desks applied to the required surfaces. In this work, Braille cells were applied by multi layered 3D printing directly to the textile surface taking into consideration the right preparation of substrates. 3D printing is created on basic cotton canvas in two variants: rough porous printing with micro roughness and smooth printing with minimal changes in roughness. A comparative evaluation for these two kinds of 3D printing was carried out to measure the micro roughness and the height using electron and confocal microscopy. Then, a qualitative study for the ability of blind people with different defects of visual impairment to recognize and read the printed Braille script was done. Blind people are using mechanoreceptors, especially Vater Pacini corpuscle, to provide information about the texture, pressure and vibration. Results of this study can define future modifications to examine influence of micro and nano structures on the tactile properties of 3D printed Braille scripts and other applications.

Keywords: 3D printing, human perception, roughness component.

#### 1 INTRODUCTION

Tactile interactions are obviously ubiquitous and essential. A person could use the sense of touch to feel for the smoother fabric of his business clothes in his closet. On the other side one of the biggest problems of blind people is visually differentiating of clothes sizes, colors and clothing maintenance [1]. Visually impaired people generally need help with these activities. because manipulation with their textile aarments becomes problematic. In the moment when color readers are expensive. these individuals need help of others. The human hand is a complex organ serving the functions of grip and touch. The mechanoreceptors of the hand can be categorised into those located within skin and subcutaneous tissues and those associated with joints and muscles providing the central nervous system with information about position of movement of hand and fingers. In addition to mechanoreceptors there are numerous free nerve endings reacting to thermal and painful stimuli generally referred to as polymodal nociceptors. They are found in the connective tissue of the locomotion apparatus as well as the skin and even enter the epidermis. Morphologically these are terminal branches of afferent nerve fibres without any specific structures around these 'free' nerve endings in marked contrast to the different types of mechanoreceptors [2].

Four types of mechanoreceptive afferents have similarly been identified by microneurography and tentatively matched to mechanoreceptors [3]. The afferents vary based on their rate of adaptation to stimuli, either slowly adapting (SA) or rapidly adapting (RA), as well as the size of their receptive field, small (I) or large (II). The slowly adapting receptors, Merkel receptors (SA I) and Ruffini cylinders (SA II), are respectively most sensitive to pressure (0.3-3 Hz) and stretching of the skin (15-400 Hz) [2]. The rapidly adapting receptors, Meissner corpuscles (RA I) and Pacinian corpuscles (PC or RA II), are on the other hand most responsive to taps on the skin (3-40 Hz) and vibrations (10-500 Hz) [2]. The neurophysiology of touch is however much less developed than vision or audition, with recent studies, for example, shedding doubt on the very existence of Ruffini cylinders in the human glabrous skin [3].

The objects which have been handled vary in shape and size. Cutaneous primary afferent responses are affected by the local shape of the object in contact with the skin. Afferent responses have been characterised for a range of shapes either scanned over the receptive field or indented into the receptive field. Local shape is conveniently expressed in terms of the local curvature of the object; the curvature at any point is the reciprocal of the radius of curvature at that point. In Figure 1a, a wavy surface of increasing curvature scanned across the receptive field of an SA I afferent results in increasingly modulated responses of the afferent [4]. For a sphere of increasing curvature (decreasing radius) indented into the skin (Figure 1b).



**Figure 1** DAI afferent responses increase as the curvature of object increase: a) wavy surface of increasing curvature scanned over the fingerpad; b) spheres of increasing curvature (decreasing radius) indented into the fingerpad

Tactile roughness is a complex, multidimensional sensation that is dependent on the physical characteristics of multiple tactile elements (e.g. grains of sand for abrasive papers), including their size, shape, density (or spacing) and composition. To assess the underlying neuronal coding mechanisms, have been used the nature of the relation between perceived roughness and surface characteristics. For relatively coarsely textured surfaces, the dominant view at present is that the neural representation of tactile roughness can best be explained by a spatial variation code whereby differences in the firing rates of slowly adapting type I. Sutu et al. [5, 6] confirm hypothesis that dot height is the critical factor underlying the shape of the psychometric curve relating tactile roughness with dot spacing: monotonic increase versus inverted U-shape. This hypothesis has been tested and confirmed in this case study by controlled measurement of surface roughness of textile 3D print allows preparing not only readable characters of Braille symbols, but also association with pattern design as integral component of whole design [7].

#### 2 **EXPERIMENTAL**

#### 2.1 Materials and methods

Surface profile measurement is achieved by measuring a line across the surface and representing that line mathematically as a height function with lateral displacement, z(x). When measuring and characterizing surface texture, use is made of the rectangular coordinate of a righthanded Cartesian set, in which the x axis provides the direction of the line, the y axis lies nominally on the real surface and the z axis is the outward direction from the material to the surrounding medium.

Samples were measured by three different systems of roughness measurement. First apparatus was laser scanning confocal microscope OLYMPUS LEXT OLS3000, second was Taylor Hobson stylusbased roughness meter TALYSURF and last method was based on 3D optical scanner ATOS 7 SR2 from GOM Company.

LSCM LEXT system 5x objective in bright field capturing mode and computer controlled moving xy stage have been used in the experiment. TALYSURF CLI 500 system was primarily equipped by Laser Triangulation gauge, which is a noncontact gauge capable of rapid 3D measurement and ATOS Compact Scan 2M optical scanner was equipped by fine optics.

In order to evaluate the surface quality, this study pointing out the importance of evaluating a set of parameters and not only one. A roughness value can either be calculated on a profile (line) or on a surface (area). The profile roughness parameter (Ra, Rq,...) are more common. Figure 2 shows five profiles characterized by the parameter set (Rq, Rsk, Rku) [8].

But what happens when it's investigated the same set of parameters, but related to 3D measurements (Sq, Ssk, Sku). Most of the 2D parameters defined in ISO 4287 have a mathematical expression that can easily be extended to 3D. For example, Sq is simply an extension to a plane of the equation of Rq that is defined for a line:

$$Rq = \sqrt{\frac{1}{lb} \int_{lb} Z^{2}(x) dx}$$

$$Sq = \sqrt{\frac{1}{A} \iint_{A} Z^{2}(x, y) dx dy}$$
(1)



a) arithmetical mean deviation of the roughness profile



c) skewness of the roughness profile Figure 2 The roughness profile



b) root mean square deviation of the roughness profile



d) kurtosis of the roughness profile

3D prints have been prepared on six different textile substrates with different roughness (twill, two canvas, knit, lining and satin) as shown on picture in Figure 3 by using of EXPANCEL microspheres.



**Figure 3** Picture of several tested textile samples with Braille symbol of "Hand Washing" and detail of Braille symbol "Non-ironing" printed on twill

An unexpanded EXPANCEL microsphere consists of a thermoplastic shell encapsulating a hydrocarbon. When this thermoplastic shell is heated it softens and at the same time the pressure of the hydrocarbon increases. This causes the shell to stretch and expand in much the same way as a balloon and resulting patterns obtain 3D character.

#### 3 RESULTS

Each tested sample has been measured by all above-mentioned methods three times. Each sample was firstly captured by mode of maximal resolution allowed by each method. In case of LSCM Olympus LEXT OLS3000 microscope has been plane resolution, which clearly resolves 0.12 µm line and space patterns of 0.01 µm height, for ultra-precise measurements of micro fabrication surfaces. TALYSURF CLI 500 system all axes can move at 30 mm/sec and data log at 0.5 µm, which allows for fast and accurate measurement and ATOS Compact Scan 2M optical scanner allows resolution range 21-615 µm (in our case 21 µm). Because resolution limit of all these systems is below tactile resolution of human touch. Gaussian filters of 0.8 mm filtered all captured data profiles. As you can see on picture in Figure 5 high resolution of confocal microscope caused number of artifact peaks in bottom part of scanned profile, which will be unrecognizable for human touch. Resulting roughness profile after Gaussian filtering appears much smoother in comparison to roughness presented on Figure 4 and it is near to probable human resolution [7].



Figure 4 Scanned profile of knit - OLS LEXT



Figure 5 Plane roughness profile OLS LEXT - knit

In case of absolute resolution was TALYSURF system 5-times worse than used confocal microscope LEXT, nevertheless on picture in Figure 5 it is visible that used final resolution of this system is sufficient. Used Gaussian filtering, which is visible on bottom graph in Figure 6, shows less change in final profile of captured sample.



Figure 6 Scanned profile of satin – TALYSURF



Figure 7 TALYSURF example of roughness analysis

Last method ATOS Compact Scan 2M optical scanner based on blue light technology allowing improvement of measuring system reliability independent of ambient light conditions is partially affected by necessity of special treatment of tested textiles. Because our samples have less reflectivity for blue light of this scanner, was necessary to cover surface of our samples by white chalk powder with high reflectivity. Resulting images were slightly smoothed by this powder as visible on picture in Figure 8, where typically pores of textile weave appear as coated by special finishing layer.



Figure 8 3D image of satin printed by Braille symbols captured ATOS Compact Scan 2M optical scanner

Powder treatment of surface tested textiles affects beside appearance of sample also measured roughness parameters as visible on graph in Figure 9, where is presented comparison of measured data of maximum peak height Rp.



**Figure 9** Relationship between maximum profile peak height (*Rp*) measured by tested profilometers

Table 1Parameters of linear regression y=a+b.xin Figure 9

Device\Parameter	а	b	R <sup>2</sup>
CompScan	90.427	0.3764	0.54
TALYSURF	28.911	0.3286	0.64

Regression budget shows that relationship between individual profilometers data is affected by flexibility of tested textiles. That means that presented measurements were influenced by insufficient flatness of tested textiles. Used method based on racks should be improved for next series of profile measurements. On the other side both compared methods show almost similar slope of trend.

#### 4 CONCLUSION

Surface topography is of great importance in specifying the function of a surface. A significant proportion of component failure starts at the surface due to either an isolated manufacturing discontinuity or gradual deterioration of the surface guality. Typical of the former are the laps and folds which cause fatigue failures and of the latter is the grinding damage due to the use of a worn wheel resulting in stress corrosion and fatigue failure. The most important parameter describing surface integrity is surface roughness. In the manufacturing industry, surface must be within certain limits of roughness. This work shows, that most important factor beside above mentioned is sample preparation procedure. In case of optical method of surface topography are results affected by flexibility and less reflectance of textiles.

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# PLASMA PREPARED SILICON-BASED THIN LAYER AS THE ANTICORROSIVE PROTECTION OF CONDUCTIVE COPPER SURFACE ON POLYESTER NONWOVEN

#### Hana Křížová, Michal Krejčík and Stanislav Petrík

Technical University of Liberec, Institute for Nanomaterials, Advanced Technologies and Innovation, Department of the Preparation and Analysis of Nanostructures, Bendlova 1409/7, Liberec, Czech Republic <u>hana.krizova@tul.cz</u>

**Abstract:** Electrically conductive nonwoven polyester fabric MILIFE® with a chemically deposited copper layer was coated by the PECVD method using the mixture of HMDSO (hexamethyldisiloxane) as organosilicate precursor and oxygen. The metallized fabric with and without silica coating was subsequently tested under strongly corrosive conditions of acid and oxidizing environment. The degree of corrosion damage of the electrically conductive copper layer was determined by changes in electrical resistance measured on its surface. We have proven that silicon-based thin layer can protect the conductive metallic layers from corrosive environmental influences. The plasma-polymerized coating of silicon-based nanolayer significantly prolongs the life of metallized polyester nonwoven and extends its use to areas of long-term corrosive conditions.

Keywords: metallized fabric, anticorrosive, conductive fabric, silicon, HMDSO, PECVD.

#### 1 INTRODUCTION

Electrically conductive fabrics have received increased attention for their high flexibility, low weight, porosity, airiness, and favorable price. A lot of ways to form conductive fabrics have been described in the literature, e.g., by adding various electrically conductive additives [1, 2], using conductive particles [3], carbon nanotubes [4], conductive polymers [5, 6], or chemically depositing metals on the fiber surface [7, 8]. New fabrics with metallic surfaces should have other properties such as physical, chemical or biological resistance, increased hydrophobicity or hydrophilicity of the surface, compatibility with the organism or environmental friendliness of their life cycles, to be widely used in industry, electrical engineering, optics or medicine and to compete with traditional materials. The corrosion resistance of materials is a typical requirement.

Copper is a metal with excellent electrical and thermal conductivity, but it decreases considerably with the content of impurities including oxygen and copper oxides respectively. Pure copper is subject to corrosion in long-term contact with the environment, where its surface is attacked e.g. by oxygen, carbon dioxide, acid rain, and other solid, gaseous or liquid substances present in the air. The changes are very slow and not entirely predictable. The composition of the verdigris that forms on the copper surface is essentially determined by the prevailing concentration of air pollution and environmental conditions. After several weeks in the air,

the reddish-orange copper obtains a brown shade (cuprous oxide,  $Cu_2O$ ), which in turn darkens to black (cupric oxide, CuO). The greenish verdigris (copper carbonate,  $(CuCO_3 \cdot Cu(OH)_2)$  will be visible after about 20 years of the action of oxygen, air humidity and carbon dioxide. Conversely, the predominantly acidic environment is not aggressive for copper, but the oxygen plays an important role in the interaction of the copper metal with acids. In conjunction with oxygen or other oxidizing agents, the oxidative corrosion of the copper surface is rapid, even in the presence of so-called non-oxidizing acids such as HCI, where copper (II) chloride (CuCl<sub>2</sub>) or basic copper chloride (Cu<sub>2</sub>(OH)<sub>3</sub>Cl) are formed. The presence of acetic acid during copper weathering can lead to the formation of copper (II) acetate. The reaction of copper, acetic acid and hydrogen peroxide involves the formation of a free radical and process. an electrochemical corrosion The mechanism includes the creation of a strong oxidizer, peroxyacetic acid (CH<sub>3</sub>COOOH), from dissolved oxygen [9]. The equation (1) shows simply the formation of copper (II) acetate:

 $Cu + 2CH_3COOH + H_2O_2 \rightarrow Cu(CH_3COO)_2 + 2H_2O$ (1)

In effect, according to reaction (2), tetraacetodiaquadicopper (II) complex is produced [10]:

$$2Cu + 4CH_3COOH + 2H_2O_2 \rightarrow$$
  

$$\rightarrow [Cu_2(H_2O)_2(CH_3COO)_4] + 2H_2O$$
(2)

All these corrosive reactions cause a loss of copper electrical conductivity, which degrades the conductive fabric and limits its life and use. Since the EU ban on the use of hexavalent chromium [11], which had previously been used in anti-corrosive coatings, came into force in 2007, environmentally friendly replacement materials and technologies are intensively sought.

The plasma deposition of silicon-based thin films from a mixture of HMDSO and oxygen by low investigated and described pressure was as a method of anticorrosive treatment of steel. plasma-assisted deposition, smooth. In the continuous and dense films with good adhesion were produced which exhibited a polymer-like structure at low pressure. HMDSO is very often used as an organic precursor in CVD (Chemical Vapor Deposition) methods because it is relatively nontoxic and has high room temperature vapor pressure (64 mbar) [12]. The scientific literature examining the deposition of thin films on steel shows a correlation between the composition of the gas phase and the structure of the coating. The structure of the deposited layer is dependent on the percentage of HMDSO in the mixture of gases supplied to the plasma chamber. A high percentage of HMDSO produces a polymer film, while a low percentage of HMDSO forms a silica-like film with only a small amount of carbon content [13]. It seems that the deposition rate of the protective layer depends on the HMDSO content in the feed gas, with its higher content and the deposition rate Also, increases the higher pressure and the associated higher process gas content in the plasma reactor (plasma chamber) usually results in a higher deposition rate of the layer. At the same time, the structure of the deposited layers and their adhesion change with increasing deposition rate [12, 13].

Plasma deposition of thin layers appears to be very promising, but conventional plasma techniques require a deposition temperature of 800 (silicon carbide) to 1100°C (silica). Logically, these high temperatures eliminate the use of most substrates for plasma deposition. For low-pressure PECVD (Plasma-Enhanced Chemical Vapor Deposition), which was used in this study, thin-film deposition place at a lower temperature than takes in the conventional arrangement. This is a major advantage of the PECVD method because low melting substrates, such as organic polymers, can also be used for deposition. Thus, besides a large number of scientific works that deal with silica coating layers on metal surfaces of steel [12-19], the studies have also emerged in which this carrier substrate is a polymeric material such as polypropylene [20], polystyrene [21] or PMMA [22]. The silica-based coating is known to have very good mechanical, tribological [23], chemical and electrochemical resistance [24].

#### 2 MATERIALS

Polyester microfiber nonwoven fabric MILIFE® (JX Nippon ANCI Corporation, JP) with a chemically metallized surface (copper layer obtained by chemical reduction process, made by Večerník Ltd, CZ).

Properties of non-metallized MILIFE®:

- chemical composition: Poly(ethylene terephthalate/ /ethylene isophthalate) copolymer
- linear density: 0.6 dtex
- weight area: 10 g.m<sup>-2</sup>
- melting point: 220-260°C
- decomposition temperature: >300°C
- color: white

Properties of metallized MILIFE®:

- weight area: 14.5 g.m<sup>-2</sup>
- color: reddish-brown
- physical properties: electric conductivity, EM shielding and thermal insulation [25]

Hexamethyldisiloxane (HMDSO, C<sub>6</sub>H<sub>18</sub>OSi<sub>2</sub>; boiling point 101°C; Sigma-Aldrich)

Acetic acid (2% solution)

Hydrogen peroxide (0.25% solution)

Paraffin oil

#### 3 METHODS

#### 3.1 Preparation of silicon-based thin layer

The polyester nonwoven MILIFE® with a chemically deposed layer of copper on the surface of the fibers was placed and fixed in the plasma chamber. Plasma excitation was obtained with use of an RF plasma generator Cesar (13.5 MHz) which provides the power in the range 0-2000 W. The deposition of thin silicon-based protecting layer was carried out by PECVD method under the following conditions: magnetron power 150 W, preload -500 V, plasma time 7 and 20 minutes, pressure in the plasma chamber 45 Pa, and 8 sccm (standard cubic centimeters or ml.min<sup>-1</sup> under standard conditions) oxygen of flow rate to the plasma chamber. The compound HMDSO was used as a silica precursor. The reactants were fed to the working chamber in a gaseous form. As mentioned in the introduction, HMDSO has a relatively high room temperature vapor pressure, so the temperature of the precursor was not increased, and its vapors were fed into the plasma chamber with nitrogen support. HMDSO vapors were fed with nitrogen at a flow rate of 3 sccm to the plasma chamber through a needle valve.

#### 3.2 Evaluation of silicon-based thin layer

The surface of the plasma protective layer on metallized polyester fibers was evaluated by electron microscope images (UHR FE-SEM Carl Zeiss Ultra Plus). The thickness of the plasma prepared silicon-based layers was measured on a flat glass surface using the mechanical profilometer Bruker Dektak XT (US). Samples coated in the range of 5-30 minutes were used to measure the thickness of layers. The roughness profile of fabrics was observed by laser scanning confocal microscopy (Olympus OLS 3100) and evaluated according to the ISO 4287:1997 standard. The chemical composition of the layer was analyzed by EDS (Energy-dispersive X-ray spectroscopy) and IR (Infrared spectroscopy). EDS (which is part of electron microscope) allows the elemental composition of the samples to be measured. Four samples coated in the range of 2-20 minutes were used for IR analysis. Infrared spectroscopy gives a more specific picture of the chemical structure of the sample, particularly as regards the typical chemical groups present in the sample using ATR technique on Ge crvstal (Nicolet<sup>™</sup> iS10 FTIR Spectrometer Thermo Scientific<sup>™</sup>).

# 3.3 Testing under corrosive conditions and measurement of electrical surface properties (electrical resistance)

Conditions that are highly corrosive to copper (acidic pH in the presence of oxygen) were simulated using a mixture of acetic acid (2%) and hydrogen peroxide (0.25%), pH 3. Three samples were tested: metallized MILIFE® without protective thin layer (sample called "blank"), metallized MILIFE® with a thin layer plasma-treated for 7 minutes (sample called "MF/Cu/SiO<sub>x</sub>/7"), and metallized MILIFE® with a thin layer plasma-treated for 20 minutes (sample called "MF/Cu/SiO<sub>x</sub>/20"). The surface electrical resistance of all samples was measured using a digital multimeter DT9205A. Device parameters: maximum measuring range 0-200 M $\Omega$  (+/-0.8%), alkaline battery 9 V as a voltage source. Twenty measurements of each sample total were performed, i.e., 5 measurements in 2 mutually perpendicular directions on both sides of each fabric (vertical and horizontal directions were selected according to the visually prevailing direction of the fibers on each side of the nonwoven fabric); spot measurements were chosen randomly across the fabric, keeping the contact electrode distance of 1.5 cm at each measurement.

The acetic acid solution was boiled briefly before the test to displace a larger part of the oxygen from the solution. Metallized MILIFE® samples were left for 48 hours in a 2% acetic acid solution at room temperature. The surface level in the test tubes was covered with a 0.5 cm thick layer of paraffin oil which prevents oxygen in the air from dissolving into the acid solution. Subsequently, the fabrics were rinsed in water, dried at 50°C and their surface electrical resistance was measured again. After that the samples were placed in a (separate) bath with acetic acid/hydrogen peroxide mixture for 2 minutes, followed by thorough rinsing in water and drying for 2 minutes at 50°C. The dried samples were re-measured, and this cycle was repeated until the final total time of 10 minutes in the acidic oxidizing bath. Each set of 20 electrical resistance measurements was evaluated statistically; the average surface electrical resistance of the fabric and the 95% confidence interval were calculated.

#### 4 RESULTS AND DISCUSSION

Figures 1-3 show the surface of the MILIFE® microfiber without coatings, with a copper-metallized coating and with plasma-polymerized silicon-based layer on the metallized surface. All three surfaces have approximately the same magnification (10 000x). The nano-roughness of the fiber surface at 10 000x magnification was investigated. It is evident that the nano-roughness of metallized fibers with silicon-based coating (Figure 3) is higher than before the plasma treatment (Figure 2).



**Figure 1** SEM image of MILIFE® microfiber with impurities on the surface (10 420x)



**Figure 2** SEM image of copper-metallized MILIFE® microfiber with copper clusters on the surface (10 000x)



Figure 3 SEM image of copper-metallized MILIFE® microfiber with plasma-prepared silica-based coating (10 000 x)

The copper clusters appear to have functioned as nucleation centers for the growth of the polymeric silicon-based layer, and thus the surface roughness of the fiber surface has increased at the nanoscale. In addition, the tendency for higher roughness of silicon-based plasma coated layers using higher radio frequency power in the presence of oxygen has already been demonstrated. The study [26] showed RF-input power determines the crosslink density and the hydrocarbon content in the layers and plays a key role in the occurrence of higher roughness. The presence of oxygen at higher RF power also significantly increased the roughness of the resulting surface.

The graph in Figure 4 shows the thickness of the plasma-polymerized silica layer as a function of the plasma time obtained from the analysis of layers deposited on glass. Each value was calculated from 5 values measured at the flat glass plasma-coated surface using the mechanical These samples profilometer. were prepared in a plasma chamber under the same conditions as plasma-coated textile samples, but different plasma times (5, 10 and 20 minutes) were used. The reason for using the glass to apply this layer was to determine more precisely the thickness of the coated layer: a flat solid object with a partial covering allows a more accurate measurement of the thickness of the thin layer than flexible textile fibers.

The graph in Figure 4 shows that the thickness of the plasma-polymerized layer coated the copper layer on fibers was approximately 120 nm (sample  $MF/Cu/SiO_x/7$ ) and 388 nm (sample  $MF/Cu/SiO_x/20$ ). Some unevenness was caused mainly by power fluctuations, which could not be kept completely constant during plasma times. Essentially, however, the thickness of the plasma-coated layer is linearly dependent on the plasma time while maintaining a stable flow rate of process gases, power of matching network, and plasma chamber pressure. The plasma deposition rate under the set conditions was approximately 0.3 nm.s<sup>-1</sup>.



Figure 4 Thickness of silica-based coating depending on the time of plasma-treatment

As for the chemical composition of the plasmapolymerized layer, the EDS analysis of the surface of plasma-prepared layer (Figure 5) shows the presence of silicon and oxygen as the main elements. This is a sample of polyester non-woven MILIFE® (non-metallized) with a thin silicon-based layer after 20 minutes of plasma treatment, i.e., a layer about 388 nm thick. The similar weight ratio of silicon to oxygen (silica 34.9 wt.%, oxygen 34.1 wt.%) represents an Si:O atomic ratio of about 1:1.7. This suggests that the formed layer contains mainly silica (SiO<sub>2</sub>). However, considering the weight fraction of carbon (29.8 wt.%), the total atom content in the deposited layer was SiO<sub>1.70</sub>C<sub>1.98</sub>. However, the EDS analysis penetrates depth to а of 1-2 microns, so the oxygen and carbon contained in the polyester of the carrier fabric could be included in this analysis as well.



Figure 5 EDS analysis of MILIFE® fabric with plasma-prepared coating from HMDSO/O2



**Figure 6** FTIR spectra of four samples (1-4) of metallized MILIFE® fabric with different thickness of plasma-prepared coating from HMDSO/O<sub>2</sub>. The purple line at the bottom of the graph ("Polyester Licensed to TU Liberec") corresponds to the material of pure MILIFE® (without copper and silicon) and is a part of the FTIR spectrum library

Figure 6 shows the IR spectrum analysis of the four samples with layers of different thicknesses prepared in a plasma chamber within 2-20 minutes by the process described above. We can observe an increasing signal response depending on the plasma time and the thickness of the formed silicon-based layer. However, for all curves, it is clear that silica (silicon oxide) is only one component of the plasma-prepared thin film. There are other peaks in the spectrogram representing organosilicon compounds, for example siloxanes. The term "silicone-based thin layer" therefore appears to be appropriate and guite apt for this hybrid thin layer, which has been prepared by the PECVD method. It has been shown that a chemically diverse mixture of silicon oxides and silicon-based organic compounds was formed. The resistivity of excellent insulators is higher than  $10^{16} \Omega$ .m at 20°C (e.g.  $10^{21} \Omega$ .m for polyethylene terephthalate), but copper as an excellent electrical conductor has a very low electrical resistivity 1.7x10<sup>-8</sup> (approximately  $\Omega.m$ ) [27]. Our measurements confirmed the pure non-metallized electrical insulator properties. MILIFE® has The electrical resistance measured on the surface was outside the measuring range of the instrument used, i.e. it was higher than 200 M $\Omega$ , and this means at least 10<sup>8</sup> times higher than on the copper metallized fabric. The electrical resistance values measured on the surface of the metallized samples (Table 1) confirmed that the acidic environment of acetic acid did not have a major effect on copper and that the corrosive conditions only occurred in the presence of hydrogen peroxide. Surface resistance values were not changed for 48 hours in a 2% acetic acid solution (pH 3) in a closed tube without oxygen. However, after the addition of hydrogen peroxide, the surface resistance of the sample without the plasma-polymerized protective coating increased significantly over for 10 minutes, due to the oxidation of copper, practically up to the values non-measurable by use of the digital multimeter. Even a thinner coating of MF/Cu/SiO<sub>x</sub>/7 sample was not sufficiently resistant to the corrosion and an increase in surface electrical resistance was apparent, although a little

slower than on the sample without the protective layer ("blank").

The surface of the metallized MILIFE® without the silicon-based layer (MF/Cu blank) and the MF/Cu/SiO<sub>x</sub>/7 sample with a thinner coating visually changed the color from the original redorange to brown-red and brown-black during the acetic acid and hydrogen peroxide treatment, while the solution was colored to light blue. This confirms the corrosion process involved both oxidative changes in the copper surface (the production of copper oxides responsible for the tarnish on the copper metal surface) and at the same time the dissolving of copper (the production of copper (II) ion accounts for the light blue color in test solution).

There was no significant increase in electrical resistance during testing of  $MF/Cu/SiO_x/20$  sample and its about 388 nm thick silicon-based thin layer was already able to effectively protect the polyester nonwoven MILIFE® with copper surface against oxidation and loss of electrical conductivity.

The porosity density of metallized and nonmetallized MILIFE® is about 80% [25]. The high porosity of the textile carrier was most likely the reason why the thinner silicon-based layer was not able to sufficiently protect the copper surface of the fabric from corrosion. Changes in porosity after plasma deposition have not been investigated in this study, but based on previous research, it is clear that the porosity decrease is directly dependent on the plasma deposition time of the HMDSO film [28]. Although the deposition of the film gradually covers the pores and reduces the porosity, the subsurface pores retain their original, open structure. The structure of the film is weakened at the pores of the fabric, and in fact there may be a film thinner than shown by measuring the thickness of the deposition layer on a flat solid surface. This caused cracks in the thinner layer of the sample  $MF/Cu/SiO_x/7$ . The corrosive medium easily penetrated the copper layer through the defects, while the thicker layer of the sample MF/Cu/SiO<sub>x</sub>/20 already acted as a reliable anti-corrosion barrier.

		MF/Cu (blank) [Ω]	MF/Cu/SiO <sub>x</sub> /7 [Ω]	MF/Cu/SiO <sub>x</sub> /20 [Ω]
Initial el	ectrical resistance	<b>1.2</b> (+/-0.1)	<b>2.1</b> (+/-0.1)	<b>1.5</b> (+/-0.1)
Time	Medium			
48 hours	2% acetic acid	<b>1.2</b> (+/-0.1)	<b>2.2</b> (+/-0.1)	<b>1.5</b> (+/-0.1)
2 min.		<b>1.3</b> (+/-0.1)	<b>4.3</b> (+/-0.1)	<b>1.5</b> (+/-0.1)
4 min.	2º/ apatia apid	<b>1.5</b> (+/-0.1)	<b>10.6</b> (+/-0.2)	<b>1.6</b> (+/-0.0)
6 min.		<b>5.4</b> (+/-1.8)	<b>13.3</b> (+/-1.4)	<b>1.8</b> (+/-0.1)
8 min.	0.237811202	<b>75.2</b> (+/-12.5)	<b>17.5</b> (+/-2.2)	<b>2.2</b> (+/-0.1)
10 min.		<b>1616.2</b> (+/-45.6)	<b>50.1</b> (+/-4.4)	<b>2.4</b> (+/-0.4)

**Table 1** The superficial electrical resistance of the samples

#### 5 CONCLUSION

We tested the metallized polyester nonwoven MILIFE®, which has excellent electrically conductive properties due to chemically copper coated fibers. The copper coating results in a very low value (1.2 of electrical resistance Ω) measured on the fabric surface by contact electrodes at 1.5 cm. We have shown that, while in the acidic environment of 2% acetic acid without air access, the conductivity (the resistance) on the fabric surface did not change even after 48 hours, this product is highly sensitive to corrosive changes in the acid environment with the presence of an oxidant. In a solution containing 2% acetic acid and 0.25%  $H_2O_2$ , the metallized surface of the fabric already chemically changed within 4 minutes, which resulted in the increasing of electrical resistance and gradual color changes of the copper surface of the fabric and of the corrosive solution itself. The silica-based plasma-polymerized layer with the thickness of 388 nm was able to reliably protect the copper surface on polyester fibers from corrosive changes even after 10 minutes in the acidic and oxidizing medium at room temperature. This protective layer was prepared from a mixture of HMDSO precursor and oxygen. Low pressure in the working chamber (45 Pa) allowed plasmapolymerized deposition already at the RF generator power of 150W. The 20-minutes treatment did not damage the nonwoven polyester carrier MILIFE®, resistance the heat of which is stated by the manufacturer up to a maximum of 300°C. We have shown that the method of deposition of a protective silica-based layer using PECVD lowpressure plasma could be a promising way to protect the metallized polyester fabric surface from the corrosive effects of the acidic and oxidizing environment with minimal consumption of the organosilicate precursor. This would extend the field of applications and the life of this product.

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# COMPARISON OF TEXTILE MEMBRANES FOR MOISTURE TRANSPORT

#### Adnan Mazari and Antonin Havelka

Department of Clothing, Technical University of Liberec, 46117 Liberec, Czech Republic mazariadnanahmed@gmail.com

**Abstract:** Membranes are commonly used in garment and especially for technical garments to allow the flow of moisture and keep the micro climate dry. There are different kinds of membranes working on unique principles. In this research we compared 3 most commonly used membranes used for different types for garments, which are hydrophilic, hydrophobic and the microporous membrane. All 3 membranes types work on different principles and help to remove moisture from the microclimate. Different tests like water vapour permeability, air permeability and drape test were performed to obtain comparable results. The research work gives a good comparison of membranes for clothing considering the flow of moisture. The results show that nano porous membranes are much more permeable and have high drape ability as compared to other membranes.

Keywords: membranes, textile structures, moisture transport.

#### 1 INTRODUCTION

Membranes are semi-permeable substrates which allow certain compounds to transport from one phase to another. Therefore, membranes act as obstacles for some species while separating others [1-2]. Polymeric membranes like polyurethane, polyacrylate, polyester and polytetrafluoroethylene are primary substrates employed as inner layer or middle layer for multilayer clothing having several applications [3]. The membrane must display certain set of characteristics contingent on application and requisite characteristics of multilayer assembly i.e. in case of protective clothing and modern sports clothes which require outstanding barrier properties along with comfort and hygienic parameters, the membranes having high water-tightness must be utilized to deliver efficient and effective shield air non permeability and soaking through and at same time must allow high amount of water vapor to pass through them [4]. In multilayer clothing, various kinds of water and wind-tight membranes are utilized which are impermeable to liquid water vapor but permeable to water vapor.

There are 2 basic types of membranes [4, 5] i.e.:

- 1- Hydrophilic solid membranes,
- 2- Hydrophobic microporous membranes with compacted configuration.



Figure 1 Mechanism of hydrophilic membrane [13] (a), hydrophobic membrane [3] (b) and nano porous membrane structure (c)

1. In hydrophilic solid membranes, a breath through procedure for absorption and migration is instigated by heat and high humidity. There is chain of chemicals groups which entice water vapor molecules. Water vapor molecules utilize these chains as stepping stones to migrate from one side towards another.

2a. Microporous hydrophobic membranes in which breathing procedure is done by permitting sweat in the form of water vapor molecules to transmit by interconnecting micro-pores instigated by heat and high humidity. Transportation of liquid water is inhibited by micro-pores (100 times smaller than droplets of water) and by surface tension effect due to hydrophobic nature of membranes i.e. repels droplets of water.

*2b. Nano porous membranes* have pore size of 1-10 nm and mostly made from polyethylene terephthalate (PET). The membranes are commonly used for filtration and moisture transport. They are famous for low weight and better performance; these membranes are commonly used as sandwich layer in many sport wares

#### 2 COMMONLY USED MEMBRANES FOR CLOTHING

Following membranes are commonly used in the field of comfort and clothing:

- 1.Hydrophobic microporous membranes of several polymers generated by perforations of compact membranes i.e. by employing micro-beams of radiation of high energy pulsation lasers or bombardment of electrons [3].
- 2. Microporous hydrophobic membranes like polyurethane (PU) membranes created by phase procedure separation (inversion) as a consequence of selective evaporation of solvent and non-solvent. Primarily there are two procedures. First one is the wet coagulation in which extraction of solvent is an inductive factor. The second way is to have phase separation procedure caused by evaporation of solvent like thermal coagulation. Membranes like Porelle membranes, are one of such kind [3].
- 3.Microporous hydrophobic polytetrafluoroethylene (PTFE) membranes synthesized by drawing procedure under critical conditions from compact membranes, resulting in creation of several micro cracks. Normally this procedure is utilized to manufacture membranes from PTFE and sold in market under trade name of Goretex XCR, Goretex Paclite and some others [6, 7].
- 4. Hydrophilic membranes mostly consist of polyester (PES) and polyurethane. Sympatex Composites Co synthesizes hydrophilic membranes from polyester under trade name of Sympatex. On the other hand, Toyo Cloth generates hydrophilic membrane from polyurethane called BION [8, 9].

5.Nano porous membranes made by electrospinning or other techniques in which multiples webs are layered above each other to achieve nano porous structure. These membranes are available in market as Goretex, Crosstech, Tetratex, Porelle, Proline, Vapro, Sympatex, Action and Neoguard [10-12].

#### 3 THERMAL CLOTHING COMFORT

One of the prime requirements of clothing is of course to provide protection from extremes of climatic conditions and it acts as a barrier between human body and the external environment [9]. The most important feature of thermal clothing is to create a stable microclimate next to the skin in order to support body's thermoregulatory system, even if the external environment and physical activity change completely [17]. The thermal comfort of clothing system is related with thermal balance of body and thermoregulatory reactions to dynamic interactions with clothing and environment. Clothing acts as a regulator of heat and moisture transport between human body and the surrounding environment [12]. Transmission of heat and moisture plays very significant role in preserving thermophysiological comfort. The fabric should permit moisture (in the form of sensible and insensible perspiration) to be transferred from the body to the environment for cooling the body and decline the possibility of thermal decrease in thermal insulation of fabric due to build-up of moisture within the microclimate environment [4]. If clothing in contact with human beings is not dry, there will be escalation of heat flow from body, consequently resulted in undesirable heat loss from the body. This ultimately creates cool feel. In reality transmission of heat and moisture through clothing system is carried out in steady as well as dynamic/transient conditions [5].

#### 3.1 Moisture transport [13]

Liquid and moisture transfer mechanisms in the fibrous textiles include:

- vapour diffusion in the void space
- absorption, transmission and desorption of the water vapour by the fibres,
- adsorption and migration of the water vapour along the fibre surface,
- transmission of water vapour by forced convection.

Water vapour moves through textiles as a result of water vapor concentration differences. Fibres absorb water vapor due to their internal chemical compositions and structures. The flow of liquid moisture through the textiles is caused by fibre-liquid molecular attraction at the surface of fibre materials, which is determined mainly by surface tension and effective capillary pore distribution and pathways. Evaporation and/or condensation take place, depending on the temperature and moisture distributions.

Moisture vapour transmission parameters are calculated by following different standard methods:

- evaporative dish method or control dish method (BS 7209),
- upright cup method or gore cup method (ASTM E 96-66),
- inverted cup method and desiccant inverted cup method (ASTM F 2298),
- the dynamic moisture permeable cell (ASTM F 2298),
- the sweating guarded hot plate, skin model (ISO 11092).

The adsorption and migration phenomenon functions depend mechanism not only on the hydrophilicity of the fibre surface but also on the extent of the fibre surface available for adsorption. All the factors we mentioned about heat and mass transfer that affects the comfort are affected by some fabric and clothing parameters. At the time of designing the textile for thermal comfort or for improvement of thermal comfort it's important to know about these parameters and their possible effects. Textile structure and chemical nature of fibres effects the thermal comfort properties of textiles such as: fibre type, fibre diameter, fibre shape, texture method of fibre yarn types and production, porosity, pore size distribution, complexity of pores (open cell or closed cells), fabric structure and thickness, clothing design, fitting and thickness of clothing, position of layers (hydrophilic/hydrophobic), sorption of fibres and fabric and finishing applied to the fabric, etc. The moisture transport proceeds generally also by other mechanisms (capillary, sorption), but at the barrier textiles we can suppose that the diffusion way will be the more dominant. It is possible to describe moisture transport by a relation for mass transport:

$$q_{dif_i} = -D_i \cdot \nabla \cdot \rho_i \tag{1}$$

where:  $D_i$  is coefficient of diffusion transport of mass for the  $i^{th}$  component [m<sup>2</sup>.s<sup>-1</sup>],  $\nabla \rho_i$  is gradient of partial mass density for the  $i^{th}$  component [kg.m<sup>-3</sup>].

For a unit flow of moisture as a compound of gaseous environs with a partial pressure of  $p_i$ ( $p_i$  – partial pressure inside of porous clothing material,  $p_i$  – partial pressure outside the porous clothing material) it is possible to use a relation:

$$q_{dif_i} = D_i \frac{M_i}{RmT} \frac{p'_i - p''_i}{s}$$
 (2)

where:  $R_m$  is universal gas constant [kJ.kmol.K<sup>-1</sup>],  $M_i$  is molar mass [mol], T is temperature [K] and s is layer thickness [m].

From this relation it is possible to determine a coefficient of diffusion transport of a mass, which determines the diffusion transport of the water vapour in a fabric.



Figure 2 Heat and moisture transfer.

 $T_1$  - temperature under cloth,  $\varphi_1$ - relative humidity under cloth (100%=extreme sport),  $T_2$  - temperature of environment,  $\varphi_2$ - relative humidity of environment

#### 3.2 Water vapor permeability

It is also known as "breathability" and is defined as capability of textile substrate to transmit water vapour from surface of skin through the fabric to the exterior climate. Diffusion of water vapor should take place instinctively due to the vapour pressure difference through textile substrate. The water vapour disperses from the region of high vapour pressure (surface of human body) to the region of lower vapour pressure (exterior drier climate). The diffusion of water vapour takes place through fabric interstices and air spaces between the skin and the textile substrate [10].

#### 3.3 Water vapor resistance

Water vapour permeability has inverse relation with water vapour resistance which is illustrated as amount of resistance against the transmission of water vapour through textile substrate. As liquid water has an excellent conductivity of heat, the thermal resistance of a garment is directly affected by quantity of moisture present in the fabric. Consequently, the more occurrence of water in textile substrate, either due to normal absorption from the air or absorption of water due to perspiration, the greater will be the rate of conduction of heat [10].

#### 3.4 Permeability index

Woodcock established permeability index which displays evaporative performance of clothing. The permeability index  $(i_m)$  can be explained by the following equation:

$$i_m = \frac{R_t}{R_{et} \cdot LR} \tag{3}$$

where:  $R_t$  is the total thermal resistance of the clothing plus surface air layer (m<sup>2</sup>.°C/W), and  $R_{et}$  is the total evaporative resistance of the clothing plus the air layer (m2.kPa/W).

#### 3.5 Air permeability of textiles

Generally, the air permeability of a fabric can influence its comfort behaviors in several ways. In the first case, a material that is permeable to air is, in general, likely to be permeable to water in either the vapour or the liquid phase. Thus, the moisture-vapour permeability and the liquid moisture transmission are normally related to air permeability. In the second case, the thermal resistance of a fabric is strongly dependent on the enclosed still air, and this factor is in turn influenced by the fabric structure.

Air permeability is an important factor in determining the comfort level of a fabric as it plays a significant role in transporting moisture vapours from the skin to the outside atmosphere. The air in the microclimate between individual items of clothing also has a physiological function. When the body is at rest, this air in the microclimate contributes up to approximately 50% of the effective thermal insulation properties of the clothing. When the body is in motion, approximately 30% of the heat and moisture can be removed by air convection in the microclimate and air exchange via the clothing. The assumption is that vapours travel mainly through fabric spaces by diffusion in air from one side of the fabric to the other

#### 4 EXPERIMENTAL PART

A total of 4 samples were chosen for the testing of water vapour permeability. All membranes were on a laminate of polyester knitted fabric with 1 mm thickness and areal weight of  $135 \text{ g/m}^2$ .

 Table 1
 Samples details

Number	Туре	Composition	Thickness [mm]
1	Microporous	ePTFE	1.22
2	Hydrophilic	PET	1.19
3	Hydrophilic	PET	1.22
4	Nano membrane	PU/PES	1.58

Multiple devices were used to measure the water vapour permeability; following standards were used for following testing devices

- 1- Sweating Guarded Hot plate ISO11092
- 2- Desiccant Cup method ISO15496(B3)
- 3- Inverted cup method ISO 15496 (A2)
- 4- Permatest

#### 5 RESULTS AND DISCUSSION

All membranes were tested for thickness and then four standard methods were used for the water vapour permeability. It is important to use different methods as it gives us a good comparison of performance. It can be seen from the Table 2, the nano porous membrane has the highest water vapour and air permeability followed by microporous membrane and then hydrophilic membrane respectively.

Table 2 Membranes resul	ts
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No.	Туре	Composition	Thickness [mm]	SGHP [m2.pa/w]	B3 [g/m <sup>2</sup> .Pa.24h]	A2	Permatest [m <sup>2</sup> .Pa/W]
1	Microporous	ePTFE	1.22 (±0.3)	4.30	5.67	5.1	2.3
2	Hydrophilic	PET	1.24 (±0.4)	8.05	1.67	1.2	9.05
4	Nano membrane	PET	1.25 (±0.54)	3.85	6.85	5.4	2.2



Figure 3 Graphical illustration of water vapour flow through different membranes

#### 5.1 Air permeability of textiles

Air permeability tester (FX-3300) and SDLMO21S by using standard ISO9237 were used for air permeability testing. Generally, the air permeability of a fabric can influence its comfort behaviors in several ways. In the first case, a material that is permeable to air is, in general, likely to be permeable to water in either the vapour or the liquid phase. Thus, the moisture-vapour permeability and the liquid moisture transmission are normally related to air permeability. In the second case, the thermal resistance of a fabric is strongly dependent on the enclosed still air, and this factor is in turn influenced by the fabric structure.

Air permeability is an important factor in determining the comfort level of a fabric as it plays a significant role in transporting moisture vapours from the skin to the outside atmosphere. The air in the microclimate between individual items of clothing also has a physiological function. When the body is at rest, this air in the microclimate contributes up to approximately 50% of the effective thermal insulation properties of the clothing. When the body is in motion, approximately 30% of the heat and moisture can be removed by air convection in the microclimate and air exchange via the clothing. The assumption is that vapours travel mainly through fabric spaces by diffusion in air from one side of the fabric to the other [14-17]. The results show that hydrophilic membrane has no air permeability and nano membranes have the highest air permeability.

Table 3 Air permeability of membrane sam	ples
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Samples	Air permeability [L/m <sup>2</sup> /s]		
Hydrophilic membrane	0.2		
Microporous membrane	550		
Nano porous membrane	720		

#### 5.2 Stiffness / bending moment

Bending properties describes stiffness of fabric. Stiffness is the ability of material to resist deformation when force is applied on it. The instrument Tuhomer TH-4 measures force required to bend specimen by 60 degree. This instrument evaluates the bending moment of textile substrates by CSN 80 0858 standard. The size of specimen was 5×2.5 cm.

This can be explained by following equation:

$$M_o = F \times K \tag{4}$$

where:  $M_0$  is the bending moment [mN.cm], F is the force applied in mN and K is constant whose value is 0.52 (from standard).

Results show that the nano porous membrane is the most flexible. The greater the bending force F required to bend the textile substrate at particular angle, greater will be the bending moment which ultimately results into greater stiffness of textile substrate.

#### 5.3 Electron microscope

The electron microscope images of all membranes give us a clear idea of the structure of the membranes, Figure 5 shows the SEM image of the hydrophilic membrane, there are no visible pores and the moisture molecules are attracted to layers and moves to other layers in steps. The close pore structure gives no air permeability to these membranes.

The hydrophobic microporous membrane are shown in Figure 6, the micro sized pores are visible which are the paths for the moisture transport. These are layers are commonly used in clothing as they are permeable to moisture as well as to the air.



Figure 4 Bending moment of membranes



Figure 5 Hydrophilic membrane



Figure 6 Hydrophobic microporous membrane



Figure 7 Nano porous membrane

The nano porous membrane shows in Figure 7, in which multiples webs are layered above each other to achieve nano porous structure, these kinds of membranes are first choice for filtration but are also used in clothing. The layers provide good air and moisture permeability.

#### 6 CONCLUSION

From the research work we are able to conclude that nano membranes has the highest air permeability, better flexibility and higher water vapor permeability followed by microporous and hydrophilic membranes respectively. In clothing the flexibility of the garment is very important and using a non-flexible membrane just not recommended.

We did mention that ePTFE is a synthetic material, as such it does affect the environment, making it the least eco-friendly of the two. It is also very slow to degrade in nature, unlike polyether and ester.

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# HALLOYSITE NANOTUBES MODIFIED BY REPELLENT IN POLYPROPYLENE FIBRES: INFLUENCE ON SUPERMOLECULAR STRUCTURE AND MECHANICAL PROPERTIES

Zita Tomčíková<sup>1</sup>, Anna Ujhelyiová<sup>2</sup>, Katarína Holcová<sup>1</sup>, Peter Michlík<sup>1</sup> and Marcela Hricová<sup>2</sup>

<sup>1</sup>Research Institute for Man-Made Fibres, a. s., Štúrova 2, 059 21 Svit, Slovak Republic
<sup>2</sup>Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Radlinského 9, 812 37 Bratislava, Slovak Republic
<u>tomcikova@vuchv.sk</u>

**Abstract:** Nowadays, there is a growing request for smart fibres therefore modification of classic fibre types is essential. Modification of the mass or surface of fibres by nanotechnologies is one of the most prospective ways how to ensure the special properties of clothing and technical textiles. This article is focused on the study of modified halloysite nanotubes by repellent (HN-R) used in polypropylene fibres (PP). The halloysite nanotubes are natural nanoadditive with porous inner surface which can be used as the carrier of chemically and biologically active agents. The influence of different content of modified halloysite nanotubes in undrawn and drawn nanocomposite polypropylene fibres on the supermolecular structure (birefringence, sound velocity in fibres, and crystallinity index), fineness and basic mechanical properties (Young's modulus, tenacity at break and elongation at break) was investigated. The obtained experimental results of nanocomposite fibres were compared with results of supermolecular structure and mechanical properties of PP fibres without additive content prepared under the same technological conditions.

Keywords: halloysite nanotubes, PP nanocomposite fibres, structure, mechanical properties.

#### 1 INTRODUCTION

Linear polypropylene (PP) is widely used thermoplastic material because it offers a unique combination of desirable chemical and physical recyclability properties, and low cost. The advantages of PP are: the high flexural strength as a consequence of semicrystalline nature, high resistance to moisture, good chemical resistance over a wide range of bases and acids, good impact strength and good fatigue resistance, and also a good electrical resistance [1-3]. However, PP lacks the melt strength and strain hardening in extensional flow required for many industrial processes as well as the absence of functional groups and low polarity makes PP difficult to dye. From chemical point of view PP is susceptible to oxidation and UV degradation; it has a high flammability and poor resistance to chlorinated solvents and aromatics [4-6]. For above mentioned properties there is still much scientific and industrial interest in modifying PP for improving its processability and properties required for more demanding applications [7, 8]. Polypropylene except to the conventional plastic applications also lends itself well in fiber applications including: ropes, carpets, upholstery, clothing what gives it a wider range of uses [3, 9]. Although the fibre production has experienced the slowest growth in the last 3 years to about

106 million tons, the man-made fibre business still 10-year continues its expansion in spite of the worsening of economic climate. For example, the filament yarns recorded the highest grow rate in 3 years to 48 million tons (PET +4.0%, PA -0.5%, CV +1.8%, PP +1.5%) [10]. This is largely due to much research which has been done in the field of fibres modification including also PP fibres. Fibre manufacturers must keep pace with the development of new polymer modifications and combinations, enabling such further functionalization of the product. The man-made fibre market needs new "intelligent" materials to continue with its growth [11].

One of the most promising ways how to ensure sophisticated properties of textiles is modification of polymer matrix by nanoparticles during fibre extrusion. Procedure, how mono- or multi- functional properties of fibres can be achieved even at low concentrations of nanoadditives, which is also very beneficial in economic terms [12]. Nanocomposite systems based on natural layered silicates, particularly montmorillonite and halloysite belongs significant to the most studied polvmer nanocomposites [13-15]. Halloysite nanotubes (HN) are types of naturally occurring 1:1 clays with nanotubular structures and similar chemical composition to kaolin.

Due to various characteristics such as nanoscale lumens, high length to diameter ratio, relatively low hydroxyl group density on the surface, etc., numerous exciting applications have been discovered for this unique clay. The results of studies suggest that these nanocomposites exhibit remarkable performance such as reinforcing effects, enhanced flame retardancy and reduced thermal expansion [15]. The shape of halloysite the hollow nanotubes with the porous inner surface, can be used as the carrier of chemically and biologically active agents [16].

In our research we used the synthetic compound DEET (N,N-diethyl-meta-toluamide) as the most effective and widely used insect repellent (R) in the world [17].

In this study, the influence of halloysite nanotubes content modified by repellent (HN-R) together with uniaxial deformation on the supermolecular structure mechanical properties basic as well as of polypropylene fibres was investigated. The repellent lost by washing were also investigated. The undrawn and drawn PP fibres modified with HN-R were prepared by discontinuous technological process of spinning and drawing. Obtained results of modified PP fibres were compared with PP fibres without HN-R nanoadditive prepared under the same technological conditions.

#### 2 EXPERIMENTAL AND METHODS

#### 2.1 Materials

Isotactic granulated polypropylene (PP), produced Company, Slovnaft Slovak Republic, bv with MFR 27.6 g/10 min (230°C/2.16 kg) and nanoadditive - halloysite nanotubes 685445 modified repellent N,N-diethyl-m-toluamide by (HN-R), prepared by company A1Synth, Ltd., Slovak Republic, were used. The content of repellent (R) inside the hollow nanotubes was 20 wt.%. The masterbatch with 10 wt.% of HN-R, developed by Research Institute for Man-made fibres, a.s. Svit, where Elvax 150W (ethylene-vinyl acetate copolymer resin) produced by DuPont Packaging & Industrial Polymers (USA), was used as a polymer carrier of HN-R during the fibre preparation process.

<u>Preparation of modified nanoadditive halloysite</u> nanoclay 685445 by repellent N,N-diethyl-mtoluamide (HN-R)

The halloysite nanotubes modified with repellent (HN-R) was prepared as follows:

Repellent was dried in the three steps before modification of halloysite nanotubes (HN). HN was activated before modification in vacuum dryer under pressure 0.1 mbar and temperature 60°C during 8 hours. Subsequently, HN was modified as follows: the activated halloysite in dry diethyl ether was stirred in a sulphonation flask by a mechanical stirrer under an argon atmosphere. Repellent was slowly added dropwise in dry diethyl ether after 30 min. The contents were stirred at slow speed for 60 minutes. The contents of the flask were transferred to an argonated closed frit and the solvent was allowed to flow slowly into a round flask of so-called "Schlenk method". After filtration, the solvent was again poured onto a frit. Finally, the solvent was filtered off, the filter cake was washed with dry diethyl ether and dried on a rotary evaporator. The resulting sample was dried in a vacuum oven. From the resulting experimental measurements, adsorption of additives about 20% into activated halloysite was evident.

#### 2.2 Fibre preparation

The modified PP fibres with content of HN-R from 0.25 to 2.00 wt.% (PP/HN-R) from mechanical mixture of PP granulated polymer and 10 wt.% masterbatch HN-R were prepared usina the classical discontinuous process of spinning and drawing. The laboratory discontinuous line has an extruder with diameter of D=32 mm, with a discontinuous one-step drawing process. The constant processing conditions spinning temperature of 220°C, spinning die plate of 25 holes with diameter of 0.3 mm, final spinning process speed of 1500 m.min<sup>-1</sup>, the drawing ratio  $\lambda$ =2.0, the drawing temperature of 130°C and final drawing process speed of 100 m.min<sup>-1</sup> were used.

#### 2.3 Methods

#### The fibre birefringence - total orientation of fibres

The orientation of macromolecular chains in fibre expresses the level of anisotropy of oriented polymer system (fibre). The total orientation of prepared unmodified and modified PP fibres was evaluated using polarization microscope DNP 714BI. The refractive indexes of light in fibre axis (n||) and in perpendicular direction of fibre (n $\perp$ ) were determined. From refractive indexes of light the fibre's birefringence was calculated according to equation 1:

$$\Delta n = n_{\parallel} - n_{\perp} \tag{1}$$

#### The sound speed in fibres

The sound speed in fibres is given by the ratio of fibre length and time needed for transfer of acoustic nodes across this length (expressed in km.s<sup>-1</sup>). It is dependent on internal structure of fibre arrangement (expressed by supermolecular structure parameter) and may be served as a measure of fibre anisotropy. The sound speed in fibres was measured by Dynamic Modulus Tester PPMSR.

#### Crystallinity index (FT-IR)

Crystallinity index  $I_k$  of PP fibres represents the fraction of the crystalline phase in PP fibres. It is determined as the ratio of integrated absorbance of absorption band of 840 cm<sup>-1</sup> (*Ai840*) characterizing the regularity of macromolecular chains segments arrangement and integrated absorbance of absorption band of 2723 cm<sup>-1</sup> (*Ai2723*) as the internal standard influencing the degree of crystallinity, (Equation 2):

$$I_k = \frac{A_{i840}}{A_{i2723}} \tag{2}$$

Crystallinity index of modified PP/HN-R fibres and unmodified PP fibres was evaluated by FT-IR spectrophotometer 8400 Shimadzu.

#### Mechanical properties of fibres

The mechanical properties (tenacity at break, Young's modulus) at break and elongation of unmodified and modified PP fibres were measured using Instron 3343 equipment (USA) in accordance with the STN EN ISO 2062:2010. A gauge length of 125 mm and clamping rate of 500 mm/min were used. The average of at least 10 individual measurements was used for each fibre. The fineness was measured in accordance with the STN EN ISO 2060:1998.

#### Washing test

For estimation of repellent stability in fibre we determined the weight loss of repellent after 5 and 20 washes. The washing conditions were: temperature 40°C, concentration of washing agent 5 g/l and washing time 30 min. After washing fibres were rinsed two times in distilled water, then in flowing water and finally they were air-dried.

The weight loss (*UR*) of repellent after the washing procedure was calculated as the weight difference between weight before washing  $m_0$  and weight after washing m (5 and 20 washes) from 10 repetitions for one fibre according to the following equation 3:

$$UR = \frac{m_0 - m}{m_0}.100$$
 (3)

For reliable estimation of repellent with nanotubes in modified PP/HN-R fibres there were determined the relevant weight loss calculated as difference between final weight loss of drawn modified PP/HN-R fibre and final weight loss of drawn PP standard fibre including also the soluble amorphous or low molecular part of PP.

#### 3 RESULTS AND DISCUSSION

Stability of the spinning and drawing process of the studied system PP/HN-R in concentration range of HN-R 0.25 - 2.0 wt.% was evaluated and compared with stability unmodified PP standard.

It was found that the studied system PP/HN-R (spinning speed of 1500 m.min<sup>-1</sup>) is fibre forming in the whole range of HN-R concentration and comparable with stability of unmodified PP standard, but process is stable only to 1 wt.% HN-R, over this content the slight odor under spinneret was felt. It was caused by the release of the repellent from halloysite nanotubes at higher HN-R content in PP matrix.

For following discontinued drawing process and the next evaluations only concentration range of HN-R from 0.25 to 1.0 wt.% in PP matrix of the studied system PP/HN-R was used. The drawing process of modified PP/HN-R fibres on the drawing ratio  $\lambda$ =2.0 was stable and comparable with stability of unmodified PP standard fibre.

By spinning and drawing processes PP/HN-R fibres were prepared to study their supermolecular structure parameters and basic mechanical properties which were compared with the unmodified PP standard.

Figures 1 and 2 show the effect of various content of halloysite nanotubes modified by repellent on the supermolecular structure parameters of undrawn and drawn modified PP fibres.



**Figure 1** Dependence of birefringence (a) and sound speed (b) of undrawn and drawn ( $\lambda$ =2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content



**Figure 2** Dependence of crystallinity index  $I_k$  of undrawn and drawn ( $\lambda$ =2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content

In case of undrawn modified PP fibres the total average orientation of macromolecular chains segments (birefringence) due to growing content of HN-R in the PP matrix was practically unchanged up to 0.75 wt.% content of HN-R. On the other side a slight decrease in birefringence with increasing HN-R content in PP fibers was observed in drawn fibers (Figure 1a) what can be the result of the steric braking effect of halloysite nanotubes modified by repellent on the orientation of macromolecular polymer chains segments in the matrix in the direction of fibre axis during the drawing process.

Similarly, also decrease of the orientation of PP macromolecular chains segments in surface layers (sound speed; Figure 1b) with growing content of HN-R significantly have been showed in drawn PP/HN-R fibres and in undrawn PP/HN-R fibres sound speed was slightly decreased only in comparison with unmodified PP standard.

From Figure 2 it is evident that the fraction of crystalline phase (crystallinity index FT<sub>IR</sub>) of undrawn PP/HN-R fibres is slightly growing with an increase of nanoadditive content. It can be the result of nucleating effect of HN-R particles on the PP matrix in the spinning process. In contrary, due to uniaxial deformation occurs the crystalline phase fraction is decreased in PP/HN-R fibres, what may be caused by steric braking effect of halloysite nanotubes modified by repellent as mentioned above.

Figures 3 and 4 show the effect of various HN-R content on the basic mechanical properties of undrawn and drawn modified PP/HN-R fibres. It was found that the content of nanoadditive HN-R from 0.25 to 1.0 wt.% in the PP matrix of fibre does not affect the fineness of undrawn and drawn modified PP/HN-R fibres (Figure 3a).

Tenacity at break respective Young's modulus of undrawn modified PP/HN-R fibres slightly decreases (up to about 20% and up to about 30%) with increasing content of modified nanoadditive, while the elongation of fibres decreases slightly (up to 40% absolute) Tenacity at break and Young's modulus for drawn modified PP fibres also decrease with growing content of modified nanoadditive (up to max 25%) as well as their elongation at break (up to approximately 30 % absolute). The decline of elongation at break together with tenacity at break in undrawn and drawn modified PP/HN-R fibres with growing content of modified nanoadditive can be a result of rising content of ethylene-vinyl acetate copolymer matrix of masterbatch in modified PP fibres.



**Figure 3** Dependence of fineness (a) and elongation at break (b) of undrawn and drawn ( $\lambda$ =2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content



**Figure 4** Dependence of tenacity at break (a) and Young's modulus (b) of undrawn and drawn ( $\lambda$ =2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content

The change of mechanical properties is also governed by the drawing process (see Figures 1-4). Uniaxial deformation of undrawn modified PP/HN-R fibres significantly increased the total average orientation of macromolecular chains segments Figure (birefringence, 1a) up to 42% and of PP the orientation macromolecular chains in surface layers (sound speed, Figure 1b) up to 38%, causing higher tenacity at break about twice (Figure 4a) and Young's modulus of elasticity about three times (Figure 4b) over the entire evaluated range of HN-R nanoadditive content.

The crystallinity index has different of trends curves undrawn and drawn fibres with increasing content of modified nanoadditive (Figure 2).

In the case of undrawn fibres the growing tendency of curve was observed with increasing content of modified nanoadditive and in the case of drawn fibres the decreasing tendency with increasing content of HN-R was observed. These results show that only up to 1 wt. % of HN-R the uniaxial deformation has positive influence on increase of the crystallinity index. In this point the curves intersect. On the other hands fall of elongation at break (Figure 3b) due to uniaxial deformation was expected, because it's generally known, that the elongation at break is reciprocal value to tenacity at break. The fineness (Figure 3a) also decreased due to uniaxial deformation of undrawn fibres. From the obtained results it is evident, that the mechanical properties of modified PP/HN-R fibres are in good correlation with their supermolecular structure parameters.

From industrial point of view, it is important to know what quantity of a repellent is released from the fibers after washing, therefore washing test modified PP/HN-R fibres was performed. of Percentual weight decrement was calculated after 5 and 20 washing cycles (Table 1). It is evident that loss weight after 5 and 20 washing cycles was observed already at PP standard fibre. It could be related to the content of finishes as well as oligomers of polypropylene which can also migrate into the water. For that reason, the reduced weight loss was calculated and was supposed that reduced loss weight of fibres during their washing tests is connected with loss of repellent content from drawn modified PP/HN-R fibres. But from the experimental results it is obvious that the values of reduced weight loss are almost higher as the values of repellent content in fibres (Table 1). This is associated with further release of finishes as well as oligomers of polypropylene, therefore loss of fibres weight during their washing is not directly proportional by the content of repellent in halloysite nanotubes. It is evident from reduced weight loss that the part of repellent stayed in nanotubes hallovsite after spinning process.

Table '	1 Relative weigh	t loss after 5 an	d 20 washes	of modified	PP/HN-R	fibres and	unmodified PP	standard fibre
Tuble	I Relative weigh	1000 41101 0 411		ormounicu	1 1 / 1 11 1 1 1	nores and	unnouncuiri	Standard libro

Carrier/modified	Banallant contant	5 wa	ashes	20 washes	
nanoadditive content	in modified PP fibres	Weight loss [%]	Reduced weight loss [%]	Weight loss [%]	Reduced weight loss [%]
PP standard	-	0.72	-	0.61	-
PP/HN-R/0.25%	0.05	0.91	0.19	0.76	0.15
PP/HN-R/0.50%	0.10	0.76	0.04	0.77	0.16
PP/HN-R/0.75%	0.15	0.75	0.03	0.74	0.13
PP/HN-R/1 00%	0.20	0.99	0.27	0.80	0.19

Weight loss [%] is final weight loss of fibre calculated after washing. Reduced weight loss [%] is calculated as difference between final weight loss of drawn modified PP/HN-R fibre and final weight loss of drawn PP standard fibre

#### 4 CONCLUSION

The nanoadditive - halloysite nanoclays modified by repellent, has been prepared with the content of repellent to 20 wt.%. Influence of different content (0.25 - 2.0 wt.%) of modified nanoadditive HN-R in PP matrix during the discontinuous spinning and drawing process was investigated and compared with the stability of unmodified PP standard. It was found that content of HN-R only up to 1 wt.% in PP matrix of the studied system PP/HN-R (spinning speed of 1500 m.min<sup>-1</sup>) is fibre forming and stable but over this content the slight odor under spinneret felt. By discontinued drawing was process at drawing ratio  $\lambda$ =2.0 and in the concentration range of HN-R from 0.25 wt.% to 1.0 wt.% in PP matrix the drawn PP fibres were prepared for evaluation of supermolecular structure and basic mechanical properties.

Addition of modified halloysite HN-R into PP matrix led to the decrease in structure parameters (birefringence, sound speed and crystallinity index) as well as in basic mechanical properties (tenacity at break, elongation at break and Young's modulus) of drawn modified fibres in comparison to drawn unmodified PP standard fibre. In undrawn modified PP fibres the results are not so unambiguous.

The content of repellent in PP modified fibres has been verified by washing process. Reduced loss weight showed that halloysite nanotubes protected some amount of repellent during spinning process because the final weight loss of modified PP fibres is higher than final weight loss of PP standard fibre, but on the other side it was found that loss of fibres weight during their washing tests is not directly proportional by content of repellent in halloysite nanotubes. Based on our result we can state that the halloysite nanotubes protect components inside hollow tubes.

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# NANOCOMPOSITE SANDWICHES CONTAINING PHASE CHANGE MATERIALS

#### Jakub Wiener<sup>1</sup>, Jiří Militký<sup>1</sup>, Jaromír Marek<sup>2</sup>, Mohanapriya Venkataraman<sup>1</sup>, Guocheng Zhu<sup>3</sup> and Juming Yao<sup>3</sup>

<sup>1</sup>Department of Material Engineering, Faculty of Textile Engineering, Technical University of Liberec, Czech Republic <sup>2</sup>Institute CxI, Technical University of Liberec, Liberec 46117, Czech Republic <sup>3</sup>Silk Institute, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou, China jakub.wiener@tul.cz, jiri.militky@tul.cz, jaromir.marek@tul.cz, mohanapriya.venkataraman@tul.cz zgg@zstu.edu.cn,

vaoj@zstu.edu.cn

**Abstract:** Energy storage has become an important part of renewable energy technology systems. The latent heat energy storage realized using a phase change material (PCM) is one of the most effective techniques of energy storage because of high energy storage density. PCM must be protected with suitable structures against water and other factors. Typical example of it is the encapsulation of PCMs into polymeric capsules. In this study, nanocomposite sandwiches composed from nanofibrous layers containing phase change materials and protective layers were evaluated. In comparison with nonporous polymeric active layers, the nanofibrous PCM rich layer have a higher capability to stabilize and separate PCM.

Keywords: phase change materials, PCM, energy storage, thermal, DSC, contact angle.

#### **1** INTRODUCTION

Phase change capability of water is one of the main factors protecting life in our planet. Without high melting heat and high thermal capacity of water, our climate will be much more extreme. Similar effects are used by many research teams to increase comfort of clothing or protect human body against extreme low or high temperatures. The latent heat energy storage realized using a phase change material (PCM) [1-7] is one of the most effective techniques of energy storage because of their high energy storage density. PCM are capable of storing thermal energy as a result of phase changes (liquid/solid or solid/solid). For our experiment we used PCM materials with high melting heat and optimal melting temperature. Application of PCMs in protected forms is necessary for clothing applications because a liquid form of PCM on textile structures are unstable and will be lost in a short time if it will be not protected. The most common applications of PCM are based on:

- (i) micro-encapsulated form,
- (ii) filling of porous structures as nano-assemblies, foams or aerogels,
- (iii) shape stabilization by forming of polymer blends,
- (iv) creation of nanocomposites with a suitable matrix.

The aim of this contribution is to describe the development of special heat storage sandwiches composed from nanocomposite layer containing PCM and nanofibrous protective layers. The nanofibrous layer is used as a loaded layer and as a barrier layer to avoid a leakage of molten PCM. These structures can be improved by addition of special components enhancing thermal conductivity and improving electromagnetic shielding. With this improvement, these composite structures can be used for development of special pockets or covers for portable electronic devices such as laptops, smartphones etc., protecting them against sudden heat shocks and avoiding identification of their presence inside.

#### 2 THEORY OF PHASE CHANGE MATERIALS

PCM functionality is based on the heat absorption or release when they undergo a phase change from solid to liquid and vice versa (Figure 1).



Figure 1 Phase change in PCM

In literature, we can find a large number of phase change materials that are organic, inorganic and eutectic which are active in different temperature ranges. The well-known organic PCMs, with solidliquid phase transition, are paraffin waxes, poly(ethylene glycol)s, fatty acids and their derivatives. Some organic PCM, such as

polyalcohols and polyethylenes undergo the solidsolid phase transition at a fixed temperature. PEGs as PCMs are very good candidates for filling of porous structures. PEGs are linear dimethyl ether chains with hydroxyl ending groups, HO-CH<sub>2</sub>-(CH<sub>2</sub>-O-CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>-OH, soluble in water and selected organic solvents. PEGs have relatively large heat of fusion, resistance to corrosion and wide melting point range adjustable by their molecular mass  $M_w$ (Table 1) [8-10].

Table 1 Characteristic of PEGs

M <sub>w</sub> [g mol⁻¹]	T <sub>M</sub> [°C]	Δ <i>H</i> <sub>fus</sub> [J.g <sup>-1</sup> ]	ΔH <sub>cr</sub> [J.g <sup>-1</sup> ]
600	22.2	108.4	116
1000	32.0	149.5	140
1500	46.5	176.3	169

Tuning of melting point is simply made by mixing of PEGs with different molecular mass. PEGs are used as PCMs in a variety of thermal storage applications ranging from building envelopes, coated fabrics, foams and fibers. They have a high heat of fusion, low and moderate melting temperature intervals, low vapor pressure, high chemical and thermal stability, non-flammability, biodegradability, non-toxicity, and non-corrosive properties [11, 12, 3, 4]. The melting temperatures  $T_{M}$ , heats of fusion  $\Delta H_{fus}$  and heats of crystallization  $\Delta H_{cr}$  of PEGs increase gradually with their molecular mass increase.

#### 3 MATERIALS AND METHODS

A "smart heat storage" nano composite structure was created from a central "active layer" containing a PCM, which was covered by "protective layers" on both sides. The "active layer" and the both "protective layers" contain a nanofibrous layer. As the core of "active layer", the polyamide nanofibrous layer with a fiber diameter approximately 200 nm in a standard planar form was used (Figure 2). The "active layer" was created by loading of the electrospun nanofibrous assembly (10 wt.%) by 90 wt.% of PEG  $M_W = 1500$  (melting temperature  $T_M = 43-46^{\circ}C$ ).

This "active layer" was covered by "protective layers". Material of the "protective layers" was selected from comparison of 10 types of nanofibrous layers such as PA, PUR and AC, with a different chemical different composition and modified by hydrophobization methods such as plasma deposition, hydrophobic finishes and oleophobic finishes. Criterion of the selection was a repellency of the melted PEG estimated by a modified method of a contact angle measurement. The melted PEG at 70°C was deposited on the tested sample in form of droplet with volume approximately 20 microliters. Droplet was held on the tested sample for 10 minutes at 70°C. The sample was then cooled at standard laboratory conditions for 2 hours and the contact angle was estimated by the optical method

with the image analysis system. For the prepared samples, the heat of fusion was evaluated using DSC measurements.



**Figure 2** Polyamide nanofibrous layer used as active layer containing PCM

#### 3.1 Thermal effect calculation

The heat evolved by the phase change is equal to:

$$Q = m L = V \rho L \tag{1}$$

where: m is mass, V is volume and L [J/g] is latent heat (e.g. for PEG it is 121).

The heat produced by heating (sensible heat storage) is equal to:

$$Q = m c dT = V \rho c dT$$
<sup>(2)</sup>

where: dT is temperature change and c [J/(kg.K)] is specific heat (for water it is 4190).

The heat transferred by conduction is equal to:

$$\frac{Q}{t} = \lambda A \frac{dT}{h}$$
(3)

where:  $\lambda$  [W/(m.K)] is thermal conductivity (air 0.026, water 0.68, skin 0.09, PES 0.2, Ag 428), *A* is cross section area, *t* is time and *h* is thickness.

Let PCM materials of mass *m* [kg] having heat of fusion per unit mass  $\Delta H_{fus}$  [J/kg], average specific heat between initial temperature  $T_i$  [°C] and melting temperature  $T_M$  [°C] is  $C_{sp}$  [kJ.kg<sup>-1</sup>.K<sup>-1</sup>] and average specific heat between  $T_M$  and final temperature  $T_f$  [°C] is equal to  $C_{lp}$  [kJ.kg<sup>-1</sup>.K<sup>-1</sup>]. The total stored heat Q [J] depends on the final temperature and its relation to initial and melting temperature.

$$Q = m \left[ C_{\rm sp} \left( T_{\rm M} - T_{\rm i} \right) + f \left( \Delta H_{\rm fus} + C_{\rm sp} \left( T_{\rm f} - T_{\rm M} \right) \right) \right]$$
(4)

where: *f* is fraction of melted PCM.

#### 3.2 Layer containing PCM

Let us assume a layer containing PCM with volume ratio  $v_{PCM}$ , density  $\rho_{PCM}$ , latent heat of phase change *L*. Fibrous layer with length  $I_F$  and width  $c_F$ , i.e. surface area  $S_F = I_{F.}c_F$  and thickness *h* composed from fibers with density  $\rho_{e.}$  Planar mass:

$$w_T = m_T / S_F = \rho_T h \tag{5}$$

(*gsm*/1000, where *gsm* is weight of fabric in grams per surface in meter squared). Total mass of fibrous layer  $m_{\tau}$  is equal to:

$$m_{T} = \rho_{T} V_{T} = \rho_{T} S_{F} h = (1 - Po) h \rho_{F} S_{F}$$
(6)

Mass of PCM  $m_{PCM}$  is equal to:

$$m_{PCM} = \rho_{PCM} v_{PCM} V_T = \frac{\rho_{PCM} v_{PCM} m_T}{\rho_T}$$

$$= \frac{\rho_{PCM} v_{PCM} m_T}{\rho_{PCM} v_{PCM} m_T} = \rho_{PCM} v_{PCM} h S_F$$
(7)

Heat due to phase change  $Q_{PCM}$  is then equal to:

$$Q_{PCM} = m_{PCM} L = \frac{\rho_{PCM} v_{PCM} m_T L}{\rho_{PCM} v_{PCM} + \rho_F (1 - v_{PCM})}$$
(8)  
=  $\rho_{PCM} v_{PCM} h S_F L$ 

For the case of heat transfer in PCM of volume fraction  $v_{PCM}$  from solid to liquid phase, when convection is governing process, is time to phase change equal to:

$$t[\mathbf{s}] = \frac{h^2 v_{PCM} \rho_{PCM} L}{\lambda \, dT}$$
(9)

#### 4 RESULTS AND DISCUSSION

The specified thermal phenomena of PCM can be characterized by using differential scanning calorimetry (DSC), determining the relevant equilibrium regions, phase transitions and related temperatures. The modulation of the thermal signal provides information about the phase transition and compositional homogeneity. The DSC trace of smart heat storage" sandwiches is shown in Figure 3. The heat of fusion 148 J/g of the three-layer composite structure was obtained as area under solid line peak on DSC trace (Figure 3).

The contact angle measurement by using of PEG droplets was complicated by spontaneous crystallization of melted PEG. In addition, there appeared higher lateral adhesion forces typical for hydrophobic surfaces [13]. Resulted droplets are then significantly asymmetric (Figure 4).

Measurement of contact angle between PEG and the nanofibrous layer showed high attraction forces between melted PEG and the nanofibrous layer. Among all the protective nanofibrous layers tested, only polyamide 6 (PA) nanofibrous layer modified by polytetrafluoroethylene (PTFE) was found effective with an estimated average contact angle between nanofibrous mat and PEG solid droplet approximately 120° (Figure 5). The "protective layers" were then in final form realized by PA nanofibrous assembly prepared by electrospinning and modified by PTFE.



Figure 3 DSC trace of smart heat storage sandwiches



Figure 4 Deformation of PEG solid droplets on nanofibrous layer



Figure 5 Contact angle measurement - PEG solid droplets on nanofibrous layer

The "active layer" containing PEG was combined with the "protective layers" (Figure 6) to build up the "smart heat storage" sandwiches.



Figure 6 "Smart heat storage, sandwiches

The protective layers protect PEG leakage present in the "active layer" not only during heat exposition, but also during washing process or during ironing process.

This "smart heat storage" sandwiches are in fact self-stabilized by the behavior of PCM rich active layer and protective layers repellency against molten PEG.

#### 5 CONCLUSIONS

In this study, the "smart heat storage" nanocomposite sandwiches containing PCM were created and tested. The contact angle between melted PEG and the nanofibrous laver showed high attraction forces between both materials avoiding leakage. Also, the influence of molecular weight on PEG, the phase transition characteristics of DSC. determined by be considered can as an efficient tool for tuning thermal energy storage range. These sandwiches can be used for selected clothing applications due to their extreme heat storage capacity, textile character of surface and water vapor permeability.

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