Three-layer knitted materials for protective clothing

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Abstract. The results of investigating multifunctional 3D knitted materials dedicated for protective clothing were presented. The 3D design structures were made on a circular knitting machine using yarns with flame retardant or electrostatic properties. The functionality imparted to each of the assortments developed was verified during the tests in accredited laboratories as well as by assessing their biophysical properties. Based on the analysis of the test results, a beneficial effect of the raw materials and the 3D structure of knitted fabrics were demonstrated. Designed garments could be useful as individual protection clothing for workers exposed to harmful occupational environment factors, such as heat and static electricity. The study was conducted within the project EUREKA E! 5799 BATAN “Multifunctional knitted fabrics with barrier properties for clothing”.

1. Introduction

The problems of human health and life protection in work environment are a current subject of studies in many research centers. One of them is the development of protective clothing and search for new technological and structural solutions in the processes of their manufacture. Textiles designed for protective clothing gain their desired properties by using proper textile raw materials, designed structures and special finishing treatments.

Among the factors mentioned, a priority issue includes raw materials and their modification to obtain multi-functional features, e.g. high strength and flame-retardant characteristics [1-5]. The analysis of raw material market allows one to select yarns, offered by manufacturers, with special properties, made of the given type of fibers in 100 % as well as in blended systems that owing to their properties can be used in specified applications, such as:

- Protective clothing against fire and high temperatures: Meta-Aramid Nomex® T450, Para-Aramid Kevlar® stretch broken, Panox®, Vectran®, Viscose FR®, Modacryl,
- High resistant clothing protecting against cutting and abrasion: 100% Kevlar®, Kevlar®/glass filament, Kevlar®/steel wire, Vectran®,
- High strength clothing protecting against abrasion and high temperatures: Kevlar®, Vectran®, polyamide, Zylon®,
- Antistatic clothing and filtration materials: 100 % Inox, polyester/Inox, Nomex®/Inox, Kevlar®/Inox, polyamide/Inox, Beltron®, Negastat®.

The use of the yarns mentioned above depends on the basic properties of fibers that are used for their production. Some essential properties for selected types of fibers are presented in Table 1. The characteristics of the given raw materials presented by manufacturers constitute a valuable assistance
for the producers of textiles, whose production is connected with fulfilling many specified requirements [6].

**Table 1.** Selected properties of special fibers used in the production of yarns designed for protective clothing

| Parameter of fiber | Most often used fiber linear density [dtex] | Specific gravity [g/cm³] | Tenacity [cN/tex] | Elongation [%] | Max. temp. that unchange the fiber structure [°C] | Temperature of essential changes in fiber [°C] |
|--------------------|--------------------------------------------|-------------------------|-------------------|----------------|-----------------------------------------------|-----------------------------------------------|
| Kevlar®            | 1.7                                        | 1.44                    | 210               | 3              | 200                                           | 680                                           |
| Nomex®             | 2.2                                        | 1.38                    | 48                | 22             | 200                                           | 640                                           |
| Panox®             | 2.2                                        | 1.36                    | 19                | 25             | 200                                           | 580                                           |
| Viscose FR®        | 2.2                                        | 1.52                    | 18                | 16             | 170                                           | 400                                           |
| Polyester          | 2.4                                        | 1.38                    | 50                | 14             | 130                                           | 220                                           |
| Polyamide 6.6      | various                                    | 1.14                    | 66                | 40             | 110                                           | 220                                           |
| Inox (metal)       | 7.9                                        | 7.9                     | 23                | 1              | 690                                           | 980                                           |
| Glass fiber        | various                                    | 2.6                     | 60-100            | 2.5            | 350                                           | 820                                           |

A significant position within a wide range of protective clothing assortments is occupied by textiles protecting against heat at elevated temperature and static electricity as well as those that meet the requirements of flame-retardant fabrics. An expected feature is also their antibacterial capacity. In this connection, consumers, in relation to the protective clothing offered, point out that their functional properties should comprise multi-functional capabilities including the physiological comport of use. The issue of multi-functionality of fabrics designed for protective clothing has been a subject of many research works at the Textile Research Institute that pays much attention to fabrics made by the technique of knitting [7-9].

In recent years, studies have been carried out on multi-functional knitted fabrics with a multi-layer structure designed for protective clothing or elements of protective, flame-retardant and antistatic clothing. This paper presents selected results of these studies concerning weft-knitted fabrics with a three-layer structure.

2. **Technological tests**

The aim of the research undertaken was to develop new assortments of knitted fabrics designed for clothing with barrier properties against elevated temperature and static electricity, showing also biological activity concerning antibacterial action. Moreover, the studies were aimed at the multi-functionality of knitted fabrics, including features of improved physiological comfort and an aesthetic appearance expected by users. In order to obtain the multi-functionality of knitted fabrics consisting in imparting to them particular properties, the following tasks were performed:

- Flame-retardant and antistatic properties of fabric were obtained by using for their production yarns of raw materials with the required features.
- To obtain antibacterial features, a chemical agent containing nanoparticles of metallic silver was use in the finishing processes of fabrics.
- To obtain the physiological comfort required with the given barrier properties, there were designed three-layer, weft knitted structures as fabrics with LR stitches (two layers) combined by a middle layer formed of a flame-retardant monofilament yarn. Designing the structures of knitted fabrics, there were used, in particular layers, such types of yarns to obtain the internal layers (in contact with user’s skin) of clothing with good properties of physiological comfort [9].
A rib knitting machine, type Ovja from Mayer Company, modernized at the Textile Research Institute, was selected to produce the knitted fabrics to be tested. Its technical parameters were adapted for the production of three-layer knitted fabrics with a set zone of distance. The modernization of the knitting machine constitutes the subject of an improvement application (submitted in 2012) and a part of Patent Application No. P 406 791, 2014, to the Patent Office of the Polish Republic; „Distance 3D weft-knitted fabric and a process and system of its making”. The invention consists in that the stitch system designed uses the technique of weft-knitted fabrics of three-layer structures, in which the layers are combined by means of tucking links of monofilament yarn, located between the needles of both beds forming the distance space [10].

In connection with this, there were designed three-layer 3D distance knitted fabrics, including a technological program of producing samples of these knitted fabric with the following compositions:

**Sample 1.** Metaaramid + metaaramid/viscose FR + monofil PES
**Sample 2.** Metaaramid + viscose FR + monofil PES
**Sample 3.** Metaaramid + Rezistat* + metaaramid/viscose FR + monofil PES
  *Rezistat – trade name of blended yarn: Vsc Lenzing + PES/carbon compounds
**Sample 4.** Metaaramid + modakryl Protex/cotton + monofil PES
**Sample 5.** Metaaramid + viscose FR + monofil PES
**Sample 6.** Metaaramid /antistatic + metaaramid + wool/viscose FR + monofil PES.

The knitted fabrics were made with the use of combined stitch that resulted in a spatially developed structure owing to the application of the stitch system in the following way: the top layer is formed by means of even RL stitch or RL plated stitch and the under surface by means of RL stitch. Both layers were combined with a monofilament yarn using a half cardigan stitches. The use of monofilament yarn to combine the layers caused the formation of spacing between the fabric layers – a distance of about 3 mm, while the links – yarn sections between the layers formed the middle layer. The preservation of distance in knitted fabrics depends, among others, on the thickness of monofilament yarn and the way of its inserting between the layers. This is essential due to the need for providing fabric elasticity. In the preparation of the sample, two methods of setting the tucking links were used: in samples 1, 2, 3 and 4, a skew roof setting of the monofilament yarn was used, while in Samples 5 and 6 – an alternating skew setting in particular fabric courses was applied.

Each of the three layers of particular fabric sample was made of different raw material. The top layers were made of aramid (meta-aramid) yarn and antistatic yarn (Rezistat, meta-aramid/antistatic), while the bottom layers – with a predominance of natural and man-made yarns (meta-aramid/viscose FR, viscose FR, modacryl Protex/cotton, wool/viscose FR). In all the samples, the distance layer was made of PES monofilament yarn.

It was assumed that the three-layer knitted fabrics designed in the way mentioned above will show particular biophysical properties creating the effect of micro-climate around the user’s body wearing the clothing made their use. In view of expected good thermo-regulating properties, the three-layers knitted fabrics have been planned to use for warming outerwear, such as waistcoats and warming elements in outerwear.

The linear density of the most multi-filament yarns used ranged from 20 to 25 tex, while that of monofilament yarn was 100 dtex. Table 2 presents the percentage content of particular raw materials in the fabric samples made.

The finishing treatment of the three-layer knitted fabrics was carried out according to the technological parameters of finishing knitted fabrics made of synthetic (aramid yarns) and natural and man-made yarns (cotton, wool, viscose yarns) in the following finishing stages: washing, neutralization, rinsing, centrifuging, strip reversing, fabric splitting along needle set-out, drying and stabilization.

- Preliminary stabilization was added to the finishing process as the first phase.
- In the finishing of knitted fabrics no softening agents were used.

In order to impart antibacterial properties to the fabrics, their selected assortments were treated with biologically active agents in the finishing process, using an antibacterial agent Ruco Bac AGP (Sample 4) or an agent containing nanoparticles of metallic silver (Sample 5).
Table 2. Percentage content of particular raw materials in the knitted fabrics

| Sample No. | Type of raw material | Content [%] |
|------------|----------------------|-------------|
| 1.         | meta-aramid          | 58.7        |
|            | meta-aramid/viscose FR | 2.6        |
|            | monofil PES          | 15.7        |
| 2.         | meta-aramid          | 58.7        |
|            | viscose FR           | 25.6        |
|            | monofil PES          | 15.7        |
| 3.         | meta aramid          | 58.7        |
|            | Rezistat             | 5.0         |
|            | meta-aramid/viscose FR | 21.0       |
|            | monofil PES          | 15.3        |
| 4.         | meta-aramid          | 58.4        |
|            | Protex/cotton        | 27.1        |
|            | monofil PES          | 14.5        |
| 5.         | meta-aramid          | 50.0        |
|            | viscose FR           | 35.0        |
|            | monofil PES          | 15.0        |
| 6.         | meta-aramid/antistatic | 26.0      |
|            | metaaramid           | 20.0        |
|            | wool/viscose FR      | 40.0        |
|            | monofil PES          | 14.0        |

As a result of the assessment of the knitting and finishing processes followed by the organoleptic evaluation of the fabric samples, especially with respect to the fabric spatial structure, Samples 3, 4, 5 and 6 were selected for the tests confirming the expected functional properties.

3. **Assessment of the functionality of three-layer knitted fabrics**

The assessment of functionality of the knitted fabrics under investigation was carried out with respect to their structural and physico-mechanical properties as well as their physiological comfort and functional barrier features concerning flammability, static electricity and biological activity [9].

The following parameters characterizing the fabric **physical and functional properties** were tested (Table 3):

- Surface mass according to standard **PN–P-04613-1:1997**
- Course and wale stitch density according to standard **PN-EN 14971:2007**
- Changes in dimensions after laundering according to standards **PN - EN ISO 5077:2011, and PN-EN ISO 6330:2002. (A1:2011)**
- Fabric thickness according to standard **PN-EN ISO 5084:1999**.

In compliance with the planned applications of the knitted fabric assortments proposed (outerwear and warming elements in outerwear), in order to assess their protective properties against hot thermal effects, we used the test methods and requirements given in standard **PN-EN ISO 11612:2011**. This standard determines the following range of tests for the parameters presented below (Tables 4, 5, 6 and 7):

- Resistance to ignition of textiles, the test method according to standard **PN-EN ISO 15025: 2005**
- Resistance to changes under the influence of hot air, the test method according to standard **ISO 17493:2000**
- Determination of the parameter of heat penetration with the action of flame, test method according to **PN-EN 367: 1996**
- Determination of the coefficient of the heat radiation transfer, test method according to standard **PN-EN ISO 6942: 2005**.
For the knitted fabrics, whose raw material system was designed to include antistatic yarns (Samples 3 and 6), electrostatic properties were determined, assessing the following parameters (Table 8):

- Surface resistance, test method according to standard PN-EN 1149-1:2008
- Volume resistance, test method according to standard PN-EN 1149-2:1999/Ap1:2001
- Half decay time and shielding coefficient, test method according to standard PN-EN 1149-3:2007.

The assessment on the parameters was performed on the basis of standard PN-EN 1149-5:2009.

The antibacterial properties of the knitted fabrics (Table 9) after finishing (Sample 4 and 5), with the use of two different antibacterial agents, were assessed by the quantitative method against gram positive bacteria, Staphylococcus aureus and gram negative bacteria, Escherichia coli. The tests were carried out according to the Testing Procedure of the Textile Research Institute, standards AATCC Test Method 100-2004 and PN-EN ISO 20743.

The physiological comfort of the three-layer knitted fabrics was determined with the use of biophysical parameters such as (Table 10):

- Thermal resistance and water vapor resistance according to standard PN-EN 31092:1998/Ap1:2004.
- Air permeability according to standard PN-EN ISO 9237:1998.
- Hygroscopicity according to standard PN-80/P-04635.

**Table 3. Physical and functional parameters of three-layer knitted fabrics**

| Sample No. | Surface mass [g/m²] | Fabric tightness | Change in dimension after washing | Average thickness [mm] |
|------------|---------------------|------------------|-----------------------------------|------------------------|
|            |                     | Number of courses/cm | Number of wales/cm | lengthwise [%] | crosswise [%] |
| Flame-retardant knitted fabrics | | | | | |
| 4. | 305 | 12.5 | 9.0 | -1.0 | 1.0 | 2.05 |
| 5. | 376 | 14.1 | 9.4 | -5.0 | -1.0 | 2.80 |
| Flame-retardant and antistatic knitted fabrics | | | | | |
| 3. | 294 | 12.5 | 9.0 | -4.5 | -0.5 | 2.44 |
| 6. | 434 | 14.2 | 9.3 | -2.0 | -4.0 | 2.88 |

**Table 4. Test results of the resistance to ignition of textiles**

| Test results according to procedure A: | |
|---------------------------------------|--------------------------------------------------|
| Does the flame reach the upper or vertical sample edge? | NO – all the samples |
| Did debris occur? | NO – all the sample |
| Was debris on fire? | NO – all the samples |
| Did a hole occur? | NO – all the samples |
| Time of consequent flame combustion [s] | 0 s. – all the samples |
| Time of consequent glow [s] | 0 s. – all the samples |

Assessment: Samples 3, 4, 5, 6 fulfill the requirements of resistance to ignition for range A1.
Table 5. Test results of the resistance of fabric to heat at a temperature of 180 °C

| Sample No. | Change in dimensions | Change in appearance | Requirements according to PN-EN ISO 11612:2011 |
|------------|----------------------|----------------------|-----------------------------------------------|
|            | lengthwise [%]         | Crosswise [%]        |                                               |
| 3.         | -1.1                 | -0.8                 | No change in appearance                       |
| 4.         | -2.4                 | -4.4                 | No change in appearance                       |
| 5.         | -1.6                 | -3.0                 | No change in appearance                       |
| 6.         | -0.5                 | -2.4                 | A light yellowing on fabric back              |

Assessment: all the fabric samples tested fulfil the required resistance to heat at a temperature of 180°C.

Table 6. Test results of the resistance of fabrics exposed to the action of thermal radiation

| Sample No. | Coefficient of thermal radiation transfer RHTI 24 | Coefficient of thermal heat transfer RHTI 12 | RHTI 24 - RHTI 12 | Requirements according to PN-EN ISO 11612:2011 |
|------------|---------------------------------------------------|---------------------------------------------|-------------------|-----------------------------------------------|
| 3.         | 21.7                                              | 13.8                                        | 7.9               |                                               |
| 4.         | 20.8                                              | 13.4                                        | 7.4               |                                               |
| 5.         | 20.9                                              | 12.5                                        | 8.4               |                                               |
| 6.         | 22.5                                              | 14.4                                        | 8.1               |                                               |

Assessment: the knitted fabrics tested fulfill the requirements for the resistance to the action of thermal radiation at an effectiveness level of C2.

Table 7. Results of testing the parameter of heat penetration with the action of flame

| Sample No. | Heat penetrating parameter HTI 24 | Heat penetrating parameter HTI 12 | HTI 24 – HTI 12 | Requirements according to PN-EN ISO 11612:2011 |
|------------|-----------------------------------|-----------------------------------|-----------------|-----------------------------------------------|
| 3.         | 11.0                              | 8.0                              | 3.0             |                                               |
| 4.         | 11.0                              | 8.0                              | 3.0             |                                               |
| 5.         | 11.1                              | 7.9                              | 3.2             |                                               |
| 6.         | 12.4                              | 8.6                              | 3.8             |                                               |

Assessment: the knitted fabrics tested fulfill the required resistance to heat penetration with the action of flame at an effectiveness level of B2.
Table 8. Test results of the parameters of barrier properties concerning static electricity

| Sample No. | Surface resistance $R_s$ [Ω] | Volume resistance $R_v$ [Ω] | Half decay time $t_{50}$ [s] | Shielding coefficient $S$ |
|------------|-----------------------------|-----------------------------|-----------------------------|--------------------------|
|            | Fabric face | Fabric back |                          |                          |                          |
| 3.         | 2.14 x 10^{12} | 2.18 x 10^{12} | 9.10 x 10^{10} | < 0.01 | 0.509 |
| 6.         | 4.72 x 10^{12} | 1.66 x 10^{12} | 9.02 x 10^{10} | < 0.01 | 0.59 |

Requirements according to PN-EN 1149-5:2009

$R_s \leq 2.5 \times 10^9$ on at least one surface

$1.66 \times 10^{12}$

$t_{50} < 4s$

$S > 0.2$

Assessment: the knitted fabric tested show barrier properties concerning static electricity, fulfilling two parameters required, i.e. $t_{50} < 4s$, and $S > 0.2$

Table 9. The microbiological tests results of three-layer knitted fabrics (quantity method)

| Sample No. | Micro-organisms used in tests according to: AATCC Test Method 100-2004 i PN-EN ISO 20743 | Parameter determined | Value of the bacteriostatic parameter $S$ | Value of the bactericidal parameter $L$ |
|------------|---------------------------------------------------------------------------------------------|----------------------|-----------------------------------------|---------------------------------------|
| 4.         | Staphylococcus aureus (ATCC 6538) Escherichia coli (ATCC 11229)                             |                      | 2.2                                     | 1.1                                   |
| 5.         | Staphylococcus aureus (ATCC 6538) Escherichia coli (ATCC 11229)                             |                      | -1.3                                    | -2.1                                  |
|            | Requirements according to JIS L 1902                                                        |                      | 6.6                                     | 2.3                                   |
|            |                                                                                             |                      | 6.9                                     | 2.0                                   |

Assessment: sample 4 shows bacteriostatic and bactericidal properties against bacteria Staphylococcus aureus, while against bacteria Escherichia coli this fabric has no biologically active properties. In the case of sample 5, its bacteriostatic and bactericidal properties were confirmed against both microorganisms.

Table 10. Test results of the physiological comfort of three-layer knitted fabrics

| Parameter                                    | Sample No. | 3. | 4. | 5. | 6. |
|----------------------------------------------|------------|----|----|----|----|
| Thermal resistance [m²K/W]                   | 0.083       | 0.070 | 0.072 | 0.090 |
| Resistance of water vapor [m³Pa/W]           | 2.87        | 6.01 | 6.11 | 7.35 |
| Permeability of water vapor [g/m³Pa h]       | 0.518       | 0.253 | 0.243 | 0.202 |
| Permeability of air [mm/s]                   | 1844        | 1766 | 1784 | 1328 |
| Hygroscopicity [%]                           | 8.91        | 9.89 | 9.97 | 9.90 |

Assessment: the values of thermal resistance indicate the thermal insulating power similar to that of fabrics used for warm outerwear (e.g. fabrics for coats – 0.093 m² K/W) – assessment in relation to standard ISO 7730. The level of air permeability obtained, in relation to the classification of textiles, qualifies the knitted fabric as „air permeable” (according to standard PN-EN ISO 9237, the required level for the class “permeable” is over 600 m/s), while the level of water vapor permeability qualifies
the knitted fabrics tested to class 3 – “permeable” (according to EN 343:1996, class 3 – resistance ≤ 20 m²Pa/W).

4. Summary
The technological and laboratory tests carried out at the Textile Research Institute indicate a chance of shaping the properties of multi-functional knitted fabrics with a three-layer structure and a specified use of them for clothing or its elements. The multi-functionality of these knitted fabrics shows protective properties against hot thermal effects and static electricity, and in the case of selected assortments, additionally biological activity against bacteria. At the same time, all the knitted fabrics tested are characterized by good parameters of physiological comfort. The analysis and evaluation of indicators characterizing the multifunctionality of developed assortments of three-layer materials has allowed them to qualify as knitted fabrics with properties:

- flame-retardant and antistatic with good properties of physiological comfort – Sample 3 and 6,
- flame-retardant and antibacterial with good properties of physiological comfort – Sample 4 and 5.

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