VLÁKNA a TEXTIL

FIBRES AND TEXTILES

3
Volume 29
November
2022

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Faculty of Textile Engineering

Trenčianska univerzita Alexandra Dubčeka v Trenčíne
Fakulta priemyselných technológií v Púchove

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CHEMOSVIT FIBROCHEM

Indexed in:
SCOPUS
Chemical Abstract
World Textile Abstracts
EBSCO Essentials

ISSN 1335-0617
print version

ISSN 2585-8890
online version

VLÁKNA A TEXTIL
http://www.vat.ft.tul.cz

PUBLISHED BY
Technical University of Liberec, Faculty of Textile Engineering
Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology
Alexander Dubček University of Trenčín, Faculty of Industrial Technologies
Slovak Society of Industrial Chemistry, Bratislava
Research Institute of Man-Made Fibres, JSC, Svit
VÚTCH – CHEMITEX, Ltd., Žilina
Chemosvit Fibrochem, JSC, Svit

PUBLISHER
Technical University of Liberec
Studentska 1402/2, 461 17 Liberec 1, CZ
Tel: +420 485 353615
e-mail: vat@tul.cz
IČO: 46747885

ORDER AND ADVERTISEMENT OF THE JOURNAL
Technical University of Liberec
Faculty of Textile Engineering
Studentska 1402/2, 461 17 Liberec 1, CZ
Tel: +420 485 353615
e-mail: vat@tul.cz

TYPESET AND PRINT
Vysokoškolský podnik, s.r.o., Voroněžská 1329/13, 460 01 Liberec 1, CZ

DATE OF ISSUE
November 2022

APPROVED BY
Rector's Office of Technical University of Liberec
Ref. no. RE 48/22, 9th November 2022

EDITION
First

PUBLICATION NUMBER
55-048-22

PUBLICATION
Quarterly

SUBSCRIPTION
60 EUR

REG. NO. MK ČR E 24338

VLÁKNA A TEXTIL

Volume 29, Issue 3, November 2022

CONTENT

PHYSICO-CHEMICAL PROPERTIES OF MAGNETITES IN NANOCOMPOSITES ON THE TEXTILE BASES

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ABSTRACT

The article is devoted to investigation of the physico-chemical properties of magnetites in nanocomposites on the textile bases. It studies of the structure and phase composition of nanocomposite materials on the polyamide and viscose textile bases. It is shown that magnetite particles synthesized in textile material with average sizes of 9.4 nm in viscose textile material and 9.7 nm in polyamide textile material. The influence of synthesis conditions on the size of magnetite nanocrystallites in textile material is established.

KEYWORDS

Textile materials; Magnetite; Structure; Nanotechnology; X-ray phase analysis.

INTRODUCTION

Today's challenges encourage the search for new approaches and methods of creating textile materials (TM) containing iron oxide compounds of nano sizes, due to the unique properties of magnetic nanoparticles [1–4], for example, their ability to absorb microwaves and have a bactericidal effect [5]. Currently, for the practical implementation of products that are nanostructured materials, it is necessary to develop new technologies for their production for the successful implementation of the potential of nanotechnology in the consumer properties of the product.

In this regard, the developer must solve the following tasks: to determine the limit of the nanoscale range of dispersed particles of matter; to work out the technology of obtaining the substance in the form of dispersed particles of the substance; to work out the technology of introducing nanoparticles into the appropriate matrix, which protects nanoparticles and preserves the properties of nanoparticles from oxidation. When choosing a method for the synthesis of nanoparticles of magnetic materials, it is necessary to implement the production of nanoparticles of magnetic materials of a given size and shape; to provide nanoparticles of a certain phase composition with reproducible and time-stable properties; to ensure technological simplicity of nanoparticle synthesis.

Many chemical methods can be used to synthesize magnetic nanoparticles [5–11]: synthesis in microemulses, sol-gel synthesis, chemical reactions using ultrasound, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow-injection synthesis, electrochemical synthesis. These methods are used for the production of nanoparticles of homogeneous composition and with a narrow size distribution. However, the most common method of obtaining magnetic nanoparticles was and remains the method of chemical coprecipitation of iron salts [12–15]. Solving similar problems is of great importance for the development of nanotechnologies for the creation of materials, in order to control the synthesis of nanoscale magnetite by in situ mechanism in nanocomposites based on textiles of different nature. Despite the large number of works performed, in general, this area of research is only at the initial stage of its development. Issues related to the synthesis of magnetite [5–15] and the study of its magnetic properties and structural characteristics in textile materials of various natures have not been studied.

The purpose of this work: study of physic-chemical properties of nanomagnetite by X-ray phase analysis, as well as establishing the influence of synthesis and nanoprocessing conditions on the structure, size of particles of the magnetite and magnetic properties of textile-based nanocomposites.

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Received June 16, 2022; accepted September 16, 2022

OBJECTS OF INVESTIGATION

For studies as textile materials (TM) was used polyamide (PA) and viscose (Vis) comprehensive threads with a linear density of 15.6 tex and PA and viscose knitted fabrics. These were obtained from polyamide and viscose threads.

EXPERIMENTAL

Textile materials with nanomagnetic particles are nanocomposites based on textiles (TM/NM). Textile materials with magnetic nanoparticles are prepared as follows. Magnetic textile materials obtained by a two-stage method. Stage 1: iron salts (FeSO4 • 7H2O and FeCl3 • 6H2O) of various concentrations from 40 g / l to 80 g / l are added to the treatment solution at a certain bath module. The resulting solution is stirred for 5 - 10 minutes until complete dissolution of salts. A sample of textile material soaked in distilled water is immersed in the prepared solution. The process of sorption of iron salts continues at a temperature of 95 - 98 °C for 60 - 80 minutes with periodic stirring. Stage 2: the process of co-precipitation of iron salts in the textile material with an aqueous solution of ammonia at pH 10-11 for 60 - 80 minutes. The final stage of processing is washing the obtained sample of textile material with distilled water.

Thus, the formation of nanosized magnetite in textile material of different nature by the in situ mechanism [2]. Textile material acts as a nanoreactor in which magnetite nanoparticles are formed. Next, the obtained magnetic textile material is washed with distilled water and dried.

X-ray phase analysis (XRD) was performed with a DRON-UM1 X-ray diffractometer using a Co Kα radiation source (l = 1.5418 A) operating at 40 kV to investigate the crystalline size and phases of the synthesized iron oxide nanoparticles in the polyamide fiber. The angular range of 10 − 80 degrees, in increments of 0.05 degrees. Diffraction patterns are recorded digitally in a file format 2θ (degrees) − I (Intensity, s-1) and shown in Fig. 1.
The study of the magnetic characteristics of the samples was performed using a magnetometer with a Hall sensor, which is designed to measure the parameters of the hysteresis loop of powder materials. Measurements of the parameters of the magnetization curves and hysteresis loops take place in an open magnetic circuit.

RESULTS AND DISCUSSION

On the diffractograms of the synthesized nanomagnetite (NM) particles in the absence of textile material, differing in the initial concentration of iron salt in the treatment bath: a) 10 (C10), b) 40 (C40), c) 60 (C60) g/l (Fig. 1), the presence of a number of reflexes with angular position 2Θ 18.3°, 30.1°, 35.5°, 37.0°, 43.1°, 53.6°, 57.1° and 62.3° was identified, corresponding to the scattering maxima of the planes (111), (220), (311), (222), (400), (422), (511) and (440) nanocrystals, respectively, according to the PDF-2 database, ICDD n. 880866).

Reflexes of the (220), (311) and (400) planes of magnetite nanocrystals are usually used to calculate the crystal size with the required accuracy.
Using the Bragg equation (1), the indices of the interplanar distance d_{hkl} were calculated:

$$d_{hkl} = \frac{\lambda}{2 sin \Theta}, \qquad (1),$$

where d_{hkl} – interplanar distance [Å], λ - wavelength used λ (CuKα) = 1.54051[Å], θ - diffraction angle [°], k = 0.89.

According to the obtained results, the values of d_{hkl} do not depend on the conditions of nanomagnetite synthesis, which indicates the same mechanism of formation of the crystalline phase of the particles. The results of the calculation of the size of nanomagnetite crystals are given in Table 1.
Using the Debye-Scherrer formula (2), the average size of magnetite crystallites was determined [10]:

$$d = \frac{k\lambda}{\beta \cos \theta}, \qquad (2),$$

where d - the average size of the crystallites [nm], λ - wavelength used λ (CuKα) = 1.54051[Å], β - width of the peak at half height, θ - diffraction angle [°], k = 0.89.

Samples C10 and C60 are characterized by the formation of larger magnetite nanocrystals (16.4 nm and 12.5 nm, respectively) with relatively low polydispersity (standard deviation of size does not exceed 5 %). Sample C40 has a smaller average size of magnetite nanocrystals (about 11 nm), but the standard deviation is much larger (~ 15 %). The most probable reason for this behavior is the synthesis conditions, such as the concentration of iron salt in the treatment bath. The lower concentration of iron salt provides fewer crystallization centers and the possibility of their growth. The high concentration of reagents (60 g/l of iron salt in the original bath), on the contrary, promotes the formation of a large number of nucleation centers and ensures uniform growth of particles and the formation of nanocrystals similar in size.

Table 1. The results of X-ray phase analysis of nanomagnetite (NM) samples

NM	2Θ [°]	Crystal lattice	d_{hkl} [Å]	D_{hkl} [nm]	d [nm]
C10	30.1	(220)	2.97	15.2	16.4±0.8
	35.5	(311)	2.53	16.7	
	43.1	(400)	2.10	17.4	
C40	30.1	(220)	2.95	13.3	10.9±1.6
	35.5	(311)	2.53	10.8	
	43.1	(400)	2.10	8.6	
C60	30.1	(220)	2.95	11.8	12.5±0.5
	35.5	(311)	2.53	12.8	
	43.1	(400)	2.10	12.9	

Diffractograms of X-ray phase analysis of samples of TM/NM composites are shown in Fig. 2. Analysis of the inorganic phase (nanomagnetite) of the viscose TM/NM composite shows that the size of nanomagnetite crystals is 9.4 ± 1.1 nm when passing an X-ray beam through the central part of the TM/NM system (designation "equator" (E) in table 2) containing NM. When transmitting a beam of radiation near the surface of the composite (through the surface layer of nanoparticles immobilized on the surface of the fibers; denoted as "meridian" (M) the size of nanomagnetite crystals is 14.7 ± 5.3 nm (Table 2).

For nanocomposite polyamide TM/NM, the average crystal size of the inorganic phase is 10.0 ± 1.42 nm (measurement in the "meridian" mode) and 9.7 ± 1.2 nm when measured in the "equator" mode. For this composite system, there is also a decrease in the average size of magnetite crystals during their formation in the volume of the fiber-forming polymer - polyamide TM. Assuming that the content of magnetite nanoparticles in the volume of different types of polymer fibers is the same, there is no doubt that cellulose macro chains are more active and affect the formation of nucleation centers of the crystalline inorganic phase and their growth. It should be noted that for both composites the values of the interplanar distance are very close, which indicates a similar mechanism of in situ formation of the inorganic phase Fe3O4.

The crystal structure of TM in the process of modification did not change (Fig. 3), which indicated the location of NM on the surface of cellulosic microfibrils (viscous TM) or in amorphous zones of cellulosic and polyamide structure. The saturation magnetization of nanocomposites based on textiles are from 2 A*m2/kg to 10 A*m2/kg.

It is important that the coprecipitation of iron salts in a strongly alkaline medium with the formation of nanomagnetite in TM occurred to a greater extent in viscous TM, given its crystalline-amorphous structure. And less in polyamide TM, which was confirmed experimentally and reflected by the lower profile intensity of the most important reflex at 2θ = 35º on the presented diffractograms (Fig. 2).

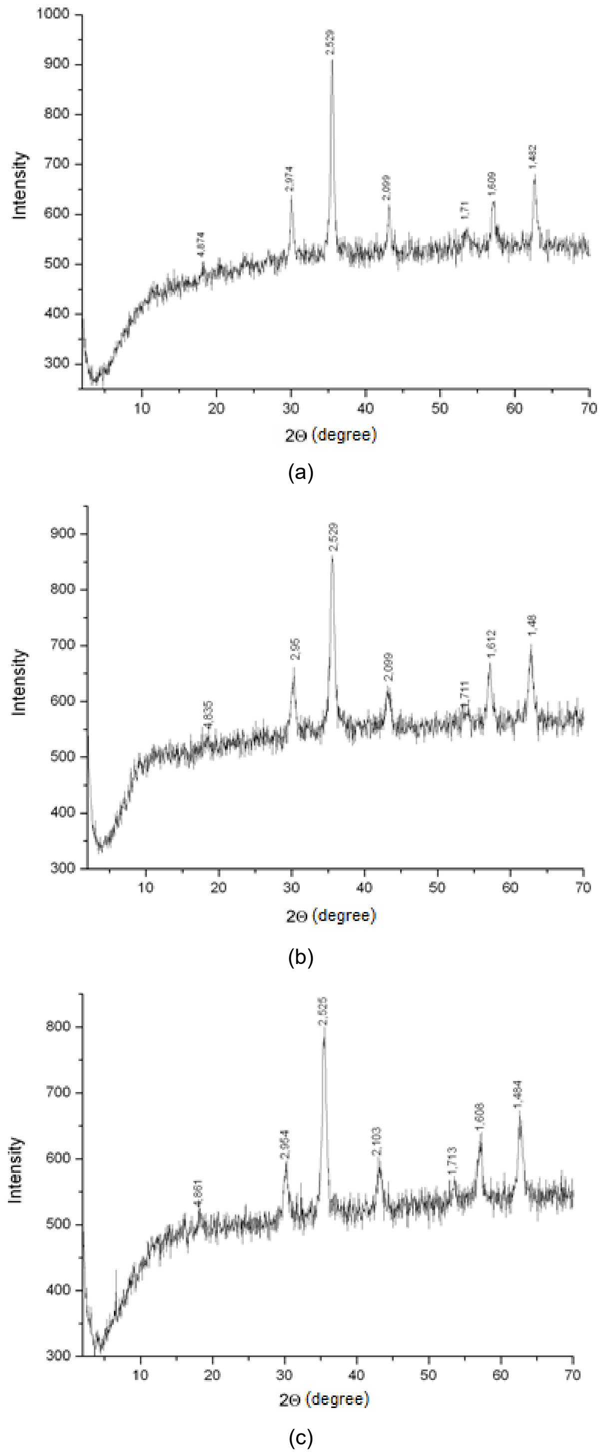


Figure 1. Diffractograms of magnetite nanoparticle samples obtained under different synthesis conditions.

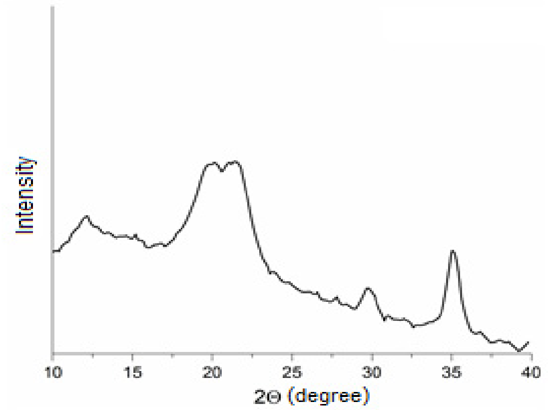
Diagrams of changes in the intensity of X-ray scattering during the rotation of TM with nanomagnetite around its own axis relative to the radiation source are shown in Fig. 4. Analysis of the scattering intensity shows the close nature of the distribution of phase inhomogeneity in both textile composites.

Table 2. The results of X-ray phase analysis of textile materials with nanomagnetite (TM/NM)

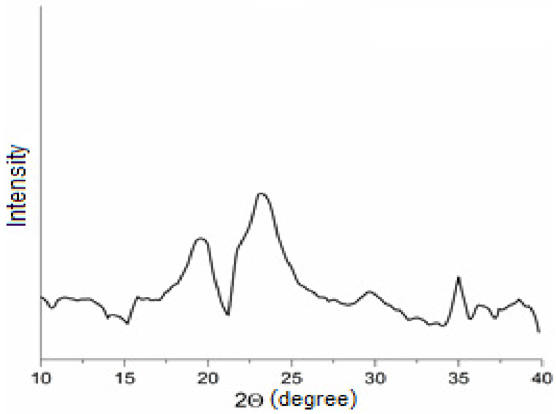
TM/NM	Mode	2Θ [°]	d_{hkl} [Å]	D_{hkl}, [nm]	d, [nm]
Viscose TM/NM	M	29.9	2.98	20.0	14.7±5.3
		35.1	2.55	9.4	
	E	29.8	2.99	9.3	9.4±1.1
		35.2	2.55	9.5	
Poly-amide TM/NM	M	30.0	2.98	10.2	10.0±1.4
		35.3	2.54	9.8	
	E	29.8	2.99	8.5	9.7±1.2
		35.0	2.56	10.9	

Since the intensity distribution is obtained by comparing the X-ray diffraction of the original TM and composites based on them, the angular regions marked on the diagram with increased scattering intensity are due to the presence of a certain structured inorganic component. For the obtained composites, the angular position of the wide scattering region practically coincides and lies in the range of 70 - 170˚ (polyamide TM / НМ) and 80 – 160˚ (viscose TM / НМ).

The reasons for the manifestation of such structural activity of the polymer fiber-forming matrix can most likely be related either to the activity of functional groups of polymer macro chains relative to the surface of magnetite nanocrystals or to the influence of polyamide TM macro chain ordering on nanomagnetite particle growth processes.



(a)



(b)

Figure 2. X-ray diffraction patterns of polyamide (a) and viscose (b) TM containing nanomagnetite.

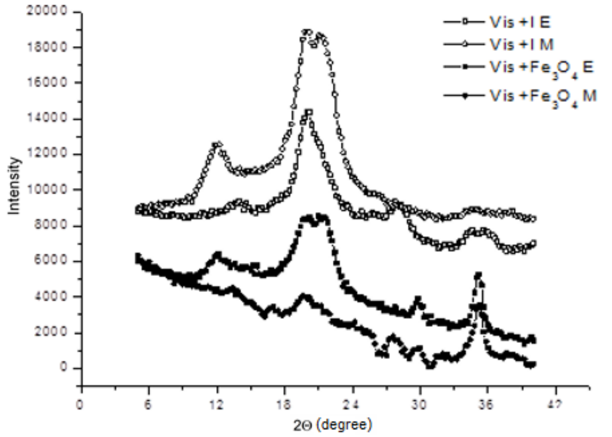


Figure 3. X-ray diffraction patterns of untreated viscose TM (Vis) and viscose TM containing nanomagnetite (Vis+Fe_3O_4).

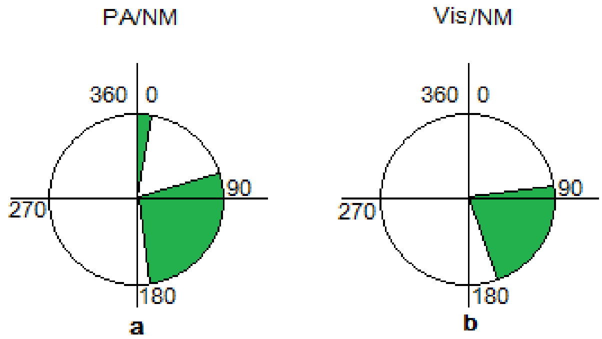


Figure 4. Distribution of X-ray scattering intensity with different orientation of the radiation source. Areas with increased, relative to the general background, scattering intensity are marked by color.

From obtained experimental data it can be stated that the structuring effect of viscose TM macro chains is more significant. This system is characterized by a more significant reduction in the size of nanocrystallites of the inorganic phase - nanomagnetite (from 14.7 to 9.4 nm). As well as a narrower range of X-ray scattering angles in determining the orientation of magnetite nanocrystals in the volume of the viscose fiber-forming matrix (Fig. 4).

Thus, it can be argued that using cellulosic (viscose) and PA textile materials is more promising because it allows more precise control of the phase and chemical composition of magnetic nanocomposites on a textile basis. The dependence of the structure, phase composition and particle size on the raw material composition and conditions of synthesis of nanomagnetite formed in the stabilizing fiber-forming matrix was established, which allowedobtaining magnetic textile materials containing magnetite nanoparticles (Fe_3O_4) with controlled magnetic properties.

CONCLUSIONS

Determination of the structure and dimensional characteristics by X-ray diffraction of textile nanocomposites revealed a number of patterns necessary for the development of scientific bases of nanotechnologies for the creation of textile materials with magnetic properties. The influence of synthesis conditions on the size of magnetite nanocrystallites in textile material is established. A significant reduction in the size of nanocrystallites of the inorganic phase (from 14.7 to 9.4 nm) and a narrower range of X-ray scattering angles in determining the orientation of magnetite nanocrystals in viscose textile material indicates that the structuring effect of macro chains of cellulose in situ mechanism in a textile-based nanocomposite.

According to the results of X-ray diffraction, it is established that nanoparticles are evenly distributed in the volume of magnetic nanocomposites on a textile basis. The average size of nanoparticles is determined by the synthesis conditions, the concentration of precursors and the nature of the textile material. With increasing precursor concentration in the synthesis of nanomagnetite, the average size of nanoparticles of magnetite Fe_3O_4 increases, while for nanocomposites based on viscose TM there is less growth than for nanocomposites based on polyamide TM in the concentration range of 40 - 60 g / l. As the concentration increases, the average size of nanoparticles increases regardless of the raw material composition of the textile material.

The influence of conditions for obtaining textile materials with magnetic properties on their structure and characteristics is determined, which allows to change: particle size from 9.4 nm to 14.7 nm and saturation magnetization from 2 A*m^2/kg to 10 A*m^2/kg. Thus, the study of the structure and phase composition of nanocomposite materials revealed the presence of magnetite particles synthesized in textile material with average sizes of 9.4 nm in viscose textile material and 9.7 nm in polyamide textile material. At the current level of methodological development for the quantitative determination of the dimensional characteristics of nanostructured materials, it is advisable to conduct a comprehensive study using various methods, such as scanning electron microscopy.

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A QUALITATIVE STUDY ABOUT INTERNATIONALIZATION OF TURKISH TEXTILE & CLOTHING INDUSTRIES

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ABSTRACT

The national textile and clothing industries do not operate in isolation anymore; they are significant parts of one global sector which serve to the whole world. The Turkish textile and clothing industries are mainly export oriented and like other developing industries, they have an important role in the internationalization of the Turkish economy with their contribution to GDP, trade and employment. This article reviews the major developments that shaped the internationalization process of Turkish textile & clothing industries. Findings from semi-structured case studies with 14 Turkish textile and clothing industries tries to highlight the changes occurring currently in the industries. The qualitative data obtained from our research gives deep and detailed understanding of the Turkish textile and clothing industries.

KEYWORDS

History of Turkish textile industry; Internationalization; Turkish clothing industry; Turkish textile industry; Qualitative study.

INTRODUCTION

The textile and clothing industries are one of the oldest and most international industries as they are the milestone industries for countires which are export-orientated and aim labour-intensive industrialisation plan [1]. Although they have totally different technological development levels, textile and clothing industries are generally metioned together as they have a strong linkage between them. This linkage is mainly from the supply demand relation between these two industries as the textile industry supplies the inputs such as yarn, fabric of the clothing industry [2]. However, clothing industry requires lower technology and it is more labour intensive where as textile industry is capital intensive and requires higher technology [3]. In the short run, textile and clothing industries are important in developing jobs and foreign currency flows whereas in the long run they give opportunity to develop a growth in economic terms [1]. The low cost of labour force is a crucial factor in the development of the textile and clothing industries. This is the main reason why development of those industries takes place mainly in developing countries. Especially clothing industry is heavily dependent on low labour and therefore the development of clothing industry takes before the development of textile industry [4].

HISTORICAL DEVELOPMENT OF TEXTILE & CLOTHING INDUSTRIES IN THE WORLD

The textile and clothing industries have been significantly important sectors in the economic development of the all countries. Indeed, they played a vital role in the period of early industrialization in the UK, North America and Japan. The textile industry is an industry almost as old as human history and the innovation in the textile industry accelerated the industrial revolution [5]. After that, the second stage of development, which emerged with the influence of capitalism on consumer culture, reached its present structure with the fashion phenomenon [6].

Until the 1940s, industrialised European countries and US dominated the textile and clothing industries and the developing countries were the suppliers of raw materials to those countries. After the Second World War, European countries and US were aware of economic gains from the liberation of trade in the world. Although developing countries and uncompetitive industries favoured protectionism, the developed countries declared a worldwide agreement called General Agreement on Tariffs and Trade (GATT) which was due between 1947 and 1995. The GATT's main aim was the reduction of tariffs, create regional free trade areas were allowed and industries such as agriculture, textiles, and clothing industries were exempted from this agreement. Since 1995,

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Received March 31, 2022; accepted September 16, 2022

GATT have favourably lowered the trade barriers and helped to move world trade clearer and more anticipated environment [7].

The textile and clothing industries are shelter industries for developing countries as they need low technology, low labour skills and low fixed costs. Beginning from 1950s, the textile and clothing industries are used as an export-led industrialization industries for internalization [8]. By the early 1950s, the textile and clothing production shifted from developed countries to Japan. The first protective measurement was put in use by USA for imports from Japan in 1955. In 1962, the Long-Term Arrangement Regarding International Trade in Cotton Textiles (LTA) was in enactment by twenty countries for five years after a year of Short-Term Arrangement Regarding Trade in Cotton Textiles (STA)'s formulation. The main purpose of the LTA was to restrict cotton- based textile imports from developing countries to USA and European countries. After renewention of LTA in 1967 and 1970, the agreement was replaced by the Multifibre Arrangement (MFA), which included the other fibres into the coverage of the agreement [8].

The MFA allows its members to impose unilaterally import quotas to protect their domestic industries. Between 1986 and 1994, the members of GATT discussed the creation of new international trading system in Uruguay Round. During Uruguay Round, World Trade Organization (WTO) was established and today it has 164 member countries. The General Agreement on Tariffs and Trade (GATT) remained to cover international trade in goods. In order to integrate the textile and clothing industries to the general rules of GATT, the members signed the Agreement on Textiles and Clothing (ATC) which was in use between 1995 and 2005. By ATC, it was aimed to forbidden the imposition of import quotas after 2005 by putting the most favoured nation clause in use for the textile and clothing industries. According to the ATC, the quotas should be abolished at four steps and but in practice that was not achieved. As a conclusion by 2005, the goal of establishing free international trade was not achieved. The major buyers of textiles and clothing countries which are USA and European Union continued restricting imports from mainly China, India, Hong Kong and Taiwan. The preferential agreements such as regional area agreements allowed countries to escape from quotas such as Mexico to the USA and Turkey to the EU [9].

In 2001, China joined to the World Trade Organization. This was an important milestone for international textile and clothing industry. After the abolishment of MFA and ATC completely in 2005, China's exports increased dramatically as China faced no more any quota restrictions. During the post MFA and ATC period, other Asian economies such as Bangladesh, Cambodia, India, and Vietnam also increased their exports especially in clothing industry. There has been a moderate grow in the export numbers of some central and south American, East European and North and South African countries compared to Asian countries [10]. During the 1970s, the production of textile and clothing industries began to shift from developed countries to developing countries because of the rising production costs in developed countries and globalization [11]. By the effect of increasing exports in textile and clothing industries, Hong Kong, South Korea and Taiwan have become newly industrialized countries of Asia, after Japan [12]. This shift enabled underdeveloped countries such as Bangladesh and Indonesia to be present in the international markets as new exporters countries by transforming their low-cost labour force into a competitive advantage [13].

After the 2007 global crisis, the share of the textile and clothing industries in global foreign trade has fallen. As developing countries are mainly exporters of textiles and agriculture and those products price flexibility is low which means they are not affected much by price and income changes compared to high-technology product lines. For the reasons mentioned, although the crisis has helped textile foreign trade recover, the share of textiles in global foreign trade has decreased sharply compared to 1995 [14].

DEVELOPMENT OF TURKISH TEXTILE & CLOTHING INDUSTRIES

Enroute to the industrialization in Turkey, textile and clothing industries have played a key role and they are defined as the "Turkey's oil" to indicate the importance of those industries [15]. These two industries are the essence of Turkish economy in terms of GDP contribution with their share in manufacturing, employment, investments and macroeconomic indicators. The Turkish clothing industry had an export of USD 17,143 billion and textile industry USD 7,287 billion which makes 14,4 per cent of all the exports of the Turkish economy [15]. The textile industry was dependent on imports until 1950s and this dependency continued until 1970s in the clothing industry whereas manufacturing of both industries was for the local market until the 1980s [16].

For more than 3,000 years, textile production in Anatolia has been known as an important trade facility. Actually, the history of textile weaving in Anatolia begins by the Hittite and Assyrian periods. In the Central Asia, weaving was used for meeting the need of basic dressing and covering. In Anatolia, Turks were encountered the old, traditional weaving industry and they developed this industry further by adding their own cultures. By the 14th century, cotton weaving industry was present in Denizli, Alasehir, Adana, Bursa, Ankara and Sivas. Especially Bursa became the Anatolian station of “Silk Way” and in the documentary of the 14th Century, it was determined that the number of silk looms in Bursa reached to thousand. By time, the wool, hemp and linen weaving developed in Anatolian cities in addition to cotton and silk weaving. Weaving industry, which continued its development until the end of the sixteenth century, experienced an unproductive period with the invasion of Indian fabrics in the seventeenth century. However, this unproductive period did not last long for Anatolian textile industry and it recovered by beginning to produce similar items like Indian textiles [17].

Later on, the Turkish textile industry is divided into sub-sectors as spinning, pattern-mould preparation, weaving and dyeing and became the one of the most important economic activity in Anatolia until the invasion of Western countries textile industries. Owing to capitulations given to foreign countries and "Industrial Revolution" that emerged in The UK towards the end of the 18th century which led to the industrialization of the textile industry in Europe, textile goods began to be produced in Europe five times cheaper than the Ottoman Empire [19]. The above-mentioned developments were the main reasons of the downturn and the subsequent collapse of Ottoman weaving industry. After the 18th century, European textile products such as British cotton wool, French woollens, which were previously afforded by the rich people in Anatolia spread in lower segments of the society as a result of the fact that reduction in the prices [18].

During the 19th century, in the major cities within the borders of the Ottoman Empire, weaving mills has largely shut down leaving only small ones operating to meet local demand. During this period, the Chuha Factory in Beykoz (1805), Feshane in Halic (1826) and Basmahane in Bakırköy continued production to meet the needs of the Ottoman army. Private establishments which were very few in number mainly bankrupt during this period and only rare existed until the Republican period. Processing of textile raw materials especially spinning of cotton yarns in cities Tarsus and Adana sustained the textile industry during that period [19].

The Turkish textile industry was seen as one of the important sectors by the state after the establishment of Turkish Republic and governments continued their support in this industry. The economic decisions taken at the Izmir Economic Congress in 1923 also played an important role in the development of the textile industry. The importance of woven industry was underlined and the Turkish woven industry was taken under protection in the Izmir Economic Congress. This declaration advanced the development of Turkish textile industry’s growth and thirteen new textile factories were established with the incentives given in the Industrial Incentive Law of 1924 [20]. Thus, in the 1930s, 23 per cent of Turkey's total industry in the economy was in the textiles industry [21].

The development of modern Turkish textile industry goes back to the early 1930s when textile mills producing cotton fabrics were established. It became the pillar industry in the “First Planned Industrial Programme” of the Turkish Republic and the textile industry has remained one of the leading industries since those years. The fact that Sumerbank was the first public economic enterprise established in Kayseri in 1933 after the Republic is an indication that the industrialization moves in textiles that started in the last days of the Ottoman Empire continued with the same importance and speed after the establishment of the Republic. With the establishment of Sumerbank, the other state-owned textile mills established during Ottoman Empire were given under the control of Sumerbank which accelerated the growth of Turkish textile industry [22]. Sumerbank had 17 mills all over the Turkey mainly producing grey fabric, yarn-dyed fabrics, piece-dyed fabrics and printed fabrics. By the mid 1950s, Sumerbank was engaged in the mass production of short staples for the Turkish domestic market and until the 1980s, it was the producer of one sixth of Turkey’s yarn and fabric production and more than one fifth of Turkish clothing output. In the 1990s, Sumerbank began to lose its competitive advantage and in 1992 Sumerbank’s annual lost reached its annual turnover and privatisation of Sumerbank took place in 1994 [23].

In the first years of the Republic, as in all sectors, there was an intensive restructuring and heavy investments in the textile industry. Therefore, from 1925 to the 1940s, exports in the textile sector lagged behind imports, while in 1940, imports more than doubled. Later, exports decreased to very low levels due to World War II, but after the 1950s, exports were more than imports [21]. In the 1960s, the textile industry is included in an intensive industrial investment support programme which was introduced by the establishment of “Turkish State Planning Organisation” [25]. In 1963, between Turkey and the European Union association agreement known as the Ankara Agreement was signed and in 1973, an additional protocol aimed at abolishing customs duties between the two parties came into force. By the additional protocol, EU abolished customs duties on industrial goods of Turkish origin from the beginning of the transition period, while Turkey was envisaged to gradually abolish customs duties on EU industrial goods. This protocol enabled Turkish textile and clothing goods to be exported to the EU countries without any tax, tariff or quota. In the 1960s, large privately-owned textile giants such as Sabancı, Koc, Cukurova for which textile industries are only a part of their activities; and firms such as Altınyıldız, Soktas, Guney Sanayi and Akın whose main and sole activities are textiles began producing man-made fibres. However, the state-owned enterprises were the major players of the Turkish textile industry until the 1980s. Afterwards, high fixed costs, out-dated technology, overmanning and poor management capabilities made state-owned enterprises to lose their competitive advantage [4].

Although the ready-made clothing industry began to develop after the 1840s in the UK and the rest of developed countries [26]. It was only over the last two centuries; the clothing manufacturing have moved tailored made products to factory production [9]. Turkish clothing industry was dominated by tailor- or home-made products until the 1970s and this began to change by the late 1970s. By the late 1970s, the Turkish clothing industry emerged as a source for foreign currency as Germany and other European countries have shifted their production to Turkey. Low labour costs and cheap raw material supply were the main reasons behind the growth of the Turkish clothing industry. However, this growth was restrained by the low quality of raw materials, lack of trained workers, inadequate supply of equipment and quota restrictions. The growth of clothing industry supported the Turkish textile industry's expansion during the late 1970s [1]. The main strength of Turkish clothing industry is the knitting sector. Despite the less value-added items in knitted garments and fabrics, the knitting sector receives more investments as it can be established on a small scale with relatively less capital in comparison to the weaving industry [23]. Single jersey, terry, pique, velour, rib, interlock and jacquard are the main types of fabrics and underwear and t-shirts are main lines produced by local Turkish knitting companies. In order to produce higher value-added products such as sweaters, cardigans and jogging wear, larger knitting companies invested on flat bed knitting machineries [27].

In the early 1980s, ex Turkish president Turgut Ozal introduced radical changes to the Turkish economy which have had a continued effect on its evolution until the 2000s. Broad-based restructuring measures were instituted, which included the opening of the economy to international competition, the liberation of foreign exchange and trade regimes and the recognition of the need to reduce the state-owned sectors of the Turkish economy. Following those changes, macroeconomic indicators were generally positive in the 1980s, expect for high inflation rates which remained around 50 per cent. Therefore, in the 1980s the Turkish economy was characterised by high economic growth and a strong balance of payments. In between 1980-1990, there was a tremendous increase in the international trade of Turkey; imports increased 300 per cent and exports increased more than 500 per cent value terms. This dramatic increase in international trade was that the Turkish governments pegged the exchange rates often at unrealistically high currency values and imports were restricted by high trade barriers. The textile and clothing exports have increased significantly by the second half of 1980 and the growth rate of those industries were higher than the average of Turkish economy. This rapid increase was stimulated by the introduction of the new-export oriented model in the 1980s and this plan aimed to export outputs of textile and clothing industries to nearby countries especially to European Union [28]. In 1983, the Foreign Investment Law was modified which offered better conditions for the foreign investors in Turkey. At the same time with this modification, a legislation was passed to encourage foreign direct investment in high technology required and export-oriented industries such as textile and clothing [29].

In order to attract the foreign investment, Turkish governments have established free trade zones and offered investment incentives such as export subsidy credits, tax and duty exemptions on the imported machinery. This government policy caused many European companies to use Turkey as a manufacturing base because of Turkey's location and low labour costs compared to Europe. In Europe, Germany is the leader of "outward processing" of manufacturing. It was the first country which began outsourcing their garment production to other countries and in order to have the control over, Germany investments were mainly established as joint ventures. In the 1980s, 35 per cent of foreign investment in the Turkish textile and clothing industry was made by German companies. German companies were followed by Italian, French and English companies and they also established joint ventures in textiles and clothing industries with a share of 40-50 per cent. The growth of foreign investment in the Turkish textile and clothing industry caused the industries to upgrade their technology and quality of the work force. Unfortunately, the levels of foreign investment were low even in 1980s compared to other developing countries because of the political and economic uncertainty [30].

By 1991, Gulf crisis and political uncertainties in Turkey caused a stagnation in the Turkish economy. The political uncertainties were solved after the 1991 election and industrial output growth accelerated in 1993 however external fiscal deficit continued to increase until 1994. In 1994, Turkish economy had one of the worst economic crises in its history due to the major external deficits and deterioration in public sector finances. In April 1994, stabilisation programme was launched following a standby agreement with the IMF. During the 1990s, the Turkish textile and clothing industries were the largest industries in terms of export with the share of 38.5 per cent of the Turkish economy. Turkish textile and clothing industries had a surplus in the 1990s and Turkish textile imports began to increase to meet the demands of Turkish clothing industry for yarns and fabrics which cannot be supplied from the local market. Turkey signed "Customs Union Agreement" with the European Union in Jan, 1996 and after this agreement, Turkey's exports were expected to increase by ten per cent, surprisingly three per cent decline occurred in 1996. The reasons behind this decline were; firstly, the economic recessions in the main European countries such as Germany, France and Italy had a negative effect on consumption patterns of consumers as fashion is accepted as a "discrete purchasing" item that consumers cut spending firstly. Secondly, new regulations imposed on trade with EU and Turkish textile and clothing manufacturers could not adopt to those changes in a short period of time. Thirdly the compensation tax imposed on raw materials of clothing exports has increased the costs of the Turkish clothing manufacturers [4]. In 1997, European Union candidate countries were exempted from import duties and quotas to EU which provided direct access for countries such as Poland, the Czech Republic and Hungary to Turkey's main export markets such as Germany. In 1999, Turkey's textile and clothing exports decreased annually for the first time after thirty years. 1999 Golcuk earthquake, economic turmoil in world markets and fluctuations in exchange rates had also an impact on this decline [22].

China's entrance to the World Trade Organization in 2001 and abolishment of quotas in 2005 are the major factors that affected the Turkish textile and clothing industries negatively. Turkey has become in direct competition in its export markets with China and other Asian industries in 2007 the economic crisis in US market made the situation worse for the Turkish textile and clothing industry. After the crisis, because of the shrank in the European market, the European Union companies revised their structures and they began to purchase in small lots rapidly from close geographies and the strength of Turkish companies in this area have increased the exports in the industry [31]. The world-wide financial crisis in 2018 hit mainly the emerging markets and Turkey was one the developing countries which is affected deeply. Turkish economy had a currency crisis followed by a recession in the second half of 2018 which had an effect on the Turkish textile and clothing industries and lowered the demand in the local market and had a negative impact on the overall performance of the Turkish textile and clothing industry [32].

TURKISH WOOL INDUSTRY

The Turkish woolen industry is smaller specialist industry compared with Australian and Chinese woolen industries which controls the world wool market [33]. The Turkish wool industry is a stable sub-sector of Turkish textile industry through the years and remained small. Turkish wool industry has few breeds of sheep compared with many other countries. The Turkish wool is mainly 30 microns thick and short-staple, therefore the Turkish wool industry mainly serves to the domestic market for carpets, blankets and other coarse fabrics [33]. The industry is mainly dependent on imports for fine wool fibres; imports were from New Zealand and Australia until the 1990s and afterwards from Turkish Republics and Eastern Europe. Unfournately, high quality wool, merino has only a 3 per cent share in total wool production. Turkey quickly emerged as the main manufacturer of woolen fabrics for clothing in the 1980s. The main market was the Centre Europe and this was hampered by the Russian financial crisis and low-priced imports from the Far East [4].

TURKISH COTTON INDUSTRY

Turkey is the 6th biggest producer of cotton, 11th biggest country in cotton cultivation area, 6th biggest country in terms of fibre cotton yield obtained from unit area, 5th biggest country in terms of cotton consumption and 6th biggest country in terms of cotton imports in the World [34]. Cotton fibre accounts more than 60 per cent of the total mill consumption in Turkey. The Turkish cotton is ranked as a medium quality cotton with a with a fibre length no longer than 31 mm and fibre thickness with a value between 2.7 and 5.0 microfiber [4]. However, only Aegean cotton is an exception in Turkey and ranked one of the best quality cottons in the international markets. Unfortunately, there has been a decline in the crop of the Aegean region related to changes in the social structure of the region such as development of tourism in the Aegean area [35].

The expansion of Turkish cotton spinning industry has begun in the 1970s. There has been massive amount of investment in the cotton spinning industry during 1990s and as a result Turkey became the biggest importer of open-end spinning machinery and third biggest importer of ring spinning industry in the world by 1995. The reasons behind those heavy investment figures were; an anticipated increase in cotton exports after custom union with EU and the start of cotton cultivation in the GAP project in South East Anatolia. GAP, which is Southeast Anatolian Development Plan is an irrigation project which made the Southeast Anatolia largest cotton growing area in Turkey. The increase in the capacity of cotton spinning was accepted to reduce the price of cotton yarn which will in turn increase the competitiveness of the clothing industry both in domestic and international markets [36]. However, the EU which is the largest export market for Turkish cotton yarns imposed a 12 per cent anti-dumping levy in 1991 and this made Turkish cotton spinners to lose their competitive advantage in the EU market as the levy was twice the levy on imports from Third World countries. Furthermore, Turkish cotton spinning industry had heavily invested on open-end carded yarn where they do not have a competitive advantage in the international markets. This excess capacity occurred because of the incentives given in Southeast Anatolia to accelerate the industrial development in that area by Turkish governments but in order to prevent unused capacity, the Turkish spinning industry should invest in ring spinning machinery [35]. Until the 1980s, the main problem of Turkish cotton weaving industry was the obsolescence of the machinery. In a 1985 dated study conducted by Boston Consulting Group, found that 60 per cent of the Turkish weaving looms were older than 25 years old. The heavy investment on the spinning industry forced the Turkish weaving industry to make complimentary investments in new technology to continue to compete in the international markets.

The Turkish cotton cultivation area continued to increase until 2006, but decreased in the subsequent years and it was only 416,000 ha in 2017 [37]. During the same period, the countries which are main competitors of Turkey supported their cotton industries with high-rate subsidies whereas Turkish governments have narrowed the scope of subsidies and also created an excessive capacity in textiles and clothing industry. As a result, the consumption of cotton increased steadily during the same time period and Turkey became a net importer of cotton in the world with approximately 500 thousand tons. As an effect of high subsides by rival competitors to the cotton lowered the prices of cotton whereas low subsidies have caused Turkish producers to stop the production of cotton which resulted in increasing numbers of imported cotton. In 2000s, Turkey imports reached to half million tons of cotton which is nearly 80 per cent of its production. Turkey mainly imports cotton from the United States which provides half of the world's cotton subsidies to its producers. The other main competitors of Turkey which are China, Greece and Spain producers also receive high rate of support and this support can reach to half of the market price of the cotton. Increasing production costs and high-rate of subsidies of competitors are the main reasons behind the decline of the Turkish cotton production and industry. This decline in the Turkish cotton industry makes the Turkish textile industry heavily dependent on foreign markets especially to the United States [37].

TURKISH MAN-MADE FIBRES INDUSTRY

The man-made fibres industries showed a tremendous development between the 1950s and 1980s in the world. The technological developments in the polymer chemistry and fibre-forming techniques were the source of those developments. During the same period, the developments in the staple-yarn manufacturing and multifilament synthetic yarns texturing technologies occurred worldwide [38].

The development of the Turkish man-made fibre industry followed the same path like the rest of the world. Until the 1960s, the Turkish textile industry was dominated by the cotton industry. In 1960s, the production of polyamide and polyester introduced the man-made fibres industry to the Turkish textile industry. The real expansion of the Turkish man-made fibre industry took place in the 1980s and the major reasons behind this growth was the growing domestic demand and an increasing export potential particularly of polyester to the West Europe, North Africa and Middle East. The development of the Turkish man-made fibre industry followed the same pattern with the rest of the world. Firstly, development of the man-made staple sector occurred and then it was followed by the introduction of man-made filament yarns as filament yarns are indicators of a more sophisticated and advanced textile industry. Since 1984, the man-made filament sector grew at a higher rate than the Turkish man-made staple industry which confirms steady transition from traditional reliance on staple activity and a move towards a filament production. In the late 1980s, in volume terms, Turkey became the 9th largest producer of man-made fibres and yarns in the World [36].

Between 1990 and 1995, production of Turkish man-made fibre doubled as a consequence of increasing demand of local textile industry. On the other hand, surprisingly, between the same time period, supply of man-made fabric showed a decline and remained the below of the local demand. After 2008 crisis, man-made fibre mill consumption had a sharp decline in 2009 and it began to recover in 2014 and nearly doubled its mill consumption compared to 2008. The mill consumption continued to increase between the years 2010 and 2020 and surprisingly in 2020 it reached to 2017 million tons even there is Covid 19 pandemic.

MILL CONSUMPTION

Mill consumption is a significant indicator of general textile activity and it is determined by consumption in the domestic textile market and consumption of fibres to resource export activity in garment and fabrics. The below Table 1 shows the mill consumptions of Turkish wool, cotton and MMF industries.

Table 1. Mill Consumption (Source:TUIK).

(Tonnes)	Wool	Cotton	MMF	Total
1980	44	282	130	**456**
1990	73	558	309	**940**
2000	98	975	813	**1886**
2010	105	1237	1136	**2478**
2015	121	1.393	1.629	**3.143**
2016	99	1.500	1.664	**3.263**
2017	96	1.548	1.762	**3.406**
2018	70	1.644	1.575	**3.289**
2019	61	1.779	1.711	**3.490**
2020	60	1.878	2.017	**3.955**

TURKISH CLOTHING INDUSTRY

Generally, clothing industry is accepted as one of the most internationalized industry [39]. The Turkish clothing industry has rapidly grown since 1970s after German companies had moved their production to Turkey. The labor-intensive characteristics of clothing industry along with the minimal technology, capital and skill requirements for its production has fostered the expansion of the Turkish clothing industry. The Turkish clothing industry has expanded more rapidly than other manufacturing industries since the 1980s for three reasons: the internalization of the Turkish economy, the rational use of investment incentives and liberalization of imports allowing the free follow of imports of machinery [40]. The relatively low labor cost is an advantage for the Turkish textile industry [41]. However, low labor productivity is one of the major problems of the Turkish clothing industry as the rate of labor productivity in the Turkish clothing industry is lower than all European countries with the expectation of Greece. After China's membership to the World Trade Organization in 2005, the quotas imposed on Chinese clothing industry was removed and the increasing shares of low labor countries such as Vietnam, Bangladesh negatively affected Turkish clothing industry. Furthermore, African countries which have been investing in the industry are expected to be important exporter countries in the sector. All of those developments will increase the competition for the Turkish clothing industry [42].

The Turkish clothing industry has enjoyed greater success in knitted garments compared to woven garments which can be linked to various factors. Firstly, the Turkish weaving companies which produce fabrics at international levels are vertically integrated and they cannot comply with the rapidly changing demand as opposed to the knitting industry because of the complexity of the production process. Secondly, most of the woven garment manufacturers have failed to create branded products. The Turkish clothing industry is mainly used as a subcontracting base by European companies for garment manufacturing, design, marketing and managerial skills are neglected.

This research aims to understand the dynamics of the Turkish textile and clothing industries and pathway of the Turkish textile and clothing industries which are mainly export-oriented. As a research method, qualitative analysis is used and 14 semi structured interviews were performed with managers from Turkish textile and clothing industries. In the light of the knowledge from the literature about the Turkish textile and clothing industries; our main research questions are formulated as follows;

Q1: What are current advantages and disadvantages of Turkish textiles and clothing industries in the internationalization?

Q2: How can Turkish textile and clothing industries can keep their competitive advantages and gain new ones in internationalization?

METHODOLOGY

In this study, a qualitative analysis approach has been adopted to investigate and understand the current situation, problems and perspectives of the companies in the Turkish textile and clothing industry. This approach is widely accepted and applied in the context of SMEs [43]. Creswell (2013) defines qualitative research as "research in which qualitative data collection methods such as observation, interview and document analysis are used and a qualitative process is followed to reveal perceptions and events realistically and holistically in their natural environments". The case study pattern is "a qualitative approach in which the researcher collects detailed and in-depth information about real life, a current limited situation, or multiple classified situations within a given period of time through multiple sources of information, presenting a situation description or status themes" [44]. In this study, as stated by Yin (2009), the "case study pattern" used when it is necessary to investigate the current context in real life or a situation within the environment is preferred [45].

Middle and senior managers working in the Turkish textile or clothing sector were selected as a sample. Within the scope of the research, officials from 14 companies were interviewed between 1 and 30 December 2021. Participants are numbered P1-P14 to protect confidentiality. The participants answered 14 semi-structured questions in interviews which conducted online and recorded with the consent of the participants. The interviews lasted an average of 25-30 minutes. Firstly, content analysis was made for the interviews which were in written format and themes and codes were created. All the necessary qualitative analyses were made in Maxqda qualitative analyses program. Maxqda is a worldwide software tool for qualitative and mixed methods data analysis. By Maxqda, different kinds of data such as texts, images, videos, tweets and focus groups discussions can be analyzed. The themes were interpreted in line with the codes they contain and excerpts from the interview texts are also included in order to support the comments.

Qualitative researches are mostly criticized for their validity and reliability. In order to ensure the validity and reliability of the research, the following studies were conducted:

- Detailed literature review was carried out during the research.
- The interviews were recorded with the consent of the participants in order to prevent data loss. The interview questions were shown to an academician who is an expert in the field and to a manager experienced in the sector and necessary arrangements were made in line with their evaluations.
- A preliminary interview was conducted with a manager to test the clarity of the interview questions. The results of the pilot interview were shared with an expert academician in the field and the validity of the questions was confirmed.

- According to the coding audit that ensures internal consistency, the consensus between coders should be at least 80 percent [46]. When the encodings made by two different encoders on the interview document are compared at the level of code presence; 14 partitions were related, while 2 sections were not. The consensus among coders was found to be 87.50 percent.

FINDINGS

The main theme of our research is the internationalization and the codes under this theme are as follows; "knowledge and experience of employees", "marketing and planning capabilities", "export commitment", "export markets information", "export experience" and "export performance". The model of the research is presented in the Figure 1 below.

The detailed code map of internationalization of Turkish textile and clothing industries is listed below as Figure 2. The numbers near the each subcode shows how many times a subcode is mentioned by the participants.

The main codes of our research are; knowledge & experience of employees, export commitment, export experience, export market information, export performance, marketing & planning capability. The details of each code are given below.

Knowledge and experience of employees

The participants mentioned that; the employees of their company have adequate knowledge and experience and the employees are sharing their experiences with their colleagues. If the top management is open-minded and promote learning in the company, the employees have continuous training. The quotes from P5 and P7 are as follows;

"… our company promotes learning and we have innovation department related to new designs and designers and export department work …" (P5).

"… our company owner promotes continuous learning in the company and we are attending a consulting programme supported by Turkish Export Promotion Centre…" (P7).

Marketing and Planning Capability

This category is defined by "strategy & plan" codes and "" change of export markets". In this code plenty of companies states that they formulate plans and strategies for each year whereas some participants declare that they do not prepare any strategic plans. However, they added that the markets are volatile and unpredictable which makes difficult for them to follow their plans.

" ...at the beginning of each year, we make yearly plans but we cannot follow all the plans because of the unexpected changes from customers such as order cancellation…" (P8) and

"… we make plans for a year and every 3 months we check if we are following our plan… "(P13) said.

Export Commitment

This category is characterized by "attending fairs", "importance of customer relations" and "retaining current customers". The Turkish textile and clothing companies are highly dependent on export sales and they have a high level of export commitment. Majority of the participants attend to the international fairs regularly however a few of them stopped attending the fairs as they do not gain new customers. As it can be understood clearly from the below quotes, the companies give high importance to their export customers and they try their best to have good relations with them;

"… some export customers request too many and detailed samples, normally we do not provide them but in order to keep good relations with our important export customers, we provide them…" (P5).

The participants have high level of apprehension about retaining their current export customers. The companies are worried about the hard competition in the international markets and they focus on the current customers rather than searching for new customers. The below example is very indicative;

"… the markets are very volatile and our target is not to lose our current customers rather than having new customers…" (P3).

Export Markets Information

Market research, target market selection, network relations, competitor analysis and distance to target markets are the codes in this theme. The market research is the most mentioned code in this theme. The participants are searching for new markets and this search is mainly through internet. On the other hand, most of the participants believe that network relations are the main source for gathering new customers and the quotes about this issue is gathered under "network relations". The participant P3's quotes are as follows about network relation;

"...we usually find new customers through our network relations; you cannot say that I want to work with this customer and knock on anyone's door. However, it is much easier if the customer representative you work with moves to another company, you begin working with the new companies by visiting him, communicating and using your personal network…" (P3).

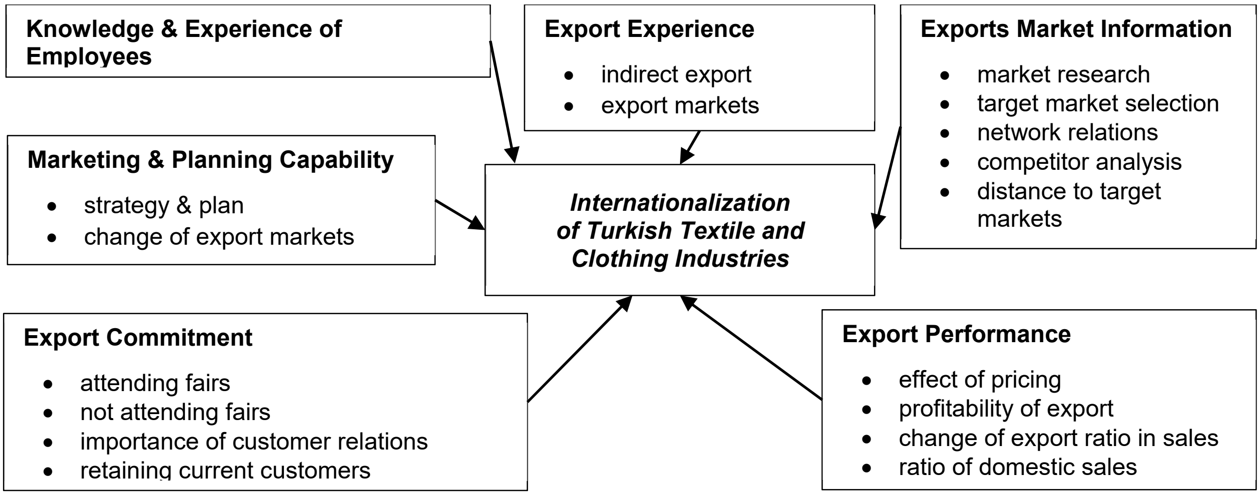

Figure 1. Model of the research.

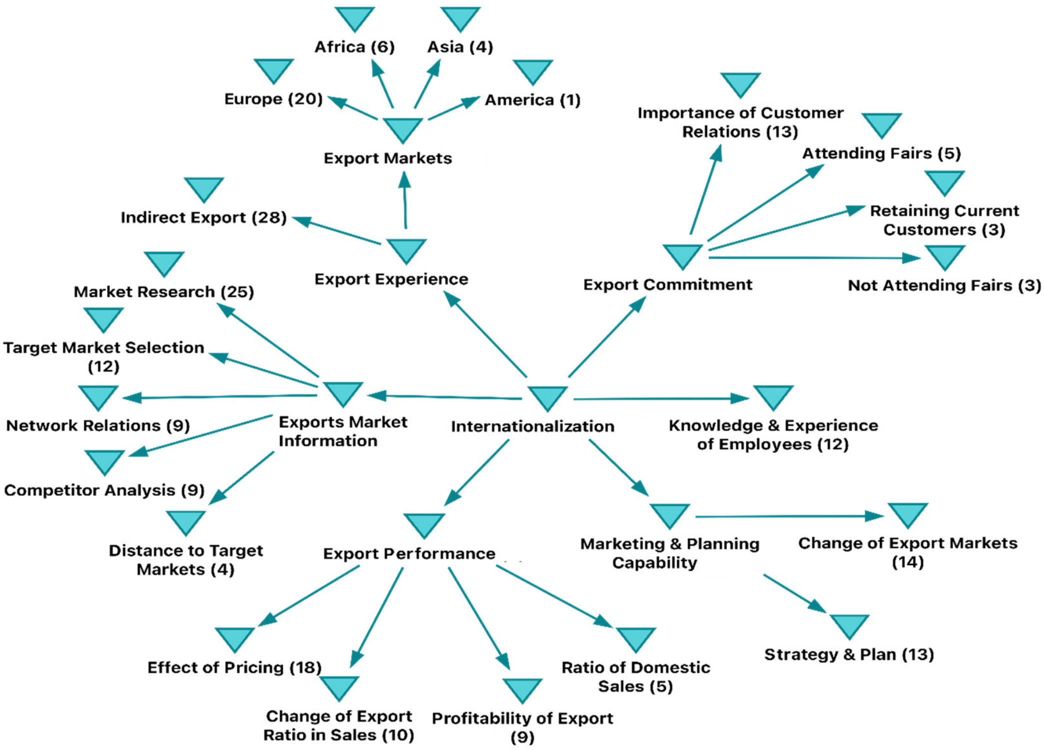

Figure 2. Detailed code map.

In market selection code, they stated that they do not prefer entering to the countries which do have developed banking system. Turkish textile and clothing industries have a substantially important exports to the Middle East and Turkic Republics and most of those exports are in the form of unregistered trade. The participants stated that they follow their domestic competitors rather than international competitors and emphasized that they are also followed by their competitors. The distance to target market is an important criterion when they are targeting new markets. The tremendous increase in the transport costs made both exporters and customers to focus more on near markets.

Export Experience

There are two sub-codes under export experience; indirect export and export markets. The indirect export is the most repeated code in our research. The Turkish textile and clothing companies are involved in indirect export either because of their low export skills or because of working with the Turkey offices of global brands.

"… we mainly work with agents especially for the Italian market…" (P5)

"… we have customers from 45 countries and we mainly work with agencies with most of those customers" (P11) quoted in" indirect export" code.

Related to “export market” code, most of the participants declared that they work with European countries. Europe is the most declared code in this theme. Europe is the largest export market of Turkey mainly because of proximity to Turkey and intensive network relations with the European countries.

Export Performance

Export performance theme has the “effect of pricing”, “profitability of export”, “change of export ratio in sales” codes. Most of the participants are complaining about the increase in the raw materials by the effect of covid-19 pandemic. The competition from Far East countries is forcing the Turkish textile and clothing manufacturers to reduce their profits. The quotes of P14 are as follows;

“… we have higher costs in zipper and we cannot compete with Chinese manufacturers but nowadays European and American companies do not want to work with China and we are trying to turn this into an opportunity…” (P14).

Export sales are more profitable compared to domestic sales according to the participants. During the periods that export ratio in the sales declines, the share of indirect export increases in their sales. Only exception is the beginning period of Covid 19 pandemic, as the exports of them were nearly stopped they stated.

The Figure 3 shows the most quoted codes in the internationalization theme. The bigger spot means “more quoted” and the numbers at the end shows the total quotation number. “Target market selection”, “effect of pricing” and “indirect export” are the mostly mentioned codes in the research. Those codes clearly indicate that the industries are searching for new markets because of the intensive competition and the Turkish textile and clothing industries are heavily dependent on indirect export.

The relation code map shows and helps to analyze the relations between the codes in Maxqda. The Figure 4 is the relation code map of the study. The thicker lines show a higher level of relation whereas thinner lines show weak relations. The strongest relation is between “change of export markets” and “effect of pricing”. The Turkish textile and clothing manufacturers are forced to change their export markets by the effect of pricing. There is also a strong relation between market research and indirect export; the manufacturers are researching for new markets to have more direct export rather than indirect export. “Effect of pricing” has strong relation with “ratio of domestic sales”. The Turkish manufacturers are forced to sell to the domestic market in order to cover general costs when they lose their customers by the effect of pricing. “Market research” has also strong relations with “competitor analysis” and “importance of customer relations”. The Turkish textile and clothing manufacturers carry competitors’ analysis and market research at the same time and they mainly focus on domestic competitors.

CONCLUSIONS

The most repeated codes in our research are “indirect export” and “target market selection. Almost all of the participants declared that they make indirect exports through agencies. Participants expressed their belief in the necessity of conducting research on new export markets and the researches are made by the help of digital Technologies such as online fairs and B2B digital platforms. The importance of customer satisfaction was emphasized in ensuring export loyalty. In ensuring customer satisfaction, positive communication with the customer and solution-oriented customer relationships have come to the forefront. The participants emphasized the importance of the knowledge and experience of the employees of the company in the process of internationalization and it was stated that people with sectoral experience were tried to be employed. It is stated that the biggest effect of the change in the export markets in recent years is the inability to compete with the prices of competing countries. Turkish textile and clothing industries main competitor is China and they cannot compete with the prices of Chinese manufacturers. However, during and after the covid 19 pandemic, European manufacturers switched their orders from China to Turkey to receive smaller and faster shipments. All participants emphasized the importance of exports and stated that export sales are more profitable than domestic market sales. Despite the difficulties they experienced in the domestic market, they added that they manufacture to the domestic market during periods when exports weakened in order to cover their fixed costs.

It was stated by the participants that the main region of export is the European Union countries. Since the European Union is the closest developed market to Turkey, it is the region where textile and clothing companies carry out the most intensive export activities. This is covered by the Uppsala Theory, which stands out in the field of behavioural-based theories in explaining the internationalization processes theoretically [47]. The participants also declared that the internationalization mainly takes place by the help of the networks of the companies.

Turkey has a location advantage exporting to Europe compared to other developing countries. Furthermore, Turkey has sent many workers to European countries mainly to Germany, Italy, France after the World War II and linkages from those people provides an important network for internationalization of the Turkish companies.

The Turkish textile and clothing industries are at cross-roads where strategic choices have to be made for the future of those industries.

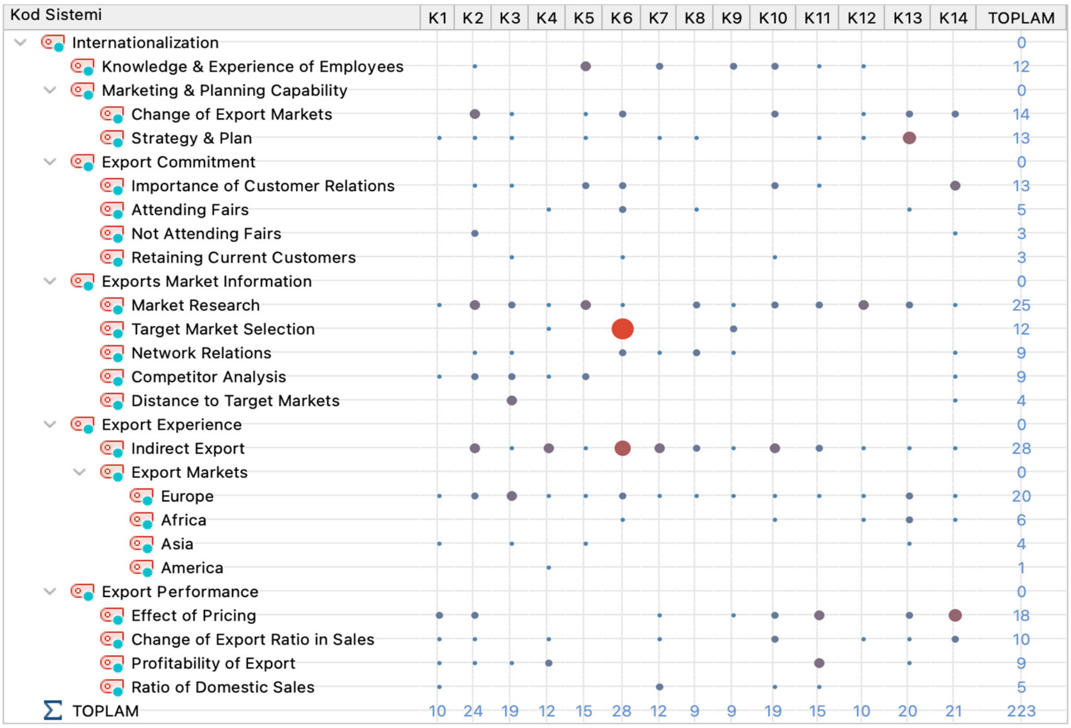

Figure 3. Most quoted codes map.

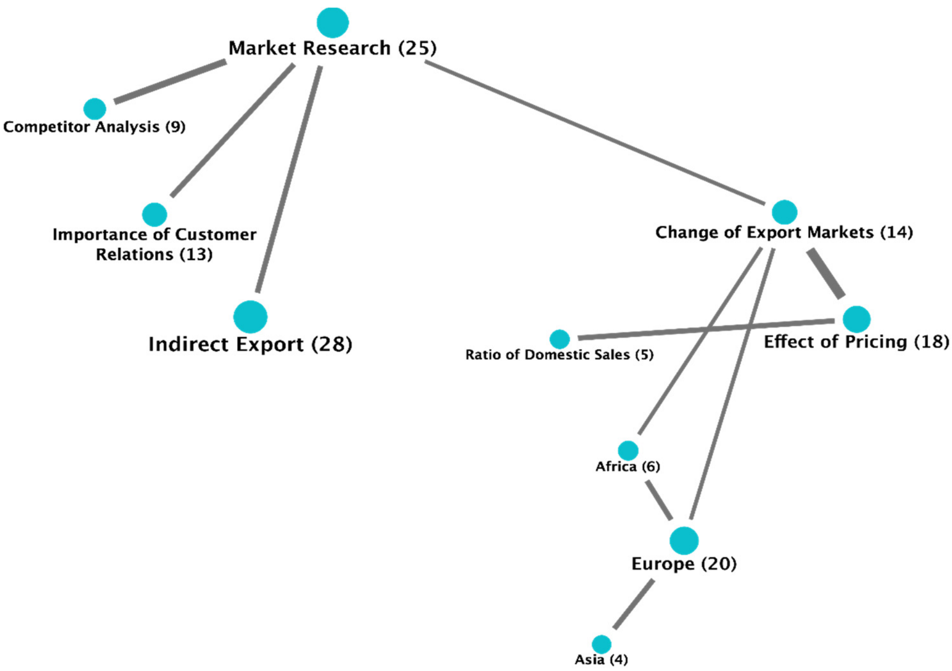

Figure 4. Relation code map.

The mix of strategies and policies will not be uniform across the country due to the radically different conditions. Turkish textile and clothing manufacturers are under intense competition from other developing countries especially from Far East competitors. Turkey has an advantage of proximity to major industrialised markets except Japan and Turkish textile and clothing manufacturers should examine opportunities to improve their distribution channels and other means to shorten lead times and services to customers. The circular fashion is gaining importance and fashion consumers are more conscious about sustainability in the main export markets of the Turkey. Therefore, all the processes in the value chain are changing and Turkish textile and clothing industries should take necessary precautions to adopt those changes [48].

The technological developments accelerated the digital transformation of the textile and clothing industries like all the other industries. Therefore, a determined effort has to be made to improve vocational education for digital transformation. Without significant improvements in digitalization of the industry, Turkey will not be able to accomplish repositioning which is crucial for the coming years. This is particularly relevant to support the emergence of middle-sized companies from the mass of fragmented manufacturers who currently exists. Without success in digitalization, a large gap is expected to open-up between the "big" private companies and "cottage" producers.

Discussion

As Turkish textile and clothing industries have a significant importance in the Turkish economy, mainly Turkish researchers had shown an interest in these industries. The researcher's main point of interest is generally the competitiveness of the Turkish textile and clothing industries. One of the most recent research in this area is by Halife (2022) and the competitive advantages of textile industries in India, China, Vietnam, Turkey, and the United States during the 2010–2019 are compared by Balassa's revealed comparative advantage approach. In this research, Turkey has less comparative advantages than Pakistan and Vietnam. Another study by Tokel et al., (2022) analyses the economic impact of Turkish cotton industry and lists the essential points for increasing the competitive advantage of Turkish cotton industry.

In the extant literature, the study of Esi (2017), which evaluates the development of Turkish textile and clothing industry is the most similar research to our study. However, in our study development of Turkish textile and clothing industries are criticised separately. The development of textile and clothing industries in the world is also evaluated and effect of the global trends to the Turkish textile and clothing industries are evaluated. In their study Uyanık and Celikel (2019), tried to point out the current situation of Turkish textile industry. Another article which was published by Onday (2005) outlines the importance of Turkish textile industry to the Turkish economy.

The other researches in this area are specifically targeting to evaluate a section or a geographic location of the Turkish textile and clothing industry. In the study of Yılmaz (2020), the historical development of Erbaa, location in the Black Sea region has been evaluated. In their study, Orhan and Ucar (2021) aimed to underline the importance of the Tarsus, Cukurova region and state the current conditions of that region. Pak and Atılgan (2021) analyzed the competitiveness of Denizli, by Porter's diamond model and found its competitiveness high.

During industry 4.0 era, like digitalization, sustainability gained importance by the development of advanced technologies. The textile and clothing industries are referred as one of the most polluting industries in the world and those industries are blamed for their effect on environmental problems such as climate change, water scarcity and chemical pollution. The value chain management is the most important part in sustainability. Turkish textile and clothing industries are important part of value chains are they are manufacturers of many international brands. Therefore, the Turkish textile and clothing industries should focus more on sustainability and assure that they get necessary measurements to develop a sustainable production. A research conducted by Kazancaoglu et al., (2022) tried to figure out the obstacles aganist the Turkish textile industry for establishing a circular economy. Their study found that unwillingness towards circular economy is the main problem of the Turkish textile industry.

In order to gain and sustain a competitive position, the Turkish textile and clothing industries should try to move upmarket which means developing their own collection with applying sophisticated marketing and merchandising techniques. The Turkish manufacturers should emphasize on concepts such as branding, design, greater flexibility, quick response, quality and service and their success will be dependent to the extent that they integrate all of those concepts which means a change to the consumer driven system.

Further Studies

Further studies should evaluate the history and developments of each sub-sectors of the Turkish textile and clothing industries in detail. The sub-sectors of the Turkish textile and clothing show significant differences amongst to their geographical location and therefore a further study based on geographical locations should be performed. Moreover, cross-cultural studies can be conducted for illuminating the possible differences between Turkish and foreign textile markets.

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RESEARCH OF WEAR RESISTANCE OF DRAWINGS PERFORMED BY ACRYLIC PAINTS IN HAND PAINTING TECHNIQUES

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ABSTRACT

The article considers a modern way of decorating clothes - hand-painted with acrylic paints based on motifs of Petrykivka's paintings. The possibility of using acrylic paints for hand painting of denim products in the technique of Petrikivka is investigated. The evaluation of the process of making drawings with different types of acrylic paint on denim fabric is performed. An experimental study of the wear resistance of the finished garment, namely: color fastness of the applied pattern to rubbing and to the washing. Based on the obtained data, a variant of acrylic paint is proposed, which provides high-quality production of competitive garments with hand-painted finishing in the technique of Petrikivka.

KEYWORDS

Properties of acrylic paints; Petrykivka paintings; Washing quality; Color fastness to rubbing; Manual application technique; Denim fabrics; Decorative painting of fabrics.

INTRODUCTION

Nowadays, changes in the world economy and, consequently, in the fashion industry against the background of restrictions related to the spread of the COVID-19 pandemic have led to a reassessment of consumer needs and changes in demand for certain clothing in the world and in Ukraine. The trade of products that are easy to use, simplified designs and shapes, and clothing for everyday use has become more widespread. This category of goods includes denim clothing, which has not lost popularity for several decades and became the classic and can be worn even at home.

On the other hand, in the era of mass production, individuality and uniqueness are the main value for a huge number of people who want to attract attention, including through appearance. The trend of customizing clothes has been and remains quite popular, which involves changing the product to the individual request of the consumer. Customization is a popular design and at the same time marketing move, which involves providing the product with certain properties to enable a person to show individuality, modify the product for the buyer or collect it completely from scratch. One of the types of customization of garments is hand-painting, which is quite popular among young people.

Today Petrykivka ornament is an artistic business card of Ukraine. This is not only Ukrainian decorative and ornamental applied art, but also modern painting, which is actively developing. Since 2013, Petrykivka painting has been included in the UNESCO list of cultural intangible heritage, which testifies to its relevance and importance in the development of Ukrainian and world culture [1].

Petrykivka motifs are actively used not only in everyday life, but also reflected in the work of world-renowned designers for decorating modern clothing. Researchers of Petrykivka painting traditions have confirmed the need to expand the implementation of Petrykivka traditions in modern clothing design from the use of traditional ornamentation to the development of new professional technologies for transferring ornamental art into clothing [2, 3]. Thus, the decoration of clothes in the style of Petrykivka with the use of hand-painted paints is modern, and the problem of studying the technology of decorating products to create competitive clothing is relevant.

REVIEW OF RELATED LITERATURE

Drawing on fabric or clothing is possible using various techniques: printing on fabric, hand-painting of details or painting the finished product. Coverage of the issues of drawing by machine printing methods is presented in works [4-8], in which the researchers analyzed the technologies of drawing images on the fabric by printing methods, methods using foil, transfer printing and more.

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Received May 20, 2022; accepted September 19, 2022

The authors [7-9] considered the issue of creating high-quality clothing of various assortments, including fabric and knitwear with drawings decorated with direct digital and transfer printing. The results of experimental studies of image quality indicators are presented and conclusions are given on the influence of various factors on the wear resistance of the image applied by direct digital and transfer printing methods.

The effect of paint on special fabrics used for sewing of working clothes of building specialties were investigated in [10]. The definition of fabrics resistance to variety kinds of paint and the rigidity of fabrics after paint's effects was assessed.

A several scientific works are devoted to the decoration of hand-painted products, which can be done with acrylic paints in various techniques: hot batik, cold batik (reservation), knotted batik, free painting, a variety of which is raw painting on moistened fabric and Petrykivka, as well as painting airbrush [11-12]. In particular, in the work [12] authors developed a specific method for simulation of the batik printing patterns with cracks. Widespread use and relevance of hand-painted types of fabric was confirmed in [13].

The authors [14-16] considered the issue of hand painting of silk and cotton fabric, the combination of traditional design methods and innovative manufacturing technologies. Different types of natural dyes for fabrics are discussed in publications, that provide them eco-textile labelling.

Scientific works [17-21] are devoted to the study of dyeing processes of natural fabrics with various types of natural dyes. The chemical technology of the dyeing materials is also considered.

The paper [22] presented a novel computational approach to simulating hand-painted printing patterns on cloth, according to the real process of this ancient folk handicraft. This method can produce vivid hand-painted printing patterns on cloth of different woven structures.

Authors [23] proposed a general classification of types of finishes for denim clothing by method of production, which also includes hand-painted paints on fabric. Confirmation of the relevance of various types of finishes, including hand-painted products with acrylic paints, is presented in [24].

The work [25] is devoted to the study of the peculiarities of hand painting in the technique of batik, in which the authors confirmed the possibility of using acrylic paints for high-quality drawing in the technique of batik on fabrics of mixed raw materials. In [26] the principles of combining batik decoration with constructive-technological methods of clothing design are proposed.

The issue of designing the author's collection of clothes with hand-painted acrylic paints on the fabric is shown in work [27], which proposed the use of acrylic paints to create the effect of a "chameleon" when manually applying paints of different shades on the surface of plain fabric.

In [28] the friction resistance of acrylic patterns made on different types of materials (denim, raincoat and silk fabrics) was studied. The authors found that the most resistant to friction was acrylic coating applied to the raincoat fabric, based on which a model of women's summer coat with decoration in the form of a floral motif, applied to the product by contour painting with acrylic emulsion.

Works [29-34] are devoted to the development of author's textiles for clothing decoration, including the application of products with applique and embroidery. In [35, 36] the authors proposed the use of acrylic paints to decorate the author's collections of products developed on the basis of a creative source.

Thus, the analysis of literature sources on the research topic shows that the problem of decorating fabrics and clothing is dealt with by many scientists. A number of works are devoted to the issues of finishing clothes with hand-painted acrylic paints. However, the issue of wear resistance of drawings made of acrylic paints requires further research.

DISCUSSING IDEAS

The research is aimed at determining the possibility of using acrylic paints for hand painting of denim products using the technique of Petrykivka drawings.

To achieve this goal, the tasks that need to be solved are formulated:

- to analyze the features of the process of painting with acrylic paints on denim;
- to carry out experimental assessment of wear resistance of the executed furnish.

METHODS

Study used a comprehensive approach, and methods of system analysis to justify the choice of quality indicators of finishing elements, made in the technique of hand painting with acrylic paints on fabric. To achieve this goal, standardized experimental methods for the study of color fastness to rubbing and color fastness to washing, as well as a standardized device ПТ-2 were used. The principles of comparative analysis were used to evaluate the process of painting with acrylic paints on denim fabric, as well as to evaluate the results of experimental studies.

EXPERIMENTAL

The quality of application of pigments on the fabric, namely, their resistance to operating conditions, is determined by the properties of film-forming substances, which have certain requirements:

- high adhesive strength, i.e., the ability to stay on the surface of the fibers of the material and firmly retain pigments;
- elasticity;
- mechanical stability;
- resistance to light and weather conditions;
- non-toxicity.

It is difficult to choose an individual polymer that would meet the whole set of requirements, so in practice, a combination of several polymers is used. Water-based acrylic paints are now the most common for hand-painted fabrics. According to the manufacturers, acrylic paints have a number of advantages. They do not penetrate into the structure of the fiber, but cover the fabric, forming a film on its surface, are characterized by a wide range of colors, mix easily with each other, creating unique shades, are not afraid of moisture. Paints are recommended for outerwear and not suitable for bed linen, which can be washed frequently. It is not recommended for products that are dry cleaned due to the possibility of wiping, as well as for children's things, as it can cause allergies. Paints are non-toxic because they do not contain harmful chemicals [11]. Thus, to make drawings on denim products, it is proposed to choose acrylic paints, the range of which is widely represented on the Ukrainian market. For the experimental study, the choice was based on paints of a similar price segment, but different manufacturers. As blue denim is chosen for the products, it is taken into account that the fabric is light when purchasing the paint. This is due to the fact that some manufacturers classify and produce paints for light and dark materials. Tables 1 and 2 show the characteristics of the selected paints and denim.

The selected paints have similar properties and methods of application, respectively, and similar methods of care for products. However, paint Javana Sunny (Kreul) in appearance is a translucent liquid in contrast to the other two, which have a more intense color.

During the study, the same pattern was made with three types of paints to assess their characteristics and properties in the process of drawing in the technique of hand painting. During the drawing, the analysis and evaluation of the consistency and properties of paints, their ability to perform the reception of the transition smear were performed, which is used in the performance of compositions in the technique of Petrykivka painting. It is also possible to apply the contours of the drawing with a thin brush. It should be noted that brushes with synthetic bristles of different thickness, length and shape were used to apply the paints. Brushes made of bleach, columnar and cat bristles did not allow to paint with acrylic paints, as there was a need for brushes with stiffer bristles.

Table 3 describes the process of drawing with acrylic paints in the technique of hand painting. Based on the results of the analysis of the drawing process, it can be concluded that the first two samples of acrylic paint allow to make drawings in the technique of Petrykivka painting. Acrylic paint Javana Sunny (Kreul) is excluded from further research as one that does not provide the possibility of drawing in the chosen technique. It is also established that when making a pattern on denim with twill weave, you must first apply the base white paint color (primer), which evens out the surface of the fabric, and only then apply a different layer of colored paint. Otherwise, the paint is absorbed by the material and loses color brightness.

It is known that the product quality is formed at all stages of design and manufacture of garments. To do this, consumer requirements for products are being formed at the product design stage. Based on these requirements, the nomenclature of product quality indicators is determined. Regarding the quality of the drawings on the clothes, indicators of safety of acrylic paints and reliability of sewing products with decoration deserve special attention. Reliability indicators determine fastness and durability of products under the influence of external factors. Indicator "color fastness to various physical and chemical influences" allows to estimate fastness of drawings made on denim fabric [37]. A group of indicators of fastness to external influences refers to mandatory indicators of the sewing product quality (according to GOST 4.45-86 "Household sewing products. Nomenclature of indicators" [38].

The indicators: the possibility of chemical cleaning, washing, and ironing and the strength of parts connection - belong to the group of indicators of resistance to external influences (according to the requirements of the standard). Denim outerwear is subject to repeated washing and rubbing in dry weather conditions during operation. The drawing is applied to products in the area of shoulders, thighs, chest and can be rubbed against the belt of bags, arms etc. [34]. Therefore, the two indicators (color fastness of drawings to rubbing and color fastness of drawings to washing) will be investigated.

The essence of methods for determining color fastness of painting to rubbing (according to DSTU ISO 105-X12: 2009 Textile materials. Determination of color fastness. Part X12. Method for determining the color fastness to rubbing (ISO 105-X12: 2001, IDT)) and color fastness to washing (according to DSTU ISO 105-C06: 2009 Textile materials. Determination of color fastness. Part C06. The method of determination color fastness after washing at home and in laundries (ISO 105-C06: 1994, IDT)) is that the samples of denim together with accompanying fabric (white calico) were subjected to appropriate physical and chemical effects [39]. Samples from denim (180x80 mm along the warp thread) were produced for research color fastness to rubbing (Fig. 1). A strip of white paint was applied as a base to the sample.

Table 1. Characteristics of acrylic paints for hand painting of fabrics.

Name of paints	Manufacturer	Country / city	Cost, [UAH]	Appointment
Acrylic for painting fabrics	Rosa talent	Ukraine, Volyn region, Novovolynsk	275 UAH / pack . (12 colors x 20 ml)	Highly pigmented water-based acrylic paints for painting light and dark fabrics of various compositions, including leather and suede
Acrylic for DECOLA fabrics	Nevskaya palette	Russia, Nevskaya Palette Art Paint Factory, St. Petersburg	275 UAH / pack . (12 colors x 20 ml)	Paints for decorative creativity for cotton and silk fabrics
Acrylic Javana sunny	Kreul	Germany by C.Kreul GmbH & Co.KG	225 UAH / pack . (12 colors x20 ml)	Water-based acrylic paints for painting light fabrics, for natural and synthetic materials

Table 2. Characteristics of the main fabric

Type of material	Raw material composition, [%]	Type of weave	Surface density, [g/m^2]	Thickness, [mm]	Yarn density, [units/cm]		Cost, [UAH]
					warp thread	*weft thread*	
Denim	Cotton - 100	Twill	350	0,72	28	19	210

Table 3. Characteristics of the process of drawing with different types of acrylic paint

Name of acrylic paint	The image of the drawing element on the fabric	Characteristics of the paint application process on the fabric
Acrylic paint Rosa talent		The paint has a dense consistency, not transparent. The white base, when applied in one layer, sufficiently evens out the surface and provides a bright and realistic color transfer when applying the next layer of paint, the color corresponds to the manufacturer's stated on the package. The consistency of the paint allows you to perform the technique in the technique of "transitional smear". After drying, the pattern has a slight gloss, the fabric at the application site has become stiffer. The surface of the figure does not form cracks and kinks when bending. With a thin brush, the contour is applied with little complication, the paint needs to be dissolved. During dissolution, a slightly grainy consistency of the paint is observed, which slightly complicates the application of a thin uniform contour. Water was used to dissolve the paint. There are no special solvents on sale from this manufacturer.
Acrylic paint DECOLA		The paint has a dense consistency, not transparent. The base of white color, when applied in one layer, sufficiently evens out the surface and provides a bright and realistic color transfer of the next layer of paint, the color corresponds to the stated on the package. The consistency of the paint allows you to perform the technique in the technique of "transitional smear". After drying, the picture has a slight gloss, but compared to the previous sample made of acrylic paint Rosa talent, less pronounced. The fabric at the application site has become stiffer. Does not form cracks and kinks when bent. The contour is applied very well with a thin brush, the paint does not need to be dissolved, at the same time from dissolving with a special solvent of the same manufacturer there is a uniform fine consistency of the paint, which allows applying thinner uniform layer and contour. Therefore, it is possible to make a finish that will not overburden the material and seal it. The image is more realistic compared to the previous version.
Acrylic paint Javana Sunny (Kreul)		The paint has a translucent consistency, which is significantly different from the previous two samples. The basis of white color put in one layer on material, after drying does not appear, is absorbed by material completely that complicates drawing of a color layer of paint on the same contour. After applying the second color layer and drying it, the paint is also absorbed and impregnated on the reverse side of the fabric. On the front surface, the color of the drawing is not bright and does not correspond to what is stated by the manufacturer on the package. The consistency of the paint does not allow to perform the technique of "transitional smear". After drying, the picture has a dull appearance, re-applying a colored layer of paint does not change the situation. Despite the technique of applying layers of paint, the image is similar to watercolor application and looks blurry. Contours with a thin brush are difficult to perform, there is a difficult application, the paint is kept on the brush with a thick drop, at the same time there is impregnation of the paint on the reverse side. The pattern after drying does not form cracks and kinks when bent.

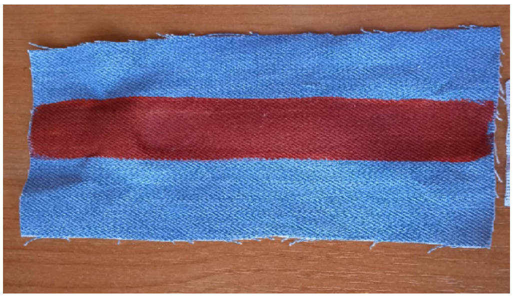
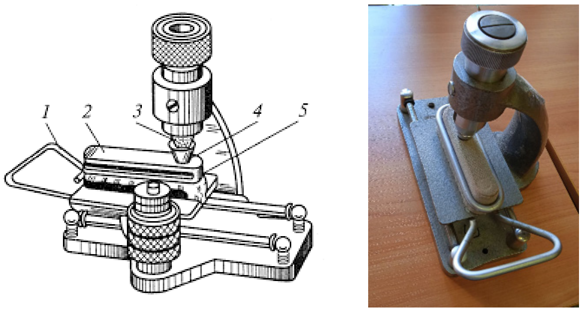


Figure 1. Sample of material with a strip of acrylic paint (Rosa talent, red)

A strip of acrylic paint with a width of 20 mm was applied in one layer evenly by hand to the sample (imitation of hand painting). Two colors of paint (green and red) were used for the experiment as the most contrasting to the main fabric.

The study of the color fastness to rubbing was performed on the device PT-2 according to standard methods (Fig. 2).



(a) (b)

Figure 2. The scheme (a) end appearance (b) of the device PT-2 to determine the color fastness to rubbing: 1 – lever; 2 – table; 3 - rod 1,5 cm in diameter with accompanying fabric sample; 4 - ring for fixing accompanying fabric sample; 5 - ring for fixing the main sample.

For an experiment, the rod with accompanying fabric sample is lowered onto the Table 2. The total pressure between the table and the rod is constant (10 N). With the help of lever 1, the table is moved along the guides at a distance of 100 mm 10 times in one direction and another for 10 seconds. The characteristics of accompanying fabric are presented in Table 4.

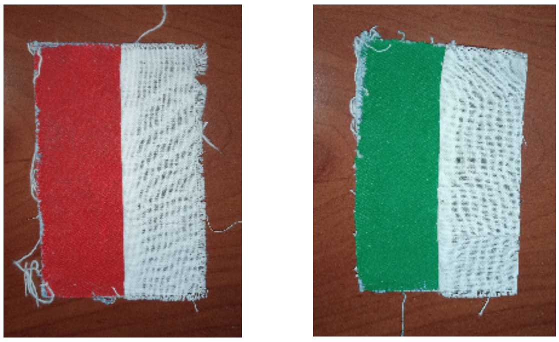
To study the color fastness of drawing after washing, samples 100x40 mm were prepared. The pattern (width of 40 mm) was applied to the entire surface of the material sample. Two colors of paint (red and green) were used to take into account the probability of different behavior of pigments to washing. The accompanying fabric sample 100x40 mm was sewn around the denim sample by hand stitches. Modes of manual washing are given in Table 5. Hand wash was carried out at the specified parameters in a glass container with a volume 250 ml with constant stirring [39].

Table 4. Characteristics of accompanying fabric.

Type of accompanying fabric	Calico
Color	White
Raw material composition, [%]	Cotton -100
Surface density of accompanying fabric, [g/m²]	120
Thickness of accompanying fabric, [mm]	0,21
Sample size, [mm]	50x50

Table 5. Hand wash modes for samples.

Type of base fabric	Denim
Raw material composition, [%]	Cotton 100
Washing temperature, [°C]	40
Washing time, [min.]	30
Rinse time, [min.]	10
The composition of the washing solution, [g/dm³]	Washing powder - 5
Type of washing powder	Persil Color (Henkel)



(a) (b)

Figure 3. Photo samples with the applied pattern after washing: DECOLA red (a); DECOLA green (b).

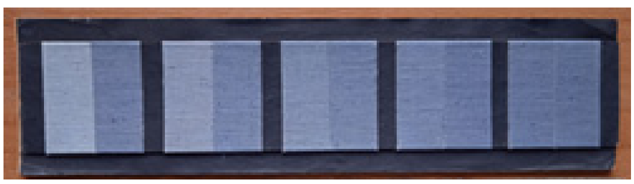
After the test, the samples are taken out, rinsed twice in cold running water for 10 minutes, wringed out, split, leaving a seam on one side, and dried in a suspended state and spread out. The image of the samples after washing is presented in Fig. 3.

RESULTS AND DISCUSSION

Color fastness to various influences is evaluated by two indicators:

- the lightening of the painted sample color (in points);
- the staining of the white accompanying fabric sample (in points).

The comparison of indicators is carried out using the scale of gray standards for evaluating the lightening of color (Fig. 4) and the scale of gray standards for evaluating the staining of the white accompanying fabric sample (Fig. 5).



1 point 2 points 3 points 4 points 5 points

Figure 4. The scale of gray standards for evaluating the lightening of color (1 point - maximum contrast, 5 points - no contrast).

Figure 5. The scale of gray standards for evaluating the staining of the white accompanying fabric sample (1 point - maximum contrast, 5 points - no contrast).

The evaluation of the research results was carried out by the contrast of the pattern before and after the test [40]. The contrast is visually equal to the scale of gray standards. The results of the experiment are presented in Table 6 and in Fig. 6. Rosa talent paint is more color fastness to rubbing.

Table 6. Color fastness of the drawings by acrylic paints to rubbing.

Name of the sample, type of acrylic paint	Paint color	Lightening of sample color, [points]	Staining of the white accompanying fabric sample, [points]
Test 1, Rosa talent	Red	4-5	4-5
Test 2, Rosa talent	Green	4-5	5
Test 3, DECOLA	Red	4	3-4
Test 4, DECOLA	Green	3-4	4

The results of the experiment on the color fastness after washing are presented in Table 7.

Based on the results of the study, it can be determined that the green color of the paints gave a more stable result. During washing samples DECOLA, red, the washing liquid was very colored. Paint residues were observed and peeled off during rinsing.

Table 7. Color fastness after manual washing.

Name of the sample, type of paint, color	Lightening of sample color, [points]	Staining of the white accompanying fabric sample, [points]
Test 1, Rosa talent, red	4	4
Test 2, Rosa talent, green	5	4
Test 3, DECOLA, red	3-4	3
Test 4, DECOLA, green	5	4

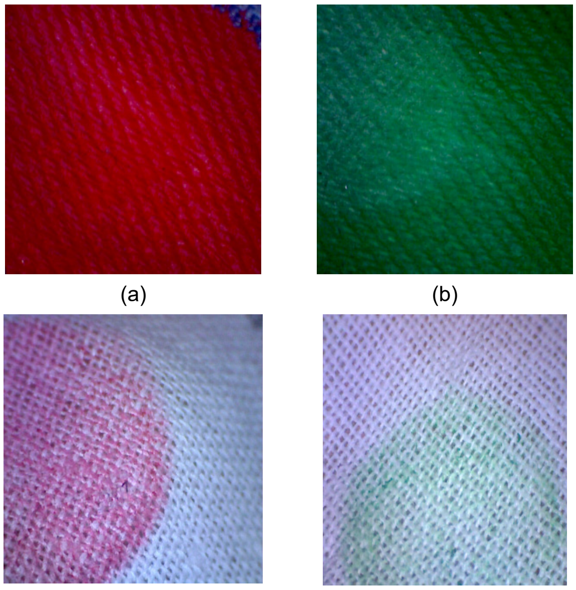


Figure 6. Photo of the material sample after the experiment (a – DECOLA, red, b - DECOLA, green) and accompanying cotton fabric (c – DECOLA, red, d - DECOLA, green) under a microscope.

CONCLUSIONS

Studies allow us to conclude that the paint Javana (Germany by C.Kreul GmbH&Co.KG) is not suitable for drawing on denim fabric in the technique Petrykivka painting. The paints are impregnated into the fabric structure, move to the reverse side of the product, give a watercolor pattern and do not cover the surface of the material with film. In addition, for a stylized drawing based on Petrykivka motifs, the paint does not allow to make a transitional stroke and draw a thin line on the material.

It is established that when making drawings in the technique of Petrikivka acrylic paints on denim fabric, you must first apply a white base, which evens out the surface of denim fabric, and then perform the main drawing.

Rosa talent (Ukraine) has more color fastness to rubbing and color fastness after washing. It is recommended for the manufacture of decoration in the technique of Petrykivka painting for denim products. It was also established that red paint from the same manufacturer loses more color after washing than green paints.

Prospects of future research include assessing the stiffness of denim fabrics with acrylic paint pattern, and determining the topography of patterns on products of various assortments.

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DESIGNING OF HEALTH-SAVING MEN'S GLOVES

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ABSTRACT

Living during a COVID-19 pandemic has negative effects on a person's psychophysiological state such as high-stress levels, leading to poor health, chronic fatigue and insomnia. As a result, the immunity is reduced, which is particularly dangerous today. One way to solve this problem is the use of health-saving clothing, which has additional features that provide the positive effect on the wearer's body. The developed gloves affect the state of the human autonomic nervous system through biological-active locations in the places of the hand and wrist. An anthropometric study of the biological-active locations of the wrist and hand is performed to construct the glove design. An algorithm for constructing a drawing of the design of the designed product based on four measurements is proposed. The effectiveness of the adaptive gloves is confirmed by studying its effect on the psycho-emotional and psychophysiological state of a person without exposure to the product and after its use by software "Intera-Diacor" and "ROFES", and a questionnaire. The evaluation is performed after wearing gloves for 20-40 minutes. It was found that 83.3 % of the wearers of the health-saving gloves showed positive changes in the body's compensatory forces (stress) and the state of internal emotional fatigue. Thus, the use of health-saving gloves has a positive social, therapeutic (health-saving) and economic effect, as the product has several functions It is an accessory fashion, has hand protection, and, has additional features to positively influence the body of the person wearing it. This allows the future to talk about the use of consumer-friendly and effective ways to correct the men's psycho-emotional and psychophysiological states, based on the safer-by-design concept.

KEYWORDS

Health-saving clothing; Health-saving gloves; Energy-information influence; Therapeutic properties clothing; Safer-by-design concept.

INTRODUCTION

Living during a COVID-19 pandemic has negative consequences on a person's psychophysiological condition, such as high-stress levels, malaise, chronic fatigue, and insomnia. As a result, immunity is reduced, which is particularly dangerous today. Therefore, it is necessary to create and develop new alternatives to improve human health and reduce the negative effects of stress.

There are many potential subjects for future research today, including the use of clothing for health savings [1-5]. An important point in improving the life cycle of clothing is providing clothing with predictable and additional functions that positively influence the body of the wearer [3, 4, 6-10]. This feature is interesting and can make clothes more effective.

Analysis of the purpose of modern gloves showed that there are products for not only one purpose. Most gloves are multifunctional. They are an accessory fashion, a means of protecting human hands, and have additional features. The use of gloves with advanced functionality saves money and time for the consumer and improves his quality of life [8-10].

Based on the analysis and systematization of information [2-12], we determined that gloves' most common additional functions are functionally compatible, adaptive, smart functions, and corrective capabilities. The wearable sensing products and sensory feedback devices that record and enhance the sensations of the hand are used in healthcare, prosthetics, robotics, and virtual reality [6, 7, and 9]. The gloves with smart functions permute continuous monitoring and treatment administered throughout an individual's daily life [8, 9]. The gloves with corrective capabilities are aimed at correcting the condition of the person wearing them due to therapeutic or prophylactic properties [3, 10].

The production methods of clothing with predictable and additional functions are the transformation of garments [13, 14]; the use of additional elements (devices, mechanical sensors, overlays, etc.) [4-11];

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Received June 23, 2022; accepted September 14, 2022

the use of new multifunctional textile (nanoparticles, modifier, etc.) [2, 12, 15].

The main characteristic of effective useful clothing is comfort [16]. Comfort is a state of mind influenced by a range of factors: physical, physiological, and psychological.

The predicted health-saving properties of gloves are the improvement of the psychophysiological state of the human body, the reduction of stress, and its negative consequences. To do this, it is proposed to influence the biological-active locations (BALs) of the hands. Such places are a set of acupoints (APs) that have a reflex connection with the internal organs and organ systems, in particular with the organs of the autonomic nervous system. Today, scientists [4, 17-20] have proven the effectiveness of the influence of elements of different origins on APs and BALs of a person. These advances are already used to create functional clothing [4, 20].

The studies [21-23] show necessary anthropometric research of hands to design gloves with additional properties, which can be used for developing health-saving gloves, 3D models of hands, and, also, for designing tools and hand protection.

Establishing textile requirements for garments is an important step in the development of health-saving gloves. Textiles should be indifferent (neutral) and not have an obvious positive or negative energy-information influence on the human body. To select indifferent textiles, it is necessary to determine the level of energy-information influence of textiles on the human body [2, 4, 16, 20].

The health-saving gloves with extended functionality should fit snugly around the palms and fingers and not exert excessive pressure on them. Such textiles must be strong, resistant to mechanical influences, to the action of water, and have high hygroscopicity, air permeability, and softness. A review [24-26] has revealed that the main textile used in the manufacture of such products are a knitted fabric.

Therefore, it is necessary to analyse in more detail the two ways to give the product additional properties - the use of nanomaterials and the use of additional elements.

Nanotechnology is widely used in the industrial and consumer sectors and has the potential to grow further and expand globally. Nanomaterials in clothing can provide him with the following additional properties: antimicrobial activity, conductivity, static electricity or UV protection, fire or water resistance, transfer of medicines, medical and cosmetics, aesthetics and self-cleaning, etc. [4, 15, 27].

The potential of nanotechnology is surely positive. However, there are also negative effects and potential harm of nanotechnology, which can be summarized:

- the possibility of nanotoxicity on human health;
- environmental implications of the nanocomposite's relation with materials and biological systems in the environment;
- dissemination of toxic, persistent nano substances originating environmental harm;
- high energy requirements for synthesizing nanoparticles;
- lower recovery and recycling rates;
- lack of trained engineers and workers [27, 28].

Many textiles with therapeutic or prophylactic properties have antimicrobial silver nanoparticles. However, some nanoparticles are harmful if released into the environment. The environment contains innumerable bacteria and other microbes, and nanoparticles designed for antibacterial activity are evidently going to continue that activity wherever they are. Being ultra-small, nanoparticles are highly mobile, and it is extraordinarily difficult to contain and control; some of them be released when the textiles are laundered [27, 29].

Besides nanoparticles, penetrating into the human body may simply dissolve, and if the dissolution products (e.g., metal ions) are toxic then the nanoparticles must be deemed toxic. If they do not dissolve (e.g., blue asbestos fibres), depending on the surface chemistry they may trigger an inflammatory immune response, which may have secondary adverse effects [28-31].

Based on this a safer-by-design concept has become increasingly important in risk assessment for consumers.

The exploration of stakeholder perceptions is essential to ensuring that robust risk governance processes are in place for nanotechnology and nano-related products. This study [31] shows to need of improving the multiparametric approaches to the safer-by-design concept of nanoproducts. The main aspect is the definition of the long-term influences of nanoproducts on people's health and the environment.

In addition, the authors [30, 31] recommended that a specific mechanism should be put in place for the safe handling, use, and disposal of nanoproducts, beginning from research and production to consumption and possible recovery or recycling.

Another product with additional properties is smart clothing, created using fusion technology, which combines electronic devices and clothing design. This design process requires a combination of several general different characteristics - electronic efficiency, electrical safety, physical comfort, and clothing aesthetics [32]. Smart clothing design is not considered in this study.

Expansion of apparel functionality, providing it with therapeutic and prophylactic properties, provides the use of medical prophylactic applicators [4, 20, 33].

Analysis of the various metal properties as a means of influence [4, 20, 33-37] shows that the use of silver allows providing energy-information influence the functional state of the human body, and improving the hygienic properties of the product. Silver has hypoallergenic and antibacterial properties.

However, the design of health-saving gloves should be performed following the general trends of sustainable fashion, so it is advisable to provide for the possibility of disassembly of gloves into components after the end of their service life.

The therapeutic and prophylactic effect of gloves is provided by the use of means of influence - the silver plates containing therapeutic information. Silver plates have a round shapes, diameter – of 5 mm, and thickness – of 0.4 mm. They locate between the lining and the main material of the product. The placement of these plates should correspond to the BALs of the human body, which have a reflex connection with the internal organs and systems of the body. The essence of information waves therapy is that information is subject to influence and control [38]. The biological information of therapeutic and therapeutic content, obtained from drugs, is stored and transmitted through bio molecular structures. At the same time, APs have a higher electrical conductivity than surrounding tissues [39]; therefore, BALs had better-perceived treatment and prevention information. The local influence of means on certain BALs of an organism causes reactions in bodies and systems of bodies, which can restore their normal functioning [4, 20, 21].

Therefore, based on the safer-by-design concept, the main goal of this paper is to develop new gloves with additional properties to reduce the negative effects of stress and improve the positive influence on the body and immunity of the owner.

METHODOLOGY

Conceptual design principles help create predictable products early in the design phase. However, a general methodology for creating health-saving clothing has not yet been proposed.

Several stages of health-saving clothing design have developed, which, in addition to consumers' basic needs, consider additional functions related to health. These stages are the establishment of primary data (predicted properties) required for the clothing production process; the establishment of the textile requirements; the development of primary and model design of clothing; the development of methods of the technological processing; and the evaluation of clothing efficiency.

The predicted health-saving properties of gloves are the improvement of the psychophysiological state of the human body, the reduction of stress, and its negative consequences.

This method is a simple and an effective therapeutic method of stress correction. Therapeutic (health-saving) properties of gloves are provided by the influence of elements of information and wave therapy on BALs of a hand and a wrist. The treatment and prophylactic information on them is written; it provides a corrective effect on an organism of wearers of the gloves.

The health-saving properties of health-saving gloves should be at the maximum contact of silver plates with BALs of the hand and wrist. The locations of such BALs for the design of health-saving gloves are described in Table 1 and [20].

The studies [2, 4, 16, 20, 33] have confirmed the effectiveness of the use of software diagnostic complex (SDC) "Intera-DiaCor" (Register of Medical Technologies of Ukraine from 30.10.2009 № 3277/2004) for textile evaluation of energy-information influence on the functional state of organs and systems of the human body on the cellular level [16]. SDC "Intera-DiaCor" consists of a device for electropuncture diagnostics (DEPD), two electrodes for local electronic diagnosis, and software installed on a personal computer (PC) (Figure 1).

The method used in this study is the following (Figure 1): on the skin areas (1) of the palms, feet, and a face of the person fix the "active" (2) and "passive" (3) electrodes for local electronic diagnosis. Through the electrodes from the device for the DEPD (4), electrical impulses are applied to the skin areas (1), and they also register the frequency-wave characteristics of organs and organ systems. Information from the device for DEPD is transmitted to the PC (5), where the data is processed using the software "Intera-DiaCor", which allows getting a beginning diagnosis of the functional state of the human body. After that, a sample of investigated knitted fabric is introduced into the contour of the "passive" electrode and the frequency-wave characteristics of the organs and systems of the human body are repeatedly recorded with the influence of investigated sample.

Table 1 Topography of the BALs of the hand and wrist of a person

Information wave therapy place – BALs	Placing of BALs
BAL-50	On the back of the forearm. The center of the place is 3 cm above the radial-carpal joint, between the radial and ulnar bones. The diameter of the place is equal to the width of the forearm at this level
BAL-51	On the palmar side of the forearm. The center of the place is on the midline, 3 cm above the radial-carpal fold. Width - 1/3 of the diameter of the forearm at this level. Length – 2/3 of the diameter of the forearm
BAL-52	The area includes the thumb and forefinger of the hand, the styloid process of the radial bone, and the radial third of the radial-carpal joint
BAL-53	The area includes the little finger and the lateral half of the ring finger, the styloid process of the ulna, a third of the radial wrist joint
BAL-54	The area includes the distal phalanx of the middle finger on the palmar and dorsal sides

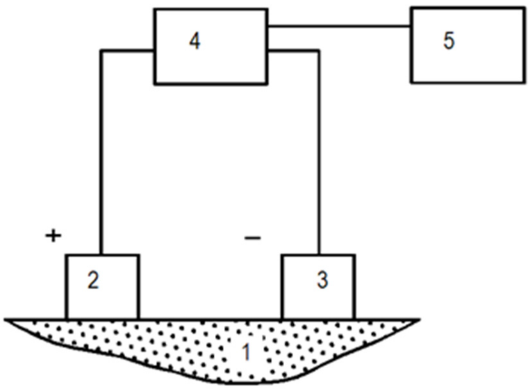


Figure 1. The scheme of SDC "Intera-DiaCor" (Ukraine): 1 – human skin; 2 – "active" electrode for local electronic diagnosis; 3 – "passive" electrode for local electronic diagnosis; 4 – DEPD; 5 – personal computer

After two complete cycles of diagnosis, the results of the evaluation of the functional state of organs and systems of the human body are compared without affecting the textile and it. For that, the histograms that reflect the three basic conditions of the organs and systems of the human body are compared to the PC monitor:

- energy lability (upper histogram columns);
- energy instability (middle histogram columns);
- energy insufficiency (bottom histogram columns).

Energy lability is the standard and reflects relatively stable energy processes in organs and systems. Energetic instability shows instability and tension in energetic processes. Energy insufficiency indicates the depression of the energy processes of organs and systems, which leads to the depletion of the functional state of the human body.

These histograms allow us to analyze the state of organs and systems of the human body, which have occurred or not occurred positive or negative changes under the textile influence. The higher the column height, the better the energy and functional state of the organ. The level of negative and positive energy-information influence of textile on the human body, as well as its inertness, is evaluated by the numerical values of the coefficients K_N, K_P, and K_i, respectively:

1) Level of negative energy-information influence of textile on the human body:

$$k_N = K_N / K_D, \quad (1)$$

2) Level of positive energy-information influence of textile on the human body:

$$k_P = K_P / K_D, \quad (2)$$

3) Level of indifferent energy-information influence of textile on the human body:

$$k_I = K_I / K_D, \quad (3)$$

where K_N – the number of organs or systems of the human body, in which functional and energy state there were negative changes, caused by the influence of the textile; K_P – the number of organs or systems of the human body, in which functional and energy state there were positive changes by the influence of the textile; K_I – the number of organs or systems of the human body, in which functional and energy state there not were changed by the influence of the textile; K_D – the number of diagnosed organs of the human body.

The value of each index is less than one, respectively, the sum of all three indexes is equal to one:

$$K_N + K_P + K_I = 1. \quad (4)$$

The next stage is the development of basic and model designs of clothing. Anthropometric research allows determining the size of BALs (Table 1) on the surface of the human body, their length, and their width. These results are required for the construction of parts of the basic glove designs [21].

A model design of gloves is developed by analyzing the range of 200 modern gloves [40-42].

For the manufacture of health-saving gloves, additional operations are performed to connect the plates to the parts of the gloves. Plates in gloves are placed in the cells formed by machine stitches, between the details of the lining and overlays. Accordingly, the technological processing of gloves performs in two stages. The first stage is the sewing of the overlays' details with the lining of the product, the placement of silver plates between them, and the making of the lining of the gloves; the second stage is the making of the main parts and the montage of gloves.

The authors of this article developed a method for evaluating the effectiveness of wearing gloves. According to the method, the assessment of the psychophysiological state of the human body is performed successively in two ways with and without the influence of the product. To do the first way, it is proposed to use the psychological questionnaire of the psycho-emotional state of a person "Well-being - Activity - Mood" ("WAM") [43]. This questionnaire is effectively used to study the psycho-emotional states of athletes and students [44, 45].

"WAM" is a complex of subjective sensations that reflect the degree of physiological and psychological comfort of a person's state, the direction of thoughts, feelings (bad or good well-being, cheerfulness, malaise, a feeling of discomfort in different body parts, etc.) [45].

For self-assessment, an answer sheet is offered with 30 opposite characteristics of well-being, activity or mood, which are characterized by polar assessments with intermediate values on a scale from 1 to 9 for each person. Three "WAM" scales determine the arithmetic average of the respondents' subjective assessment. The obtained points for each of the three states in the range from 4.0 to 9.0 indicate the optimal state of the

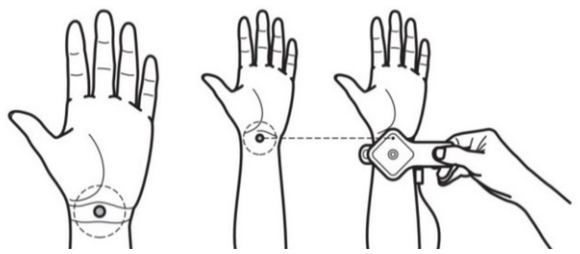


Figure 2. The location of the electrode before the scanning of psychophysiological state of the respondent by the device "ROFES".

respondent. Values below 4.0 points indicate a decrease in well-being, activity and a mood of the respondent [44].

The second way involves assessing the psychophysiological state of man with the device "ROFES" (Certificate of Conformity No. TA 380 14 2243, Tüv Austria CERT GMBH). The device determines psychophysiological indicators: the tension of the body's compensatory forces (the presence of stress), the state of internal psycho-emotional fatigue, the presence of signs of neurosis and irritability [46].

The effectiveness of wearing health-saving gloves is determined by the evaluation in two ways without the influence of the product and with it.

At first, the researchers notify the respondents about the conditions of the experiment to avoid stressing in the face of the unknown.

The first cycle of assessment of the psychophysiological condition of the respondent is carried out without health-saving gloves. For an assessment of the state of well-being, activity, and a respondent's mood the respondent chooses for himself the number that best reflects the relationship between these indicators.

After that, the psychophysiological state of the respondent is assessed without the influence of health-saving gloves by "ROFES". To do this, the "ROFES" electrode is fixed at the level of the APs or BALs on the wrist of the left hand of the person (Figure 2), and the process of scanning the state of the respondent's body begins.

The device is fixed to the left hand so that an active electrode is situated on the APs on the left wrist. After the device has been turned on, it sends a weak electric signal and registers how it is changing. After that, the computer program compares the obtained result with the standard one, which is typical of a healthy person of the same age. The results of the study are displayed on the PC screen in the form of a five-point assessment of the body. In addition to assessing stress, fatigue, and nervous tension, "ROFES" assesses the general state of health and 17 organs and systems [47].

The second cycle of assessment of the psychophysiological state is carried out after the subject has worn gloves minimum of 15 minutes. The respondent takes off the product and the researchers evaluate its state in two ways. However, first, assess the psychophysiological state of the human body using "ROFES", and then conduct a second interview with the questionnaire.

The analysis of the diagnostic results using "ROFES" is carried out by comparing the five-point scales of the psychophysiological state of the examined person before and after the application of the product.

The authors propose to determine a complex indicator of the state of people Kr, which is calculated as the arithmetic mean for three measured values:

for assessing by "WAM"

$$K_{r\,\mathrm{WAM}} = (I_W + I_A + I_M) / 3, \quad (5)$$

for assessing by "ROFES"

$$K_{r\,\mathrm{R}} = (I_s + I_e + I_n) / 3, \quad (6)$$

where I_W – assessment of the psycho-emotional state of person's "Well-being", score; I_A – assessment of the psycho-emotional state of a person "Activity", score; I_N – assessment of the psycho-emotional state of a person "Mood", score; I_s – assessment of compensatory forces (the presence of stress), score; I_e – assessment of the state of internal emotional fatigue, score; I_n – assessment of the presence of signs of neurosis, irritability, score.

The value of the complex indicator of a person's psycho-emotional state ("WAM") shows that at 6.5...9.0 points, the respondent's emotional state according to subjective feelings is at a high level. With 4.0...6.49 points, a person has an average level of well-being, activity and mood, which may indicate the development of fatigue processes according to their own feelings. The low levels of values of the complex indicator of a person's psycho-emotional state (at 0...3.99 points) indicate that, according to self-assessment, a person at the time of the survey has difficulty adapting to psycho-emotional loads or stressful situations and needs help.

The scale for assessing the complex indicator of the psychophysiological state of man is given in Table 2.

The proposed method makes it possible to study the psycho-emotional and psychophysiological state of the human body, identify the presence of stress, and assess the effect of the developed products on the psychophysiological state of the human body.

Therefore, the methodology for designing clothing with extended functionality has been developed and described. At the same time, particular attention is paid to the needs of consumers to improve the psychological and physiological state of the owner while wearing clothes, including health-saving gloves.

Table 2. Scale of a complex indicator of a person's psychophysiological state by "ROFES" [46].

The value of the complex indicator ("ROFES")	The level of compensatory forces of the body	Interpretation of state assessment
4.4…5.0	high	The energy organs' resources is high, optimal loading. The risk of disease development is minimal or a compensated process, lack of internal emotional fatigue, no stress, neurosis
3.5…4.3	the medium is close to high	The energy organs' resources is good, insignificant loading. Low risk of disease development or a compensated process, no stress, neurosis, there is slight psycho - emotional fatigue
2.6…3.4	average	The energy organs' resources is decreased, which is a loading consequence. There is a middle risk of disease manifestation, internal emotional fatigue, minor signs of stress, and neurosis
1.7…2.5	the middle is close to the bottom	The loss of energy organs' resources is a heavy loading consequence. The risk of disease development with prolonged exposure to this state is increased, and there are significant psycho-emotional load, signs of stress, and neurosis
1.0…1.6	low	The large loss of energy organs' resources is observed as an excessive load consequence. The risk of disease development with prolonged exposure to this state is high, state of overexertion (stress, neurosis), strong psycho-emotional stress

RESULTS AND DISCUSSION

Materials

The gloves are made from the top material, lining, overlay parts, interfacing, finishing materials, etc. According to [10, 12, 19], the textiles for the men's health-saving gloves were selected as knitted fabrics.

Earlier it was noted that textiles should be neutral to the human body. Since the lining and the overlay details have close contact with the BALs, the energy effect of these materials on the human body is evaluated in the paper. We chose three ready-made samples of knitted fabrics for the lining and the overlay parts of gloves, which we named KF1, KF2, and KF3. Next, we determined the properties of these fabrics (Table 3).

In order to choose thin knitwear for the lining of the gloves, the thickness and weight were investigated. To ensure high hygienic properties, the hygroscopicity and normal moisture of the selected knitted fabrics are determined. For the selection of allowances for the construction of the gloves, breaking load and extensibility were investigated.

Studies have shown that knitted fabrics with such properties (Table 3) can be used for the lining and the overlay parts of gloves. To select indifferent textiles, it is necessary to determine the level of energy-information influence of knitted fabrics on the human body by "Intera-DiaCor" according to the method described above. The results of the study are presented in Table 4.

The analysis showed that the highest level of indifference for the functional state of the human body (0.86…0.97) has a knitted fabric KF1 (Table 4). Such results indicate the absence of excessive positive or negative energy-information influence on the state of organs and systems of the human body caused by knitted fabric. Therefore, we recommended textile KF1 (Table 4) as the lining and the overlay details for the manufacture of health-saving gloves.

As result, the men's health-saving gloves are made of a package of materials: layer 1 (top) - knitted fabric "Double knit interlock" (weight 680 g/m2, 80 % Polyester, 20 % Cotton), layer 2 - overlay parts (Table 3, option KF1), and layer 3 - lining (Table 3, option KF1). Also, the health-saving gloves can have artificial or natural leather overlays. They make it possible to extend the time of wearing gloves.

Development of design of men's health-saving gloves and their technology

To design health-saving gloves, an anthropometric study of the size of the BALs of the men's wrist and hands was conducted.

To find the relationship between the area of the bases, and the necessary measurements for the manufacture of gloves, we chose wrist circumference, hand girth, hand length, hand width, thumb length and little finger length [8-10]. In addition, we proposed to measure thumb circumference, middle finger circumference and forearm width. These measurements are needed to determine the place of BAL-50 and BAL-51. The results of the anthropometric study are presented in Table 5.

We determined the high correlations between wrist circumference and forearm width (0,98), hand length, and thumb circumference (0,71). Therefore, we obtained the values of main and additional measurements that allow you to set the size and place of the required BALs.

Table 3. Some properties of knitted fabrics for the men's health-saving gloves (lining and overlay parts).

Designation, structure of knitted fabrics ISO 8388: 1998 [E/F]	Code of knitted fabrics	Raw material composition, [%]	Thickness [mm] DSTU ISO 5084:2004	Weight [g/m²] DSTU EN 12127: 2009	Hygro-scopicity [%] DSTU GOST 3816:2009	Normal moisture [%] GOST 8845-87	Breaking load, [N] DSTU EN ISO 13934-1:2018		Extensibility, [%] GOST 8847-85	
							Wales	*Courses*	*Wales*	*Courses*
plaited jersey fabric	KF1	CO 100	0.8	214.6	15.3	0.2	586	368	1.0	11.0
plain jersey fabric	KF2	CO 92 / EL 8	0.8	361.6	6.1	4.5	156	239	7.5	8.2
plain jersey fabric	KF3	CO 93 / EL 7	1.4	365.7	12.2	3.2	274	168	29.5	26.0

Table 4. Levels of energy-information influence of knitted fabrics on the human body.

Levels of energy-information influence of knitted fabrics on the human body	Number of person					
	1	*2*	*3*	*4*	*5*	*6*
KF1						
negative (k_N)	0	0	0.02	0	0.07	0
positive (k_P)	0.07	0.03	0.03	0.05	0.07	0.09
indifferent (k_I)	0.93	0.97	0.95	0.95	0.86	0.91
KF2						
negative (k_N)	0	0.02	0.02	0	0.12	0.02
positive (k_P)	0.12	0.02	0.02	0.23	0.12	0.18
indifferent (k_I)	0.88	0.96	0.96	0.76	0.75	0.8
KF3						
negative (k_N)	0	0	0.03	0	0.21	0.02
positive (k_P)	0.13	0.04	0.02	0.13	0.15	0.20
indifferent (k_I)	0.87	0.96	0.95	0.87	0.64	0.78

Table 5. Statistics of anthropometric study of the men's wrist and hands.

Statistics	Wrist circum-ference	Hand length	Hand width	Hand girth	Thumb length	Thumb circumference	Little finger length	Middle finger circumference	Forearm width
Arithmetic mean, cm	18.40	19.70	9.44	21.15	8.37	6.3	6.73	3.72	9.65
Standard deviation, cm	1.33	1.38	0.98	1.45	1.49	0.75	0.93	0.67	1.12
Standard error of the mean	0.24	0.25	0.17	0.26	0.27	0.13	0.17	0.12	0.20
Median, cm	18.00	20.00	9.20	20.85	8.00	6.50	6.70	5.70	10.00
Mode, cm	18.00	20.00	0	20.50	8.00	6.50	7.00	6.00	9.50
Excess coefficient	0.35	0.62	1.29	1.31	-0.11	1.46	-0.14	0.28	-0.60
Asymmetry coefficient	0.63	-0.76	0.27	0.15	0.51	-0.89	0.21	-0.10	-0.56
Sample minimum, cm	16.00	16.00	7.00	17.20	6.00	4.00	5.00	5.00	7.00
Sample maximum, cm	22.00	22.00	12.00	24.20	12.00	7.50	9.00	7.00	11.10

Analysis of the range of 200 modern products of hand wear [8-10, 26, 40-42] demonstrated that the vast majority of them 155 (77.5 %) are gloves. The methods of fixing modern gloves on the wrist are a cuff with a textile fastener (37 %). Other closures include an elastic fastening (22 %), an elastic cuff (19 %), an inelastic cuff (7 %), and 15 % of the gloves do not have a wrist fastening placket.

Analysis of the most popular model designs of gloves shows that the most common model design of gloves is model that has sewn back and palm parts, arrow-strip between them, thumb part with an insert (finger wedge), which is sewn to the palm part of the gloves. Frequency of occurrence this model design is 33.5 %.

Due to that, the most common model design is MC4, we chose it as basic to design men's health-saving gloves. To improve the aesthetics of gloves, it is recommended supplement them with finishing materials and sewing accessories. They can be placed on the palm part or back [8-10, 26, 40-42].

The four main measures of the men's hand and obtained anthropometric correlations were used to construct the design of men's gloves according to the method "M. Müller & Sohn" [48].

Thus, when constructing a drawing of the glove, we took into account the sizes of BAL-50 and BAL-51, which are placed on the back and the palm of the forearm, respectively. We also recommend making gloves with a 7.5 cm wide cuff ready-made. This width of the cuff allows you to completely close these areas and ensure the necessary fit of the influence elements on the body. Places BAL-52 and BAL-53 fully correspond to the measurements used in the construction of gloves. Place BAL-54 is located on the distal phalanx of the middle finger; its length is 5.0 cm. To ensure the effectiveness of the functions of the gloves, their details are constructed taking into account the size of these places.

The sketch of appearance of men's health-saving gloves for correction of a psychophysiological state of an organism is presented in Figure 3.

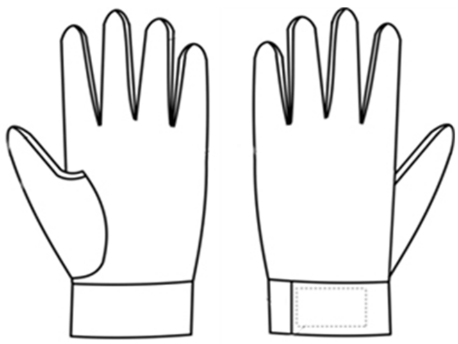


Figure 3. Men's health-saving gloves.

The scheme of construction a drawing of a top, a lining and overlays of gloves (Figure 4) was developed. Areas of gloves with the influence elements are shaded on Figure 4.

Based on the received drawing of men's health-saving gloves, derivative patterns of overlay details are made. The necessary quantity of silver plates and their placement on details are calculated. Silver plates are located between the lining and overlay details of men's health-saving gloves in places that are projections of the corresponding BALs of the human body. We chose the distance between the plates of 30 mm accordingly to [4, 20] (Figure 5).

The appearance of men's health-saving gloves from the inside out showed the places of the BALs after the operations to connect the plates with the part of the gloves (Figure 6).

The plates were placed in the cells formed by machine stitches between the lining and overlay details. The proposed methods of technological processing of men`s health-saving gloves are presented in Figure 7.

In the work [4], the technology of joining materials and influence means of the men's underwear is justified.

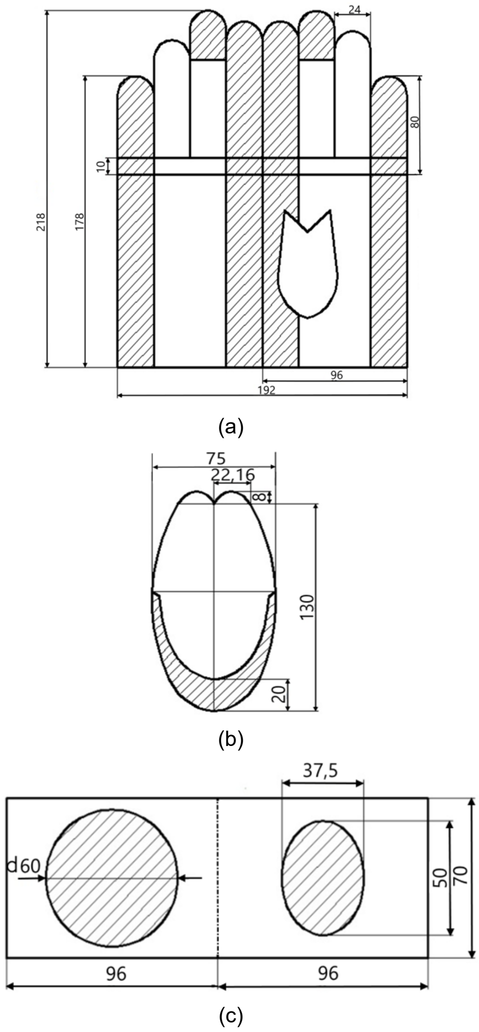


Figure 4. Drawings of a top, a lining and overlay details of men's health-saving gloves: (a) a back part and palm part; (b) thumb insert; (c) cuff.

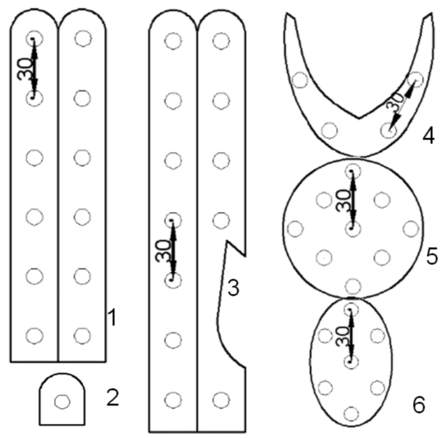


Figure 5. The location of the influence elements on overlay details of men's health-saving gloves: 1 – the little finger overlay (BAL-53); 2 – the middle finger overlay (BAL-54); 3 – the index finger overlay (BAL-52); 4 – the thumb overlay (BAL-52); 5 – the palmar forearm overlay (BAL-51); 6 – the back forearm overlay (BAL-50).

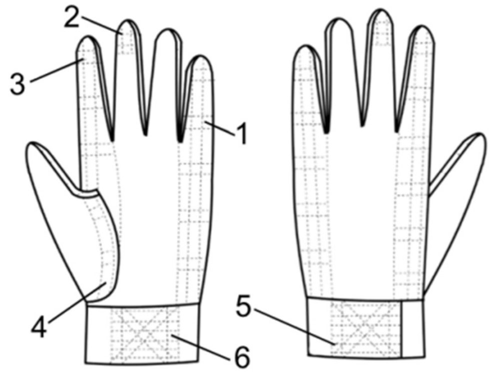


Figure 6. The appearance of men's health-saving gloves from the inside out: 1 – the place of the little finger overlay; 2 – the place of the middle finger overlay; 3 – the place of the index finger overlay; 4 – the place of the thumb overlay; 5 – the place of the palmar forearm overlay; 6 – the place of the back forearm overlay.

The connecting layers of clothing details are fastened with thread stitches. Since the silver plates are inserted between the materials after the stitching, the materials are stretched, and the seam thickness of underwear is increased by 28.2...37.9 % [4]. Besides, it was found that silver plates do not cause discomfort for the consumer and do not deform during the operation of the men's underwear for an hour. Thus, the chosen technology of joining materials and means of influence ensure the clothing's comfort during a use.

Therefore, the method for constructing a drawing of men's health-saving gloves has been improved by using correlations between measurements in the design. This made it possible to develop an ergonomic design of men's gloves with the influence elements in contact with BALs of the human body. The elements create the necessary energy-informational effect and have a therapeutic and corrective effect on the body of the wearers of the gloves.

The gloves were made in two stages. According to the results of the research, the first stage of making gloves was developed. It includes sewing the details of the lining with the product lining, placing silver plates between them and the brand of the lining of the gloves; the second stage – the manufacture of basic parts and installation of gloves (Figure 7).

The evaluation of gloves efficiency

As the design of men's health-saving gloves is a pilot study, a preliminary study was conducted to determine the nature of the energy-information influence of gloves on the consumer's body after their use. For the previous study, 10-th men were selected who used gloves for 15 minutes at rest without emotional communication - walked, sat, and did not watch the news.

The assessment of the energy-information influence of men's health-saving gloves was carried out according to the method described above. The study consumer survey results on the psycho-emotional state are presented in Table 6.

According to the results of the self-assessment of the psycho-emotional state of the respondents after using the men's health-saving gloves at rest for 15 minutes, 80 % of people improved their well-being, 70 % – activity, and 50 % – mood.

Positive changes from the energy-information influence of men's health-saving gloves were found in one of the studied states in 40 % of people, in two states - in 20 %, and a positive effect was found in all three states - in 40 % of consumers.

The results of diagnosing the psychophysiological state of 10 people by "ROFES" without the influence of men's health-saving gloves and after wearing them for 15 minutes are shown in Table 7.

The analysis of the obtained values of the complex indicator state of the people ("WAM") (Table 6) showed that 90 % of the respondents before wearing gloves have a high level of "WAM", and 10 % have an average level. After wearing men's health-saving gloves, the value of this complex indicator increased in 50 % of respondents, 30 % - decreased, in 20 % of respondents - did not change. But each of the interviewees remained in the group with the same level of the complex indicator of the state of people ("WAM").

At the same time, the results of a study by "ROFES" (Table 7) showed that, at first, 60 % of respondents have a state level of "the medium is close to high" (Table 2). After 15 minutes of using health-saving gloves, the group of men with this level already included 90 % of respondents. Before using gloves, 40 % of respondents have average levels. After wearing them, the values of the complex indicator state of the people ("ROFES") increased in most people. Hence, the group of people with an average level decreased and contained only 10 % of respondents.

The results of a previous study in Tables 6 and Table 7 showed that using men's health-saving gloves affects the states. People experienced this effect in improving their mood and well-being as a result of the self-assessment (50 % of respondents). After wearing gloves, the psychophysiological state of 30 % of people (№ 3, № 6, and № 10) improved. Their level grew from the average level, which has the presence of signs of stress (Table 2), to the level of "the medium is close to high". In general, the positive effect of wearing gloves on the psychophysiological state of people by "ROFES" was found in 50 % of respondents.

At the same time, a previous study shows that it is difficult to clearly describe the effectiveness of the gloves on a person's condition after 15 minutes of wearing.

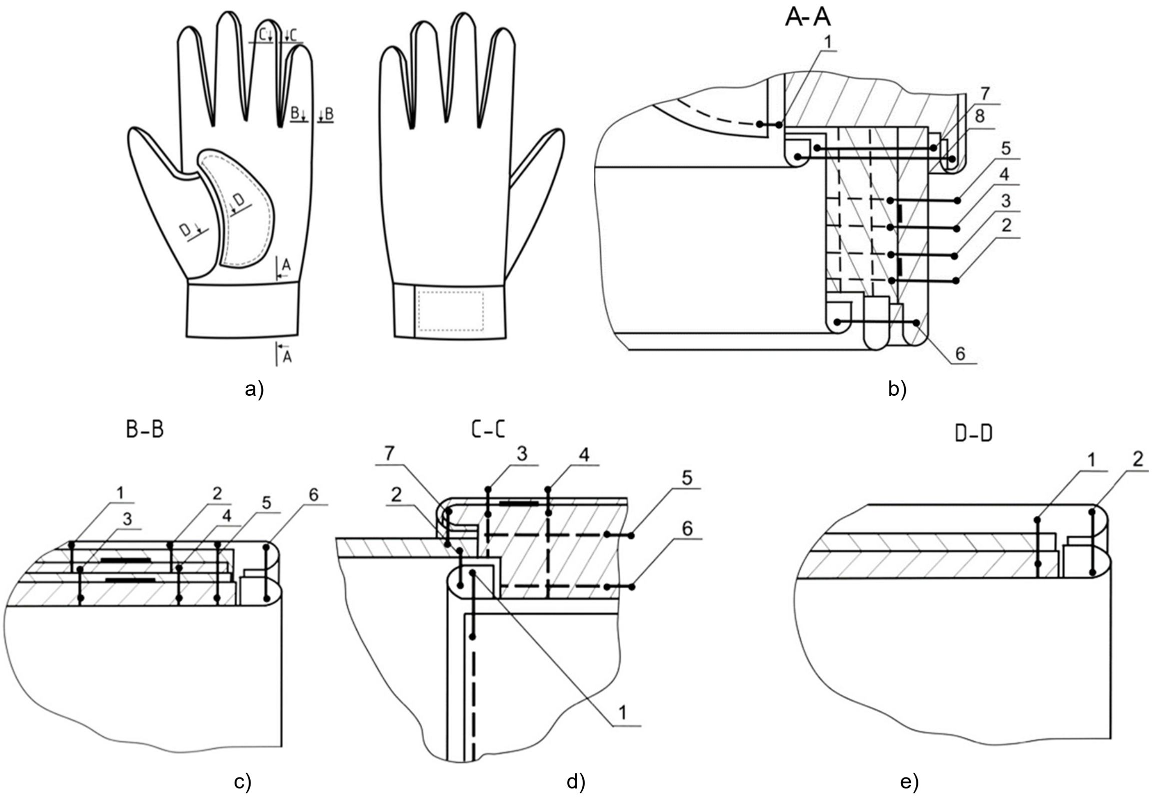


Figure 7. The illustrations of methods of technological processing of men's health-saving gloves: (a) location of the cross-sections on the gloves; (b) to cross-section A-A; (c) to cross-section B-B; (d) to cross-section C-C; (e) to cross-section D-D.

Table 6. The results of the self-assessment of the respondent's psycho-emotional state

Number of person	The self- assessment of the researched person						Complex indicator state of the people ("WAM") (formula 5)	
	Well-being		*Activity*		*Mood*			
	Without gloves	*With gloves*	*Without gloves*	*With gloves*	*Without gloves*	*With gloves*	*Without gloves*	*With gloves*
1	8.4	8.0	6.6	6.8	8.7	8.5	7.90	7.77
2	5.5	5.8	5.1	3.9	6.4	6.2	5.67	5.30
3	6.6	6.9	6.3	6.4	7.5	7.2	6.80	6.83
4	6.8	7.5	6.8	7.6	7.3	7.8	6.97	7.63
5	8.0	8.2	7.9	8.2	8.6	9.0	8.17	8.47
6	7.7	6.9	6.3	6.4	6.0	7.5	6.67	6.93
7	6.3	6.6	7.8	7.3	7.4	7.1	7.17	7.00
8	7.1	7.3	6.7	6.7	7.2	7.1	7.00	7.03
9	6.8	6.9	7.5	7.7	7.4	7.5	7.23	7.37
10	7.1	7.4	6.9	7.3	7.2	7.4	7.07	7.37

Table 7. The results of the previous study on the state of the people by "ROFES"

Number of person	Evaluation						Complex indicator state of the people ("ROFES") (formula 6)	
	The state of compensatory forces (stress)		*The state of internal emotional fatigue*		*The state with signs of neurosis*			
	Without gloves	*With gloves*	*Without gloves*	*With gloves*	*Without gloves*	*With gloves*	*Without gloves*	*With gloves*
1	3	4	5	5	4	4	4.0	4.3
2	3	4	5	5	4	4	4.0	4.3
3	3	3	3	5	4	4	3.3	4.0
4	3	3	3	3	4	4	3.3	3.3
5	3	3	5	5	4	4	4.0	4.0
6	3	4	3	5	4	4	3.3	4.3
7	3	3	5	5	4	4	4.0	4.0
8	3	3	5	5	4	4	4.0	4.0
9	3	3	5	5	4	4	4.0	4.0
10	3	3	4	4	3	4	3.3	3.7

For that reason, the authors decided to study the effectiveness of wearing gloves for a longer time. The intervals for determining the nature of the effect of the men's health-saving gloves were 20, 40, and 60 minutes.

The continuation of the experiment revealed difficulties in the application of the "WAM" questionnaire, since the questions were repeated every 20 minutes, and the respondent's self-assessment lost its adequacy due to the increase in the subjectivity of the survey.

Therefore, only a hardware device "ROFES" was used for further research, which, unlike a subjective assessment, allows quantifying the effect on the three states of the body during selected time intervals.

To minimize the influence of variables and increase the reliability of the results of evaluating the impact of gloves, the authors decided to exclude such a factor as previous use of the product. Because of that, for further research, the respondents were 12 men who never used health-saving gloves before.

The results of diagnosing the psychophysiological state of 12 people by "ROFES" without the influence of men's health-saving gloves and after wearing them for selected time intervals are shown in Figure 8.

Evaluation of the energy-informational impact of men's health-saving gloves (ROFES) (Fig. 8) showed that after 20 minutes of using the gloves, improvement occurred in 50 % of respondents. When the time of using gloves is increased to 40 minutes, a positive effect is observed in 71 % of people.

Initially, 50 % of the respondents have a state level of "medium close to high", and 50 % of the respondents have average levels. After 20 and 40 minutes of using health-saving gloves, the group of men with an average level was only 16.67 % of the respondents. At the same time, 83.33 % of respondents had a level of "the medium is close to high". After wearing it for 60 minutes, a positive effect was found in 50 % of people (Fig. 8).

The analysis of the study showed that the psychophysiological state of the respondents improved in at least one of the three states in 50 % of men (Fig. 9).

In general, a positive impact of the men's health-saving gloves on the psychophysiological state of 10 out of 12 studied people was noted. It has been established that positive changes in the psychophysiological state of most respondents occur after 40 minutes of using health-saving gloves.

According to the results of the study, reliable positive changes in indicators of compensatory forces of the body (stress) and the state of internal emotional fatigue were found in 83.3 % of people who wore men's health-saving gloves for 20 and 40 minutes. It was established that is after putting on gloves, the state with signs of neurosis remains unchanged at the level of "medium close to high". Therefore, this state was not taken into account in the furthest analysis of studies.

Research results confirm the effectiveness of using the men's health-saving gloves.

The appearance of the men's health-saving gloves is shown in Figure 10.

The health-saving gloves are made of black knitted fabric. The top layer of the gloves is made of black double knit interlock, and the lining is made of grey plain jersey fabric.

The gloves are recommended to wear in the cold season. To improve the aesthetics and strength of the product, a leather insert is proposed on the palm of the gloves (Figure 10, b).

To the aesthetic appearance of the men's health-saving gloves can use other products for dressmaking such as webbing, tapes, zippers, snap buttons, etc.

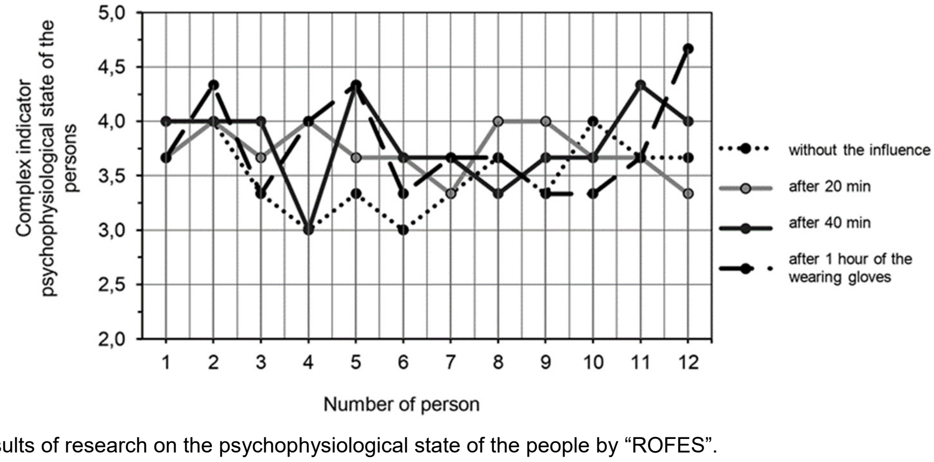
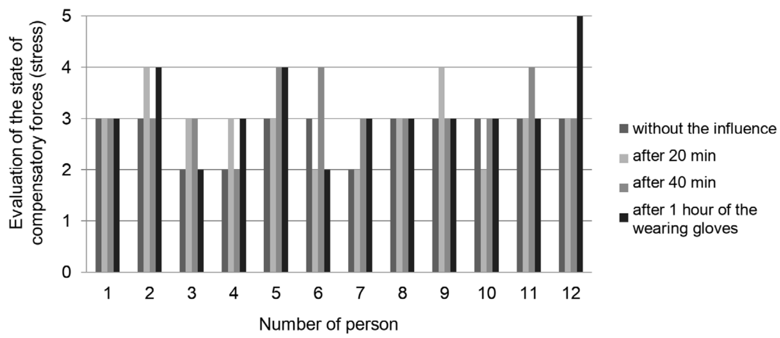
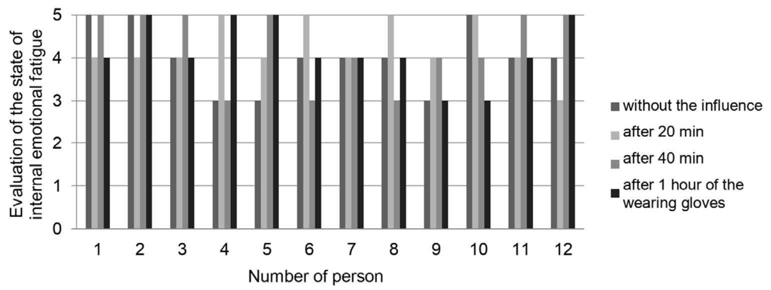


Figure 8. The results of research on the psychophysiological state of the people by "ROFES".



(a)



(b)

Figure 9. The results of the diagnosis of the psychophysiological state of people after wearing health-saving gloves over time: a – the state of the compensatory forces; b – the state of internal emotional fatigue.

a) b) c)

Figure 10. Appearance of the men's health-saving gloves: a - the back side, b - the palm side, c - the inside of the cuff of the glove with a clasp.

The color does not affect the functional properties of the product. The color of the men's health-saving gloves can change depending on the fashion and personal preferences of the consumer. Color can also have a positive effect on the psycho-emotional state of a person. We didn't investigate the effect of color on the functional properties of the product. But this is a promising direction for further research.

The study confirmed that silver plates are elements of positive energy-information impact on BALs. They are located between the substrate layers and fixed by parallel stitches (Figure 10, c). The results of the respondents' survey showed that the presence of plates in the men's health-saving gloves does not reduce hand motility, and they are not felt in the product on touch.

The results of evaluation are to be used as a data set to fill the database with knowledge of the previously developed expert system to support clothing design process [49]. In addition, the system can be used for the designing and for the selection of ready-made garments that meets predefined customer's impressions (e.g., in the shops, including online stores) and to select a prototype to develop new model of clothing that meets the wishes of the consumer.

As part of this study, we obtained results reflecting the psycho-emotional and psychophysiological characteristics of the consumers, as well as their dynamics in conditions of use. Since it was a pilot study, the sample size was not huge. These results are difficult to generalize to a broad sample. However, they are a start for further research on the states of more people after the use of gloves for a longer period.

CONCLUSION

The study's results of the state of tension of the compensatory forces of the organism by "ROFES" indicate the presence of an average stress level for 86 % and a significant level of stress for 14 % of the people. Such results show the need to wear products to reduce the negative effects of stress. The effectiveness of the proposed health-saving gloves was confirmed experimentally. We noted a decrease in the level of stress after their use for 83.3 % of the people.

Thus, the use of men's health-saving gloves has a positive social, therapeutic (health-saving), and economic effect, as the product has several functions It is an accessory fashion, has hand protection, and has an additional positive influence on the body of the person wearing it.

This allows the future to talk about the use of consumer-friendly and effective ways to correct the men's states, based on the safer-by-design concept.

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Fibres and Textiles **29**(3), 2022, 43-50 DOI: 10.15240/tul/008/2022-3-005

DEVELOPMENT OF A METHOD TO DIGITIZE CLOTHING PATTERNS

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ABSTRACT

The study aims to develop a method to digitize a clothing pattern without a digitizer. For this study, we address the following objectives: formulate a hypothesis of the method, describe the method's algorithm, and perform testing and evaluation of the developed method. The idea of the developed method is as follows: digitizing the clothing patterns might be achieved without digitizer by applying modification tools of the pattern design systems to the digital simple geometrical forms constructed directly in the graphical environment of the system. Testing and evaluation of the developed method confirmed the initial hypothesis. The achieved result of the current study is the alternative method to digitize clothing patterns when it is necessary to avoid additional costs.

KEYWORDS

Digitizing, Pattern; Coordinates; Modification; Pattern design system.

INTRODUCTION

In the clothing industry, design, development, and procurement teams have been affected more than any other industry and are constantly under pressure to present more products with fewer resources in a shorter time. The diversity of garment designs created as new products is not found in any other industry and is almost independent of the size of the business.

With the rapid development of digital technologies in apparel design and manufacture, clothing enterprises have ushered in development opportunities in recent years. For clothing enterprises, digital transformation is an inevitable step to meet the development requirements of the information age. However, some clothing enterprises still adopt the traditional management concept [1]. Slow adaptation leads to the low efficiency and quality of enterprise management.

The skilled labor-dependent nature of apparel design, the globalization of the market, the proliferation of information, the typical iterative "optimization" trial-and-error process of apparel product development, the reduced time to market, and continuous pressures of cost are just some of the factors that add to the fashion industry's already complex activities. Digital prototypes in the textile and clothing industry are part of the technology adoption in the product development process, which involves various operators in different stages and places, with multiple skills and competencies and other necessities of formalizing and defining the results of their activities [2].

Recently, the growth of IT technology has created new products and service methods in various industries, including the apparel industry. Especially, technologies for automating apparel manufacturing are steadily being developed. The automation of apparel manufacturing is divided into two main groups: the automation of pattern-making and sewing. Again, the automation of pattern-making for ready-to-wear and custom-fitted clothing forms the automation of pattern-making [3].

Moreover, COVID-19 has increased the digitalization of the fashion market and the rise of the virtual world. As COVID-19 locked down many countries worldwide and prevented physical contact between designers and manufacturers, the crisis forced fashion industries to inevitably turn to digital and virtual fashion and provided an opportunity to redefine business models toward more sustainable digital innovation [4].

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Received July 29, 2022; accepted September 15, 2022

CAD/CAM (Computer Aided Manufacture) systems allow rapid generation of a garment design. It can be adjusted quickly without diminishing creativity. Since any cost saving through computer-aided design has become a requirement in gaining a competitive advantage in clothing design, most universities have included CAD and pattern design systems education as a part of their clothing technology courses. They have been instrumental in reducing lead times, improving accuracy, and putting apparel products in retail stores closer to when consumers need them [2].

CAD systems are widely used in apparel design since they allow interactive manipulation of garment pieces faster and more efficiently than the normal drafting process for pattern making and grading. The CAD software shows advantages in avoiding manual work, raising precision and productivity, and organizing information flow. The computer systems integrate all processes into one joint flow, thus excluding the time-consuming manual preparation of patterns, creation of layouts, and relocation of written information.

The development of the CAD systems attempted to eliminate manual and time-consuming operations in the textile and apparel industry. Many researchers assume that the CAD/CAM technology would eliminate the need to manufacture multiple prototypes. However, clothing designers did not wholly accept this scenario except during garment construction and design.

Nowadays, a lot of effort is placed in designing CAD systems, which could be easily modified to meet individual specifications of individual garment manufacturing companies. With the current trends of production customization, the reduction in the numbers of models made for each clothing line and each clothing collection, the increase in the diversity of fabric and construction patterns, and due to global changes in fashion market trends, the use of the CAD/CAM systems will inevitably broaden in terms of applicability to new production stages. The general trend in improving the industrial apparel CAD systems is to alter pattern design to facilitate quick responses to market change [5]. Reducing the time to develop a model and the cost of material reduces the cost and production and provides additional time for the designer's creative part to create clothes [6].

ANALYSIS OF PUBLISHED DATA AND STATING THE PROBLEM

Digital transformation of apparel design

The digital transformation of apparel design and manufacturing has been under discussion for at least a decade. Several scientific works are dedicated to this question [1-6, 15]. They discuss different aspects of clothing digitalization: from sketch vectorization [3] to CAD/CAM applications in textile research [5] and garment development [2, 4]. Some researchers focus on the digital fashion market [1] and its virtual representation based on 3D scanning and 3D dynamic model development [4]. They are unanimous on the advisability of digital transformation of apparel design on all steps of garment development and its manufacturing.

On the other hand, each one focuses on one specific design procedure [3, 5] or the general aspects of the management while implementing digital solutions in apparel design, manufacturing, and online marketing [1, 2, 4, 7].

The paper [1] introduces the basic concept of digital enterprise management, analyses the shortcomings of the current clothing enterprise management, and discusses the key points of digital transformation of clothing enterprise management combined with the characteristics of clothing enterprises. Another work [7] describes the results of the patterns of digitization survey designed to assess how companies are implementing digital transformation. The survey covers the various strategies companies employ, the technologies they invest in, and, in particular, the actions they take to overcome the organizational resistance that is common in most large-scale transformations.

Several works focus on the comparative analyses of the popular CAD systems [6, 8]. The rapidly evolving software market offers a wide range of clothing CAD systems to consider when choosing one. The developers provide both initial application systems that serve as practical help in individual activities, such as housewives, and powerful complexes of clothing and material support for large enterprises, providing the ability to adjust to the regional market characteristics and take into account the features of the enterprise. Such systems are functional but usually not cheap. Consequently, making the right choice when choosing a CAD system is sometimes difficult. According to [6], when considering several factors, the most important are cost and functionality.

The CAD system usually includes the cost of the computer, digitizer, plotter, etc. While the computer is necessary, a digitizer is needed when a clothing enterprise has a lot of paper patterns requiring digitalization. Due to the COVID-19 pandemic, engineering professions adapt to the new working conditions at home. It means having digital patterns and CAD systems at home for clothing patternmakers. Consequently, from time to time, they need to digitize some clothing blocks at home, while the digitizer is usually a massive and very costly thing. Besides that, reducing time spent digitizing is crucial since it directly translates to improved productivity.

Ways of digitizing patterns

Pattern digitizing is a vital step of manufacture process in multiple industries, such as apparel. Researchers compare and discuss various ways of digitizing patterns and their advantages and disadvantages [8].

There are numerous ways to digitize patterns. Among them are digitizer tables, roll-up digitizers, scanners, pattern digitizing software (photo digitizing software).

Every clothing designer / patternmaker and design studio should be seen as a different case as they have unalike requirements and priorities. Therefore, one of the methods above may better meet their digitizing needs. However, most users will have similar advantages and disadvantages while digitizing by each method.

Digitizing tables or “Table digitizers” are electromagnetic tables used with a particular mouse to traverse the patterns’ outline one point at a time. There are various buttons on the digitizing mouse for inputting a different type of point to the pattern design system that runs on the computer linked to the digitizer. Before starting to digitize, a user must calibrate the digitizer. Accuracy depends on the user’s attention and experience and the pattern itself. Patternmaker fixes patterns on the table surface using adhesive tapes and then remove them.

Although it is among the most widely used digitizing methods, table digitizers have some crucial disadvantages. Probably the most crucial aspect is speed. Digitizing is slow since a patternmaker does it manually, one point at a time, and also due to the usage of adhesive tapes. Users lose considerable time, especially when there are many patterns to digitize in one batch and such batches are repeated often.

Table digitizers are also expensive and heavy devices, making them inconvenient, particularly in small workplaces. Transferring pattern pieces into a CAD system via a digitizer is tedious and frustrating. The fact that one can evaluate the result only after the digitizing process is finished leads to inaccuracies or untidy curve runs. Purchasing a digitizer table is expensive and requires a significant amount of space.

Roll-up digitizers are thin, flexible, and lightweight. They are stretched on a flat surface and rolled up after finishing digitizing. Roll-up digitizers cost less compared to table digitizers. Although users can roll them up, they still require a flat surface of their size, and digitizing speed is as slow as table digitizers.

Scanner digitizers are scanner-like devices that scan the image of patterns from a close distance and employ image processing techniques to process the scanned image. They are much faster than the previous three digitizers but also come at a higher price. Depending on their size, they may claim some of the workspaces. Also, they may not always fit all the patterns, so patterns may have to be digitized one or two pieces at a time.

Pattern digitizing software (photo digitizer) uses image processing algorithms like scanner digitizers, but the difference is that it captures the image using a digital camera rather than a scanner. The software processes the captured image. It extracts features such as pattern outlines, notches, internal lines, and grain lines from the image. Using a camera means the captured image’s quality will depend on the lighting conditions, camera quality, and camera position, demanding more sophisticated image processing algorithms.

Several programs provide a solution to the inconvenience and inaccuracy of tablet digitizers. Among them are ProfileFitPattern Photo program [9], JULIVI “Fotodigitayzer» [10], Kuris Photo Digitizer [11], Eastman Photo Digitizer [12], Autometrix Photo Digitizer [13], and others. The digitized outcome matches the accuracy of measurements of a result digitized with a digitizer tablet. A patternmaker can compare the digitized curves directly on-screen with the original, so the accuracy of the curve is significantly greater. The advantages of photo digitizers are that no expensive digitizer table is required, the space requirement for a digitizer tablet is omitted, and flexible and location-independent digitizing. One may expect that this kind of digitizing system may be costly. It is partly actual since each vendor may charge a different amount for calibration-free photo digitizers. Besides that, clothing patternmakers do not have enough methods to implement such digital tools at home when necessary, for example, due to the force majeure conditions such as the COVID19 pandemic, etc.

That is why it is advisable to have a method to digitize a clothing pattern without any pattern digitizer when it is necessary to avoid additional costs.

THE PURPOSE AND OBJECTIVES OF THE STUDY

The study aims to develop a method to digitize a clothing pattern without a digitizer. For this study, we address the following objectives:

- to formulate a hypothesis of the method;
- to describe the algorithm of the method;
- to perform testing and evaluation of the developed method.

METHODS

The hypothesis of the developed method is as follows: digitizing of the clothing patterns might be performed without any digitizer (tablet or photo, etc.) by applying modification tools of the CAD/CAM systems (pattern design systems) to the digital simple geometrical forms that are constructed directly in the graphical environment of the PDS. We consider a rectangular as a chosen form for the alteration. “Julivi” is the pattern design system selected for the study. The system “Julivi” allows constructing the rectangular patterns using built-in macros. Moreover, a range of system tools enables measurements and any possible alterations of the clothing blocks.

The main points and lines that construct a pattern are defined, and names are assigned to apply the alteration method, as shown in Figure 1.

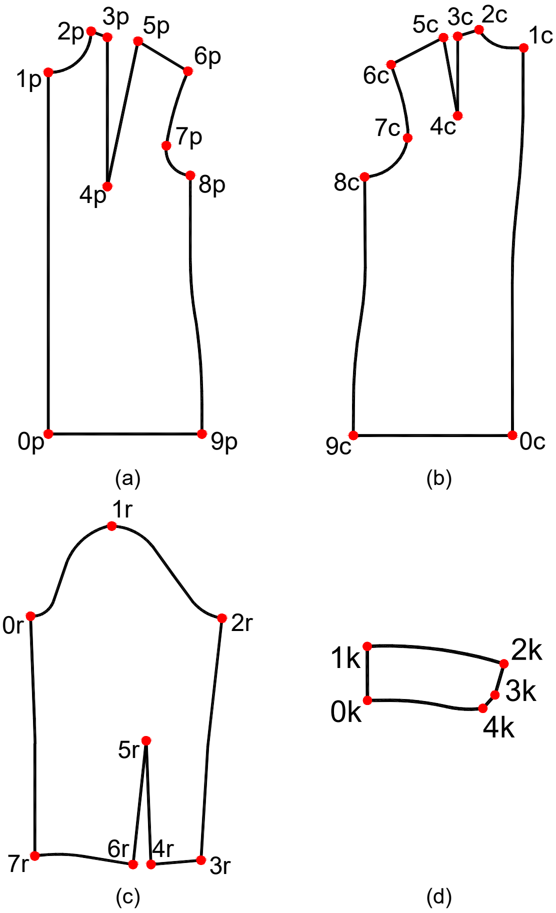


Figure 1. The main points of the original patterns: front, back, sleeve, and collar.

We used two different digitizing methods, such as photo digitizing and digitizing by graphic tools of PDS itself. We performed a comparative analysis of measurements for the patterns of women's clothing. The original patterns were compared to their digital twins to compare the accuracy of the developed method. The lengths of the digital patterns' constructive lines were measured by PDS "Julivi" tools and compared to the measurements of the same lines of the original patterns. Besides that, a comparison of the clothing blocks' areas was performed. Pattern design system "Julivi" automatically forms a "Specification" that lists the areas of digital patterns.

RESULTS AND DISCUSSION

Algorithm of the method

The algorithm of the developed method is as follows.

1. Constructing a simple geometrical form in a graphical environment of a pattern design system by its tools (figure 2, a)
2. Determining the number of main points of the pattern and inputting the same number of points to divide the lines of the original rectangular into the number of segments (figure 2, b). The names of the points are the same as those assigned for the actual pattern points.
3. Determining the coordinates of the points of the original pattern in the Cartesian coordinate system. The center of coordinates is one of the main points, which a patternmaker may choose as they see fit.
4. Determining the coordinates of the points of the digital rectangular in the Cartesian coordinate system. The center of coordinates is the point of the same name as in the original pattern.
5. Calculating Δx, Δy – the difference in coordinates of the points of the same names belonging to the original pattern and the digital geometric figure.
6. Shift the points of the digital geometric figure by the value of Δx, Δy using the pattern design system.
7. Determining the minimum number of additional points on the curved sections of the original pattern and inputting them into the curved sections of the original patterns and their digital twins.
8. Determining the coordinates of additional points, calculating the values Δx, Δy for them, and shifting the extra points of the digital geometric figure by the value of Δx, Δy using the pattern design system (figure 3, figure 4, c).

An example of using the method is at the link https://youtu.be/d1Fya_F8uqg.

Testing the method

The first step of testing the method is digitizing the original patterns (Figure 1) with a photo digitizer using the pattern design system "Julivi" (Figure 5).

The second step of testing is digitizing the patterns of the front, back, sleeve, and collar, using the developed method (Figure 6(c), Figure 7(c) and comparing the patterns' areas and segments' lengths (Table 1, Table 2).

Table 1 and Table 2 compare the method of digitizing; one can see that the developed process guarantees a higher digitizing accuracy than a photo digitizer.

Red marks in the tables show the differences that overcome the permissible rates. As the differences ensured by the developed method are acceptable, we may conclude that this method may be used as an alternative method of digitizing patterns instead of the photo digitizer or any other digitizer.

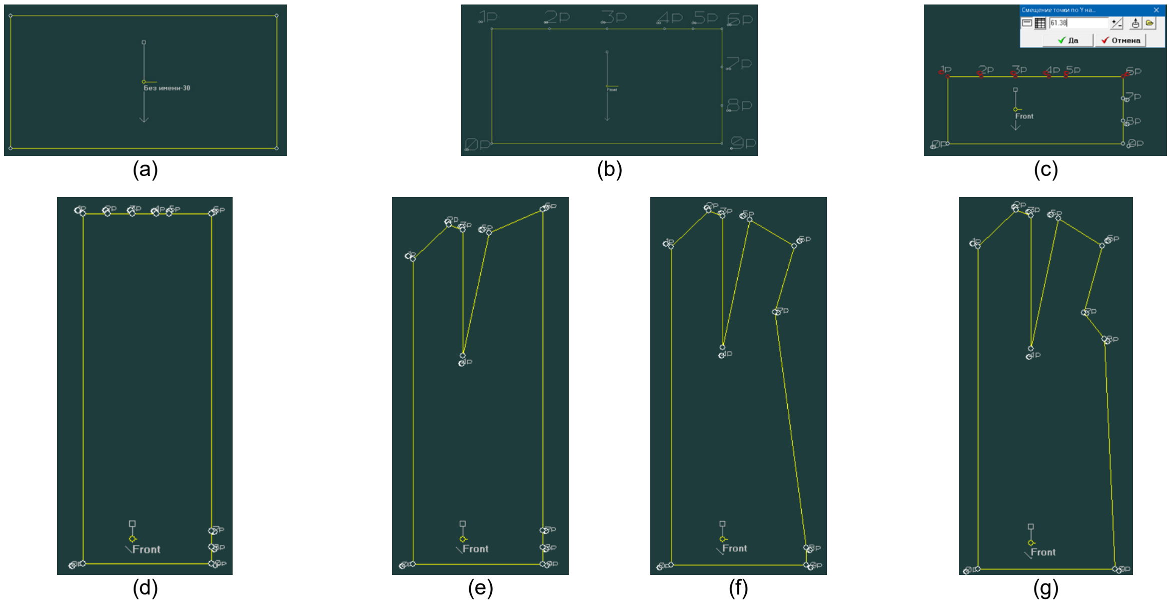


Figure 2. Digitizing the front block: (a) a rectangular (step 1); (b) main points (step 2); (c)-(g) shifting the points (step 6).

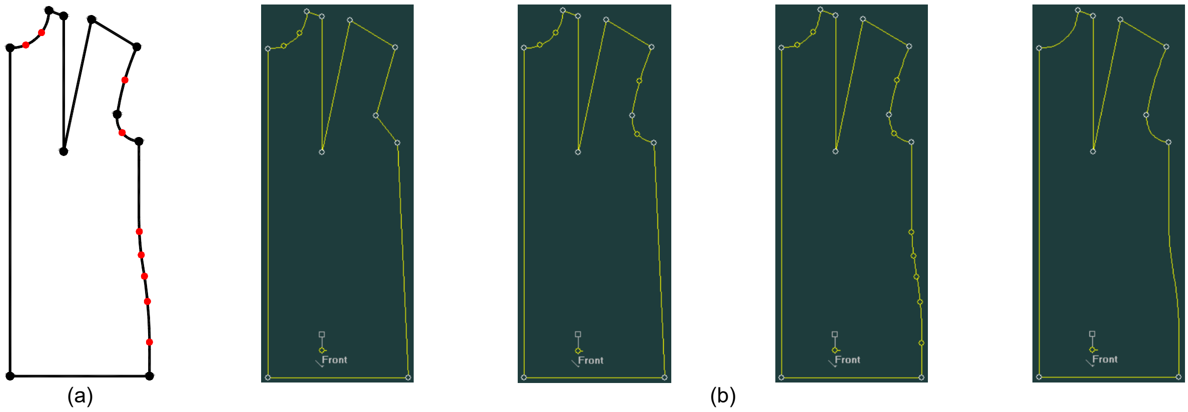
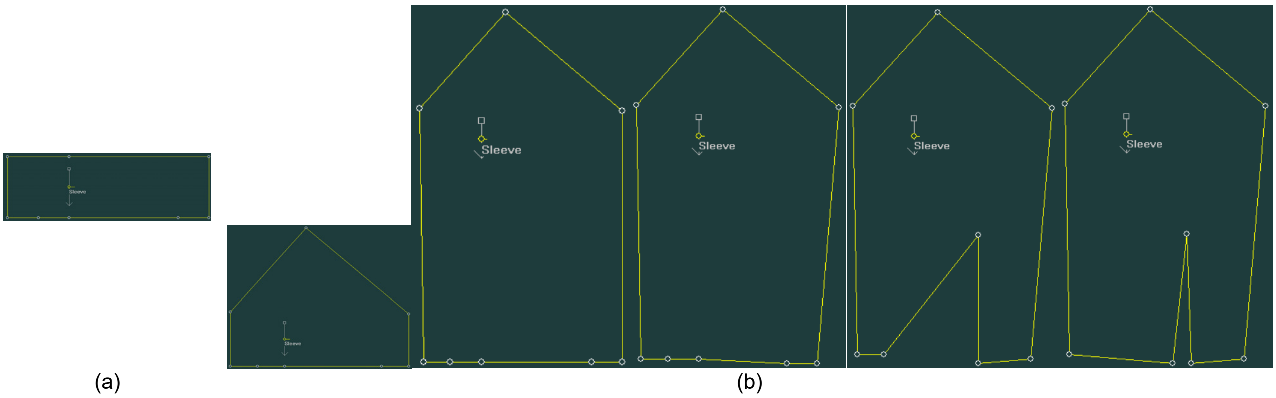
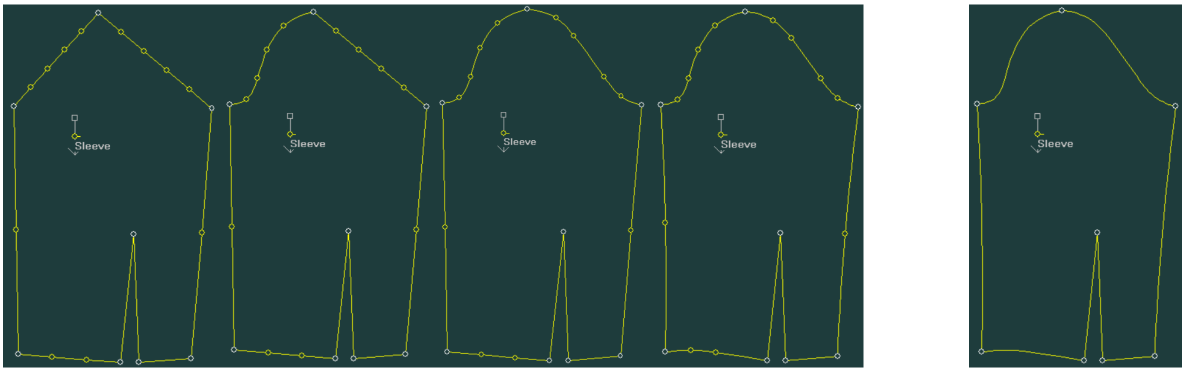


Figure 3. Alteration of the curved sections of the pattern: (a) inputting the extra points (step 7); (b) shifting the extra points (step 8).





(c) (d)

Figure 4. Digitizing a sleeve pattern: (a) an initial rectangular pattern; (b) points relocations; (c) digitizing curves; (d) completely digitized pattern of the sleeve.

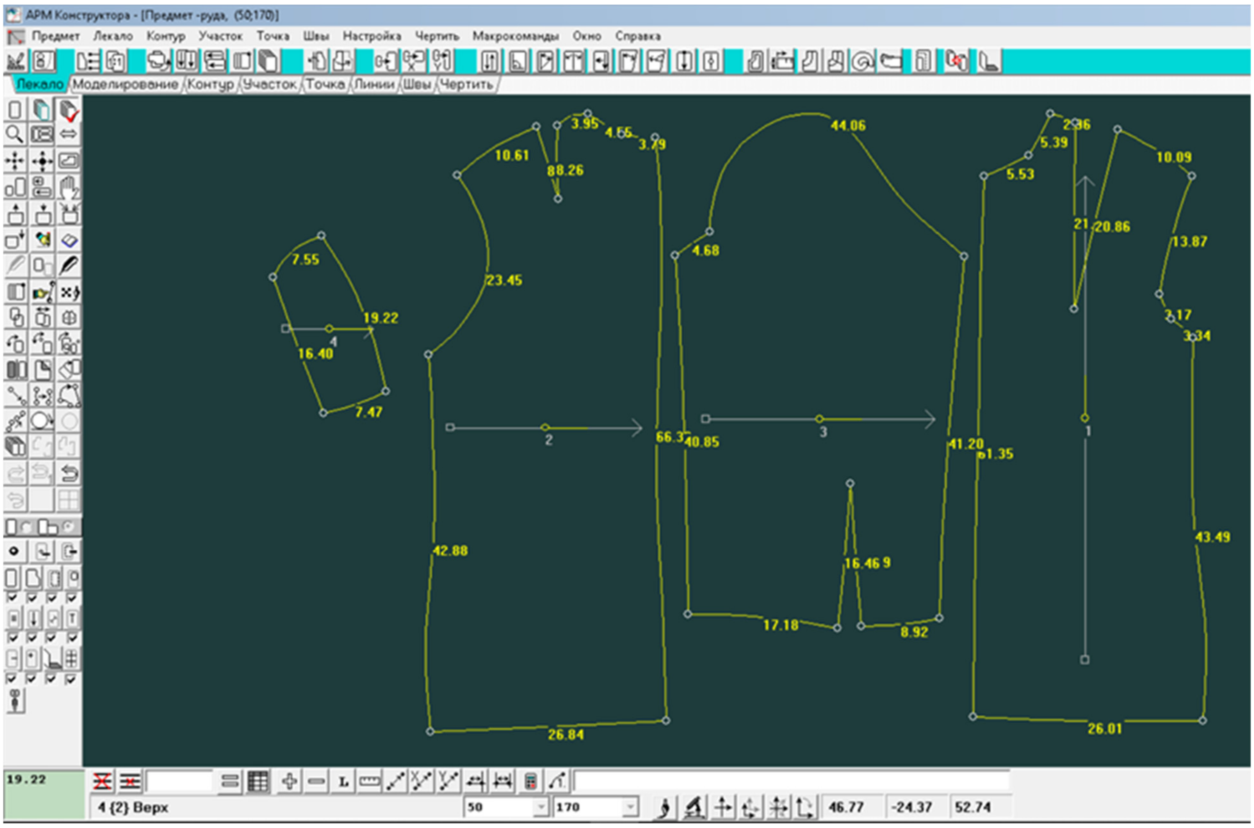
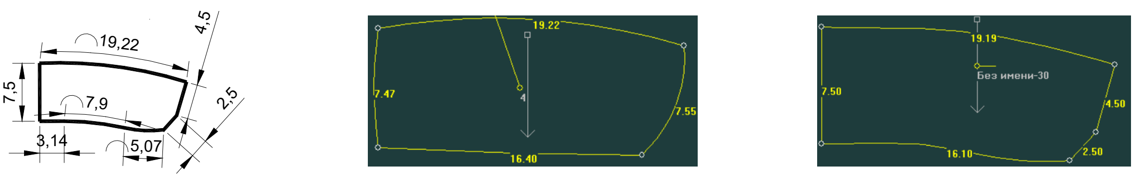
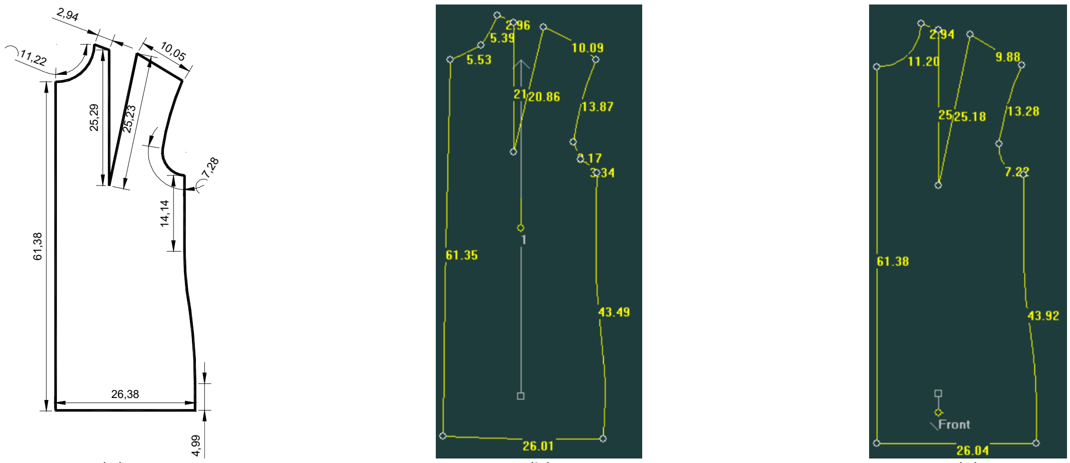


Figure 5. Digital clothing blocks obtained using photo digitizer (M2).



(a) (b) (c)

Figure 6. Collar: a) original pattern (M1); b) digitized with photo digitizer (M2); c) developed method (M3)



(a) (b) (c)

Figure 7. Front: a) original pattern (M1); b) digitized with photo digitizer (M2); c) developed method (M3).

Table 1. Comparison of the segments' lengths.

Part	Line	M1, cm	M2, cm	M3, cm	$\Delta_{1\text{-}2}$		$\Delta_{1\text{-}3}$	
					cm	*%*	*cm*	*%*
Front	0p-1p	61.38	61.35	61.38	0.03	0.05	0.00	0.00
	1p-2p	11.22	10.92	11.20	0.30	2.67	0.02	0.18
	2p-3p	2.94	2.96	2.94	-0.02	-0.68	0.00	0.00
	3p-4p	25.29	21.05	25.29	4.24	16.77	0.00	0.00
	4p-5p	25.23	20.86	25.18	4.37	17.32	0.05	0.20
	5p-6p	10.05	10.09	9.88	-0.04	-0.40	0.17	1.69
	6p-7p	13.18	13.87	13.28	-0.69	-5.24	-0.10	-0.76
	7p-8p	7.28	6.51	7.22	0.77	10.58	0.06	0.82
	8p-9p	43.91	43.49	43.92	0.42	0.96	-0.01	-0.02
	9p-0p	26.38	26.01	26.04	0.37	1.40	0.34	1.29
Back	0c-1c	65.77	66.30	65.76	-0.53	-0.81	0.01	0.02
	1c-2c	8.71	8.34	9.07	0.37	4.25	-0.36	-4.13
	2c-3c	3.79	3.95	3.78	-0.16	-4.22	0.01	0.26
	3c-4c	13.48	8.26	13.47	5.22	38.72	0.01	0.07
	4c-5c	13.48	8.51	13.48	4.97	36.87	0.00	0.00
	5c-6c	9.99	10.61	9.99	-0.62	-6.21	0.00	0.00
	6c-7c	12.81	13.05	12.81	-0.24	-1.87	0.00	0.00
	7c-8c	10.70	10.49	10.63	0.21	1.96	0.07	0.65
	8c-9c	43.95	42.88	43.94	1.07	2.43	0.01	0.02
	9c-0c	26.97	26.84	26.97	0.13	0.48	0.00	0.00
Sleeve	0r- 1r	21.91	24.29	22.41	-2.38	-10.86	-0.50	-2.28
	1r-2r	26.25	24.5	25.62	1.75	6.67	0.63	2.40
	2r-3r	41.62	41.20	41.62	0.42	1.01	0.00	0.00
	3r-4r	8.61	8.92	8.61	-0.31	-3.60	0.00	0.00
	4r-5r	21.21	16.19	21.21	5.02	23.67	0.00	0.00
	5r-6r	21.32	16.46	21.31	4.86	22.80	0.01	0.05
	6r-7r	17.00	17.18	16.98	-0.18	-1.06	0.02	0.12
	7r-0r	41.09	40.85	41.09	0.24	0.58	0.00	0.00
Collar	0k-1k	7.50	7.47	7.50	0.03	0.40	0.00	0.00
	1k-2k	19.22	19.22	19.19	0.00	0.00	0.03	0.16
	2k-3k	4.50	5.13	4.50	-0.63	-14.00	0.00	0.00
	3k-4k	2.50	2.42	2.50	0.08	3.20	0.00	0.00
	4k-0k	16.11	16.40	16.10	-0.29	-1.80	0.01	0.06

Table 2. Comparison of the patterns' areas.

Part	Line	S_{M1}, cm^2	S_{M2}, cm^2	S_{M3}, cm^2	$\Delta_{1\text{-}2}$, %	$\Delta_{1\text{-}3}$, %
Front	0p-1p	1478.138	1523.120	1481.360	-3.043	-0.218
Back	0c-1c	1591.888	1627.370	1592.230	-2.229	-0.021
Sleeve	0r-1r	1503.026	1549.050	1496.460	-3.062	0.437
Collar	0k-1k	134.326	146.960	133.440	-9.405	0.660

CONCLUSIONS

The achieved result of the current study is the alternative method to digitize a clothing pattern without any digitizer. Testing and evaluation of the developed method confirmed the initial hypothesis.

The implementation of the method slightly increases the duration of the digitizing while the accuracy is assured at the highest level of precision. The most prominent advantage of the method is no need to purchase the digitizer.

It is necessary to highlight that the method is compatible with any pattern design system available at the design studio or even at a designer's home.

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USE OF CHITOSAN AS ANTIMICROBIAL, ANTIVIRAL AND ANTI-POLLUTION AGENT IN TEXTILE FINISHING

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ABSTRACT

With the industrial developments in recent times, the textile industry also needs sustainable and environmental-friendly resources. Today's world has been overburdened with the use of synthetic or hazardous materials in day-to-day life. Chitosan polymer obtained from chitin deacetylation, having a lot of properties beneficial to mankind without being hazardous to environment and humans is currently gaining popularity for research and development all over the globe. Antimicrobial and antiviral textile finishing with the help of chitosan is a new trend in the textile field. Also, chitosan having good adsorption properties finds its application in textile effluent treatments. This review reports and discusses multifunctional finishing and dyeing of textiles with chitosan and highlights its application for textile wastewater treatment.

KEYWORDS

Chitosan; Textile; Antimicrobial; Antiviral; Dye.

INTRODUCTION

Last years, in addition to the growing interest in natural eco-friendly agents, there has also been a drive toward the introduction of green processing techniques in textile manufacturing due to rigorous ecological legislation and growing environmental concerns [1]. Turning from established hazardous synthetic value chains towards more sustainable bio-based products is one of the key factors to achieve these goals. This means to substitute petrol based agents with reactants and products derived from renewable resources. Searching for materials and reagents that could contribute to functionality and sustainability of textile products, researchers identified chitosan as an agent of choice [2].

Chitosan, poly-(1,4) 2amido-2-deoxy-ß-D-glucose, is a renewable polymer derived from deacetylation of the polysaccharide chitin. Chitin, poly-(1,4)-2 acetomido-2-deoxy-ß-D-glucose, is found throughout the biosphere. Its estimated production is 1012 tons per year. Chitin is the second most abundant polymer after cellulose. Sea animals, insects, and micro-organisms are the sources of chitin (Table 1).

In more than 90 % of all animal species and insects, chitin-based composites are the major constituents of the exoskeletons of arthropods (Figure 1). A critical evaluation of potential sources of chitin and chitosan [3] concluded that crustaceans, fungi and insects were, respectively, the principle source of chitin and chitosan and would remain so for the immediate future. However, it was envisaged that both krill and cultured fungi would complement these major sources of raw materials [4].

Table 1. Sources of chitin and chitosan.

Sea Animals	Insects	Microorganisms
Crustacean	Scorpion	Green algae
Mollusc	Spider	Yeast (β-type)
Coelenterate	Gnathopod	Fungus
Annelids	Ant	Penicillium
Lobster	Cockroach	Brown algae
Crab	Beetle	Chytrid
Shrimp		Ascomycetes
Krill		Spore

The generation of the highly reactive amino groups in the chitosan polymer imparts versatility in its use for food, textile, cosmetics, environmental, biomedical and pharmaceutical applications. Due to the presence of these amino groups, chitosan is easily soluble in weak acids and forms viscous solutions that can be transformed into films, sponges, beads … etc.

We recognize the importance of chitosan in eco-friendly textile finishing processes. Therefore we present our review paper as follows. Initially we introduce a general overview of chitosan and its properties. Second, we highlight the use of ChSN as an antimicrobial and antiviral finishing agent of textile materials. The next part will be dedicated to present research investigations where chitosan was used as

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Received May 5, 2022; accepted October 12, 2022

an anti-pollution dyeing agent. Finally we discuss the advantages and limitations of ChSN polymer and we suggest future research trends.

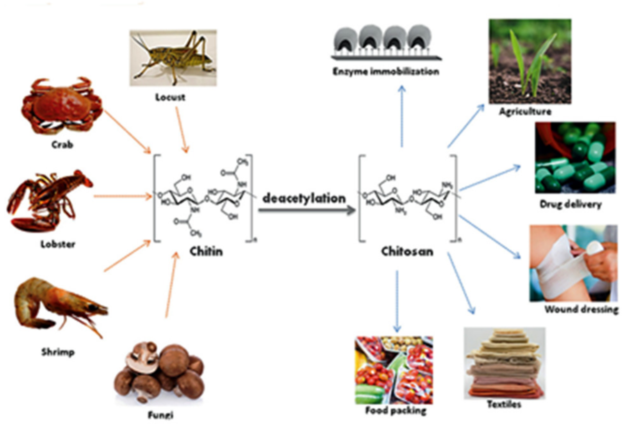

Figure 1. Main sources of chitin and chitosan and their potential applications [4].

CHITOSAN PROPERTIES

Chitosan is obtained by deacetylation of chitin biopolymer. Crustacean shells are the most important source of chitin for commercial use due to their high chitin content and availability. Chitin is isolated from crustacean shells in three steps: demineralization (DM), deproteinization (DP), and elimination of lipids and pigments. The chemical methods for the preparation of chitin from crustacean shell waste consist of mechanical grinding, DM with strong inorganic acids, and DP with alkali at elevated temperature. The chemical DM and DP processes have several drawbacks such as poorly controlled depolymerization, resulting in the reduction of molecular weight and viscosity and hydrolytic deacetylation. In addition, chemical treatments engender hazardous environmental problems such as disposal of wastewater, making this process ecologically aggressive and a source of pollution to the environment because of the high concentration of mineral acids and caustic chemicals employed [5]. Along with increased demands for an environmentally friendly society, eco-friendlier processes using enzymatic and microbiological methods for producing chitin have attracted great interest in the field of green biotechnologies. As an alternative to chemical processes for extracting chitin, fermentation processes using proteolytic microorganisms or proteolytic enzymes have been studied for decades for various crustacean shells. Procedures for chitin and chitosan production by chemical and biotechnological treatments are briefly compared in (Figure 2).

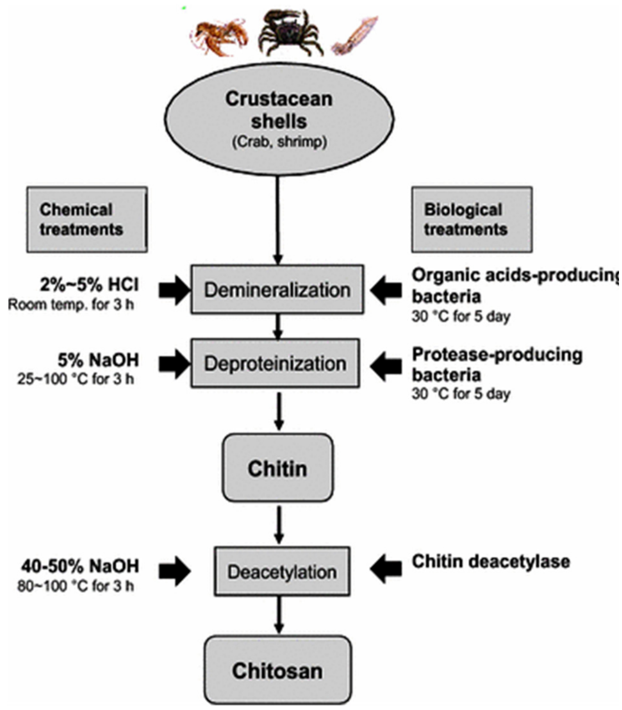

Figure 2. Chemical and biological methods for the extraction of chitin and its conversion to chitosan [6].

Obtained chitosan is a linear polyamine with too much nitrogen content and reactive amino and hydroxyl groups (Figure 3). The amino group of chitosan is not protonated in neutral medium and therefore it is insoluble in water. Chitosan dissolves readily when electric repulsions (corresponding to cationic charges) are more important than the attracting interactions (such as hydrogen bonding and Van der Waals interactions).

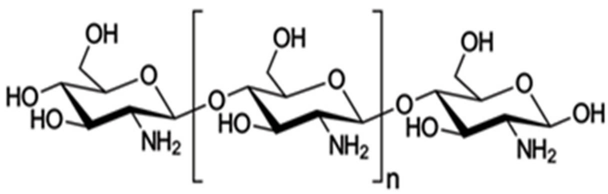

Figure 3. Chemical structure of chitosan.

The physicochemical characteristics (Figure 4) determine the relationship that exists between the structure of chitosan compounds and their potential uses. Deacetylation degree (DD) and molecular weight (MW) are the most important parameters affecting ChSN properties [7]. Often analyzed are other characteristics such as solubility, crystallinity, viscosity, nitrogen and ash contents and water retention value [8].

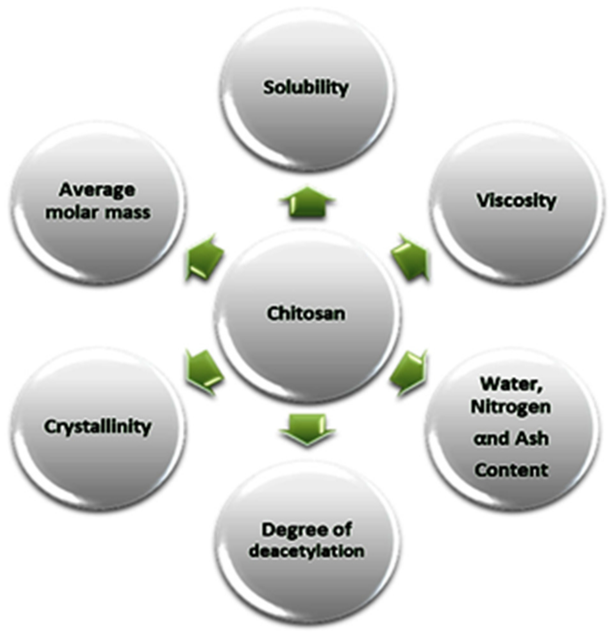

Figure 4. Physiochemical characteristics of chitosan [9].

Deacetylation degree

The degree of deacetylation of chitosan is defined as the ratio of the number of glucosamine GlcN groups to the overall number of N-acetylglucosamine GlcNAc and glucosamine groups [10]. The DD value of a ChSN sample is one of the most important factor in assessing its applications in the medical, nutritional, environmental and biotechnological fields [11]. It can also be related back to the specific biological and structural properties and functions of chitosan. It should be clear that chitosan is the deacetylated form of chitin and it must be characterized by a degree of acetylation when a degree of deacetylation is valid for chitin, the initial form of the polymer nearly fully acetylated. For chitosan, measurement of the DD is crucial in determination of its chemical structure, physical properties and interrelation. It is also essential in providing a basis from which the functions and applications can be predicted and optimized [12]. Therefore, a suitable method of obtaining reliable DD values is essential for diverse researchers working in those fields. To date, several techniques have been developed and applied for determination of the DD of chitosan, such as proton nuclear magnetic resonance (H NMR, solid C NMR and N NMR), UV spectrophotometry, conductometric and potentiometric titration, differential scanning calorimetry (DSC) or CHN elemental analysis among others [13].

Molecular weight and viscosity

Knowledge of the molecular weight of chitosan is of fundamental importance for the understanding of its applications and its role in living systems. The molecular weight of ChSN depends largely on the conditions of deacetylation and can be determined by several methods such as chromatography, light scattering and viscometry [14]. The latter is the simplest and most popular method to determine molecular weight of chitosan. The average MW is determined by the Mark–Houwink–Sakurada equation which relates this parameter with the intrinsic viscosity: $[\eta] = k\ MW^{\alpha}$, where k and α are empirically determined coefficients. However, this method has the disadvantage of not being absolute because it relies on the correlation between the values of intrinsic viscosity with those of molecular weight. ChSN is available commercially with molecular weight ranging from 5 to 1,200 kDa.

Viscosity of chitosan increases with increase in its molecular weight and concentration. Increasing the degree of deacetylation also increases the viscosity. This can be explained by the fact that high and low deacetylated chitosan have different conformations in aqueous solution. ChSN has an extended conformation with a more flexible chain when it is highly deacetylated because of the charge repulsion in the molecule. However, the chitosan molecule has a rod-like shape or coiled shape at low degree of deacetylation due to the low charge density in polymer chain. The viscosity of chitosan solution is also affected by factors such as concentration and temperature. As the chitosan concentration increases and the temperature decreases, the viscosity increases. Chitosan viscosity decreases with an increased time of demineralization due to depolymerization.

Physical characteristics of chitosan

The principle physical parameters of ChSN polymer and their methods of determination are summarized on table 2:

Table 2. Main physical properties of chitosan with corresponding measuring methods.

Property	Values	Measuring methods
Deacetylation degree	66 – 99 %	Fourier Transform Infrared [15] Potentiometric Titration [16]
Macromolecular weight	5 – 1.200 kDa	Gel Permeation Chromatography [17] Viscosimetry [18]
Particle size	< 30µm	Optical microscopy [19]
viscosity	< 5cps	Capillary test [20]
Density	1.35 – 1.4 g/cm^3	Density meter [21]
Melting point	152-159 °C	Differential Scanning Calorimetry [22]
Crystallinity	57 %	X-Ray diffraction [23]
Ash value	> 1 %	Gravimetric analysis [24]
Moisture content	> 8.5 %	Gravimetric analysis [25]

Chitosan chemistry

The chemical behavior of ChSN includes [26]:

- Linear amino polysaccharide with too highly nitrogen content

- Insoluble in organic solvents and water
- Highly soluble in acidic solutions
- Reactive amino and hydroxyl groups for chemical activation and cross-linking
- At weak base, deprotonated amino group acts a powerful nucleophile
- Enable to form hydrogen bonds intermolecularly.
- Forms salts with inorganic acids and organic.
- Form chelates and complexes with many transitional metal ions
- Cationic biopolymer with rise charge density (one positive charge per glucosamine residue).
- Flocculating agent that interacts with negatively charged molecules.

The presence of large amounts of protonated -NH2 groups on the chitosan structure accounts for its solubility in acid aqueous media since its protonation constant (pKa) value is approximately 6.5 [27]. Chitosan solubility depends on different factors such as polymer molecular weight, degree of acetylation, pH, temperature, and crystallinity. When around 50% of all amino groups are protonated, chitosan becomes soluble [28]. This behavior is explained by the fact that deacetylation leads to an increase in the number of glucosamine units and a modification in the crystalline structure of the polymer. On the contrary, a reduction in the crystallinity is observed for high acetylated ChSN samples [29]. Chitosan can easily form quaternary nitrogen salts at low pH values. So, organic acids such as acetic, formic, and lactic acids can dissolve chitosan. The most commonly used solvent for chitosan is 1 % acetic acid at about pH 4.0. Chitosan is also soluble in 1 % hydrochloric acid and dilute nitric acid but insoluble in sulfuric and phosphoric acids.

As seen in Figure 5, the reactive groups found in chitosan are a primary amino group (C2) and primary and secondary hydroxyl groups (C6, C3). Glycosidic bonds and the acetamide group can also be considered functional groups. These functional groups allow for a great number of modifications, producing polymers with new properties and behavior. ChSN derivatives have been produced, aiming to improve chitosan's properties, such as solubility or biodegradability, or to introduce new functions or properties. For instance, solubility has been improved in water aqueous media by deacetylation, depolymerization or quaternisation among other processes [30].

Interactions of chitosan with textile materials

The backbones of chitosan and cellulose are similar which has been postulated as a reason for their mutual affinity.

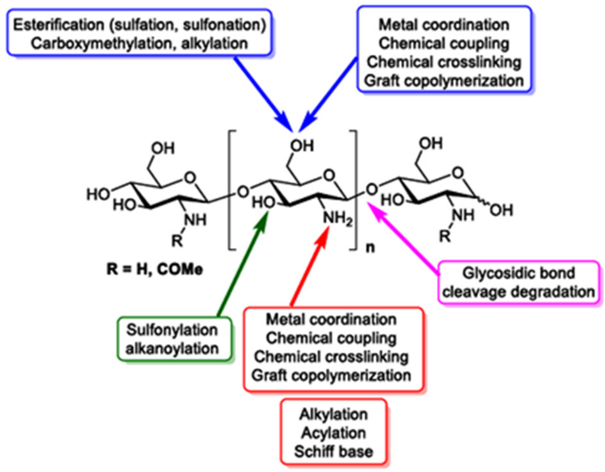

Figure 5. Chemical modifications of ChSN functional groups [31].

In acidic solution, chitosan's amine groups are positively charged; while in alkaline conditions, chitosan is uncharged and its solubility in water is diminished. It has been observed that chitosan adsorbs on textile cellulosic materials (cotton, viscose, jute …) in both acidic and alkaline conditions [32]. The more possible cellulose-chitosan intermolecular interactions are based on hydrogen bonds and Van der Waals forces. However, ionic and/or covalent bonds can be formed under special conditions and cellulose treatments [33]. For some applications, the irreversible binding of ChSN to the cellulose substrate is extremely important, especially when the bio-activity of a material should appear only at the interface on the biological medium. The functional groups of cellulose, such as carboxylic and aldehyde groups, contribute to the binding. The COOH groups provide electrostatic attraction between cellulose and ChSN as an adsorbent, while aldehyde groups allow covalent binding of ChSN via Schiff base formation [34]. These chemical interaction mechanisms between chitosan and cellulosic fiber were investigated by Grande et al. [35] using FTIR spectra analysis. The strong absorption in the region 3500– 3100 cm−1 signifies the strong hydrogen bonded ChSN and cellulosic material and also the existence of primary –NH2 and secondary –NH groups. The absorption peak that appeared at 1640 cm−1 for chitosan-treated cellulose suggested the formation of Schiff base (C=N double bond) between aldehydic carbonyl group of cellulose and amino group of ChSN corroborating the formation of a donor–acceptor interionic complex between the cellulose and ChSN.

It is known that the binding of chitosan to wool is due to ionic interactions, such as carboxyl groups in wool forming salts with the free amino groups in chitosan and hydrogen bonding interactions between hydroxyl and amide groups of the wool with the hydroxyl groups of the chitosan [36]. These chitosan-protenic fibers interaction was confimed by Silva et al. [37] using X-ray photoelectron spectroscopy (XPS) analysis of chitosan coated soybean fabrics. They noted that after the addition of chitosan there was a positive shift in the binding energies of the C–O/C–N and O–C–O/C=O peaks. The presence of chitosan significantly increases the relative percentage of binding energy area of these two peaks displays also a positive shift of the carboxylic component peak from 288.5 to 288.9 eV.

The above mentioned weak ionic interactions between chitosan and proteinic fibers limit the application of the former to proteinic textile materials. Chemical modification of chitosan can create a strong chemical bonding between chitosan and wool, which consequently increases the washing durability. Glyoxal or glutaraldehyde or citric acid has been used as crosslinking agents. Chitosan has also been grafted to wool after acylation with succinic anhydride and phthalic anhydride [38].

Biological properties of chitosan

Chitosan is not only a naturally renewable resource but also a low-cost polymer and very versatile material. Much of the recent interest in chitosan and its derivatives arise from the fact that they combine several favourable biological characteristics, including biodegradability, biocompatibility and non-toxicity, making them valuable materials for pharmaceutical, biomedical as well as textile applications. Besides these properties, chitosan-based materials present antibacterial, antiviral, hemostatic, antioxidant and anti-inflammatory activities [39].

- **Hemostatic effect**

One of the biggest challenges for the modern medicine is massive blood loss, which is responsible for the highest number of deaths resulting from various injuries. Until now, no functional, food or drug administration-approved artificial blood substitutes have been developed. Thus, the ability of fast and efficient inhibition of bleeding is an issue of a great importance. Currently, the most popular methods of hemostasis restoration is the application of an hemostatic agent. An ideal hemostatic agent should have antimicrobial property. This can be achieved by applying a textile matrix (dressings and sponges) containing antibiotics that are effective against most bacteria species. Due to its proved antimicrobial, antioxidant and anti-inflammatory properties, chitosan has been considered as an attractive candidate for hemostasis in medical applications [40]. In general, ChSN can enhance the hemostatic activity by attracting the negative charge erythrocytes and red blood cells, plasma, activation and aggregation of platelets, and blood coagulation [41]. As a result, chitosan is normally used as hemostatic dressing for wound healing in clinic instead of a blood-contact medical device. The hemostatic property was attributed to the polycationic characteristic of chitosan

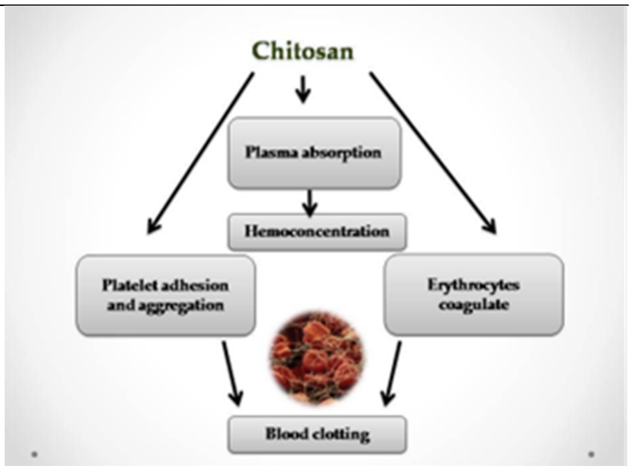

Figure 6. Mechanism of chitosan hemostatic effect [43].

and its non-specific binding to cell membranes resulting from the positively charged amino groups along the molecular chains [42]. In fact, the positively charged chitosan enhanced platelet adhesion, aggregation and activation of intrinsic blood coagulation (Figure 6).

- **Antiviral activity**

There are reports of antiviral properties of chitosan and its modified forms. In the report of Ai et al. [44] chitosan extracted from the larvae of Musca domestica exhibited inhibition of infectivity of two baculo viruses, autographa californica multiple nucleopolyhedro virus (AcMNPV) and bombyx mori nucleopolyhedro virus (BmNPV). In another study by Davis et al. [45], 53 kDa chitosan showed a reduction in the growth of surrogate enteric viruses, feline calicivirus FCV-F9 and murine norovirus MNV-1. Derived 3,6-O-sulfated chitosan was shown, by Gao et al. [46], to exert broad antihuman papillomavirus (HPV) activities in vitro, by targeting the viral capsid protein, known to play a role in viral replication inside a host cell. Li et al. [47] showed that sialyllactose (SL)-incorporated chitosan based materials are able to inhibit viral adhesion of influenza virus to a host cell. The SL-chitosan binds to hemagglutinin protein on the surface of an influenza particle, which is responsible for viral attachment to the host cell surface via binding with surface glycoligands. Guo et al. [48] reported on antiviral mechanism of a combined biological agent consisting of chitosan oligosaccharide and cytosinpeptidemycin (CytPM-ChSN). CytPM-ChSN effectively inhibited tobacco mosaic virus (TMV), suppressed viral RNA and capsid protein accumulation. Davydova et al. [49] reported that low molecular weight derivatives of chitosan especially with decreasing degree of polymerisation showed antiviral property against TMV by inhibiting the development of necrosis caused by the virus.

Figure 7 summarizes the general antiviral mechanisms of actions of the chitosan and chitosan derivatives. Broadly, chitosan based materials act on non-enveloped viruses (murine norovirus-1, MS2, feline calicivirus F-9, human papillomavirus, hepatitis A virus, Coxsackie virus B4, phi X174) through viral capsid interaction. One or more mechanisms of action may take place. The positively charged chitosan has been postulated to bind to viral nucleic acid and reduce the viral genome integrity [51]. With respect to enveloped viruses, chitosan may stimulate the immune system to inhibit Newcaste virus, bind to envelope glycoprotein to inhibit viral entry (of HIV-1, influenza) and/or inhibit the virus growth (of herpes simplex virus) in a nonspecific manner. The antiviral actions of such therapeutics and their respective physicochemical constructs can be exploited to eradicate the SARS-CoV-2, another variant of enveloped virus.

- **Antioxidant property**

The body maintains an oxidation balance under normal physiological conditions. When the antioxidant capacity is not adequate to combat the sudden increase in free radicals, the surplus free radicals lead to cell injury, metabolic disorders of the cellular macromolecules, and the occurrence of skin and soft tissue diseases. The antioxidant properties of ChSN are attributed to the amino and hydroxyl groups in its molecular chain, which can effectively scavenge excessive free radicals in the human body [52]. The antioxidant activity of chitosan mainly depends on its relative molecular weight and the level of acetylation. Chitosan shows a greater ability in scavenging free radicals having relatively low molecular weights and higher levels of acetylation [53]. In addition, chitosan derivatives containing Schiff's base and a quaternary ammonium salt exhibit stronger antioxidant capability than chitosan due to the presence of hydroxyl and halogen groups [54]. The antioxidant capacity of ChSN can be regulated by adjusting its molecular weight, acetylation level, and the extent of chemical modification, thereby conferring tremendous application prospects in medical cosmetology and the treatment of soft tissue diseases [55].

- **Anti-inflammatory effect**

Inflammation is the first protective response to infection or injury of human body driven in a tissue compartment by a specific set of immune and inflammatory cells with the aim of restoring its structural and functional integrity after exposure to an adverse stimulus [56]. It is known that chitosan and its derivatives, which interact with eukariotic cells, stimulate the synthesis of anti-inflammatory cytokines, causing different directions in the effect on immunity, both stimulating and inhibitory. Thus, it was established that chitosan contributes to the decreased synthesis of anti-inflammatory cytokines by human astrocytoma cells, without affecting time their vitality at the same. It also prevents the development of chronic inflammation, which can cause severe diseases [57]. When studying experimental bronchial asthma in mice after intranasal introduction of ChSN, the anti-inflammatory effect of water soluble forms of chitosan manifested itself in a decreased degree of infiltration of the bronchial epithelium by leukocytes and inhibition of the synthesis of various anti-inflammatory factors of the immune-response [58]. Davydova et al. [59] tested the anti-inflammatory activity of chitosan with high molecular weight (115 kDa) and low MW (5.2 kDa), and both chitosan samples presented an intensified induction of anti-inflammatory IL-10 cytokine in blood and suppression of colitis progress. The authors concluded that the main contribution to anti-inflammatory activity of chitosan was driven by structural elements comprising its molecule, but not depending on MW. Oliveira et al. examined the inhibition of pro-inflammatory cytokines and anti-inflammatory activities of chitosan [60]. From the achieved results, a reduction of TNF-α (pro-inflammatory cytokines) in 3~10 days of cells cultured on ChSN material and significant increase of anti-inflammatory cytokines IL-10 and TGF-β1 were presented.

- **Antimicrobial activity**

The antimicrobial activity has been considered the most essential and influential bioactivity of chitosan and employed not only to the preparation of biomedical materials but also to the functionalization of other materials including textiles. The mechanism of antimicrobial activity of chitosan is not yet fully understood although numerous researches have been carried out so far. The antimicrobial effect of chitosan is much higher comparing to chitin due to the numbers of the amine groups that is responsible for cationic property of chitosan. Positively charged chitosan at acidic condition might interact with negatively charged residues of carbohydrates, lipids, and proteins located on the cell surface of bacteria, which subsequently inhibit the growth of bacteria [61]. Thus, the electronic property of chitosan plays a very important role in the inhibition mechanism of microorganisms (Figure 8). The high density of positive charge on the structure of chitosan or its derivatives generates strong electrostatic interaction that is affiliated with DDA. With this theory, chitosan is more promising for the inhibition of Gram-negative than Gram-positive bacterium since the negatively charged cell surfaces interact more with positively charged chitosan [62-63]. However, many researches demonstrated that the chitosan was a more efficient inhibitor against Gram-positive compared to Gram-negative microorganism in their experimental results [64-65].

The use of chitosan an antibacterial finish of textile materials is discussed in the next section.

ANTIBACTERIAL FINISHING OF TEXTILES WITH CHITOSAN

In the textile industry, there is a growing demand for new medical textiles and textiles related to health care. The development of research in this field was largely due to the events associated with the rapid propagation of dangerous pathogens that may cause epidemics. Until now, many chemicals have been used in antimicrobial textiles such as phenols and thiophenols, antibiotics, heterocyclic compounds with anionic groups, nitro compounds, urea, formaldehyde and amine derivatives, which show bactericidal effect, but in most cases are toxic to humans and harmful to the environment. That is why the textile industry is looking for new, ecofriendly solutions that are non-toxic to people and are safe for the environment. The most studied natural polymer for antimicrobial finishing of textiles is chitosan. ChSN is a wide-spectrum biocide with high antimicrobial efficacy against both Gram-positive and Gram-negative bacteria, as well as fungi and yeasts [67]. Chitosan inhibits the growth of a wide variety of bacteria and fungi, showing broad high bacteria killing rate and low toxicity toward mammalian cells [68].

In textile field, the most common way to apply chitosan to fabrics is by wet thermal curing, involving relatively high temperature with energy consumption, costs and possible fabric degradation; moreover, the addition of toxic reagents, such as glutaraldehyde, is requested as cross-linking agent. In recent research works, ultraviolet radiation in the presence of a suitable photo initiator was proposed as an alternative process to graft chitosan molecules to textile fibres by radical process [69-70]. In detail, in case of a cellulosic substrate such as cotton, the same cellulose molecule can be involved in the reaction by the formation of radicals, which can react with those formed on the chitosan molecule, conferring a strong fastness to the finishing. Moreover, UV grafting is a fast and eco-friendly process, carried out at room temperature, with lower cost than the traditional thermal process. Cotton, silk and synthetic fabrics were considered as substrates. Obtained results showed that chitosan UV curing yielded strong antimicrobial properties, reaching near 100 % reduction on all considered fabrics. In order to have a good treatment fastness, chitosan has to be diluted with acetic acid solution before spreading on fabrics and an impregnation time of 12 h at an ambient temperature or 1 h at 50 °C is necessary before the curing to ensure a good penetration inside the fibres [71]. The homogeneous distribution of chitosan on fabrics was confirmed by dyeing tests with an acid dye and by SEM analysis (Figure 9), which showed the optimal distribution of the finish on single fibre surface.

Erdogan [73] studied the antibacterial effectiveness against *E. coli ATCC 8739* of cotton fabrics coated with crayfish and shrimp chitosan/nanosilver composite. The antibacterial efficacy of chitosan/nano-Ag coated fabric samples against E. coli ATCC 8739 was tested by the JIS L 1902-2015 standard test method (it is a quantitative method used to test the ability of antibacterial finished fabrics to inhibit microbial growth and kill microorganisms). The crayfish and shrimp chitosan formed a colorless film and coated the nano-Ag particles homogeneously on the cotton fabric. Antibacterial activity values were calculated as 3.10 and 5.74 for crayfish and shrimp chitosan coated cotton fabrics and as 5.37 and 5.10 for crayfish and shrimp chitosan+nano-Ag coated cotton fabrics, respectively. Their experimental results showed that chitosan/nano-Ag coating exhibited a good antibacterial activity (99.99 % reduction) against E. coli ATCC 8739 and can be used in the manufacture of garments such as medical textiles, baby clothes and underwear.

Several textile fabrics made from natural and synthetic materials were coated with ChSN to achieve antimicrobial property. Table 3 summerizes results gathered from literature of textile substrates treated with chitosan to impart them antibacterial activity.

CHITOSAN AS AN ANTIVIRAL AGENT

A normal textile fabric does not have any antiviral properties but the incorporation of chitosan into textiles can make them antiviral. ChSN make the treated textiles antiviral by employing either of the following two mechanisms or by combining them. In the first mechanism, the applied biopolymer makes the surface energy of a textile surface relatively low. Doing so will stop the viral transmission via textiles by restricting viruses to the textile surface. This low surface energy of textiles can also destroy the outer lipid barrier of a virus which will make the viral genome inactive by making it unable to penetrate into a host cell [81]. In the second approach, when a virus comes in contact with a textile surface treated with ChSN, the latter bind with the outer layer of the virus and inhibit its vital mechanisms. Chitosan oxidize and dissolve the lipid or the glycoprotein layer and enter inside the virus structure and adhere to the genome (i.e. with the virus DNA or RNA) and deactivate the same by breaking it into fragments. As a result of these interactions, the disintegration of the virus ensues, manifesting itself in the leakage of the viral genome and a loss of infectivity, leaving the viral particle inactive on the treated textile surface [82]. A schematic diagram explaining the antiviral mechanism through virus destruction (i.e. through the second approach) is shown in Figure 10.

To date, the incorporation of chitosan into the textiles can be done at different stages and in different ways. ChSN antiviral finishing on the textile material can be done onto the textile fibre, yarn and fabric depending upon the application technique.

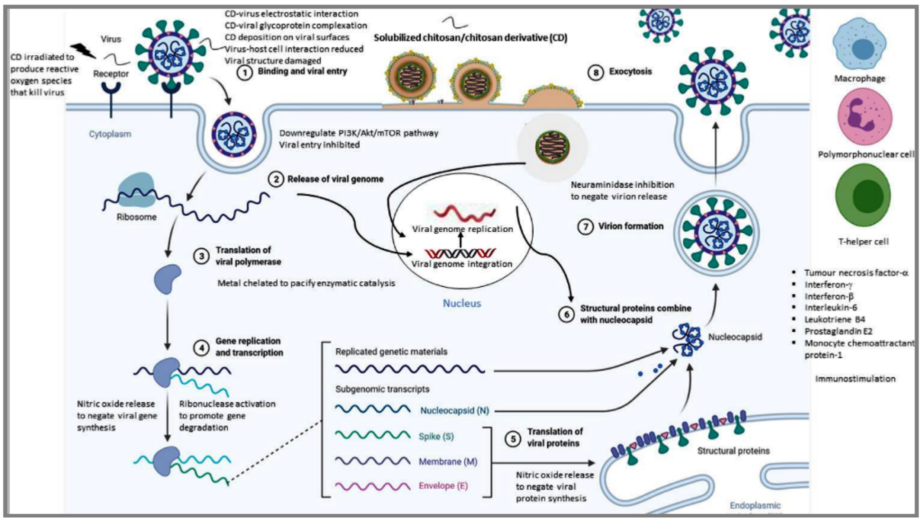

Figure 7. General antiviral mechanisms of actions of the chitosan and its derivatives [50] .

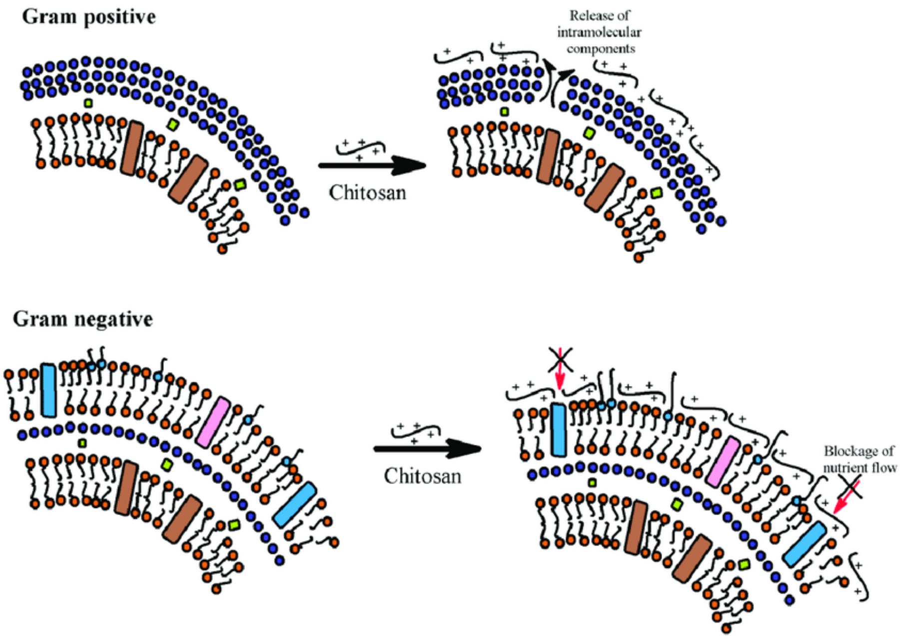

Figure 8. Action modes of chitosan on Gram positive and Gram negative bacteria [66].

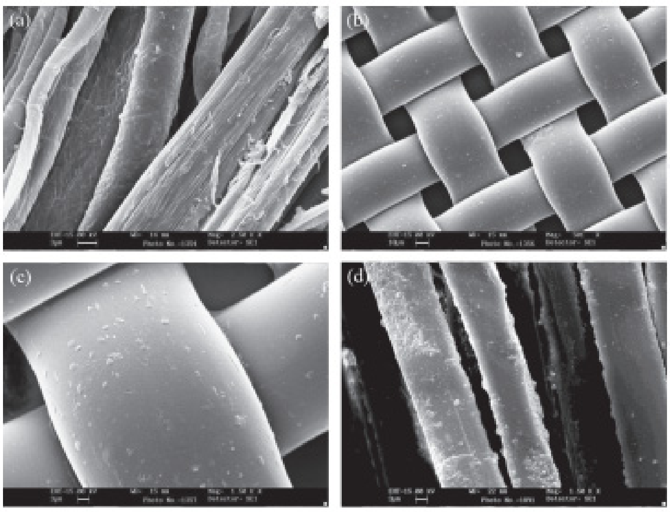

Figure 9. Chitosan UV grafted to fibres: cotton (a), PET (b), PA (c) and silk (d) [72].

Table 3. Antibacterial efficiency of chitosan treated textiles.

ChSN material	Substrate	Bacteria	Efficiency	Test method	Reference
ChSN/ZnO nanoparticles	Cotton	S. aureus E. coli	98.48 % 99.88 %	Shake flask method (ASTME2149-01)	[74]
ChSN	Silk	E. coli ATCC 11229	100 %	ASTM E 2149-01	[75]
ChSN/Copper nanoparticles	Polyester	E. coli ATCC 25922 S. aureus ATCC 25923	99.9 % 99.9 %	AATCC 100-2004 AATCC 100-2004	[76]
ChSN nanoparticles	Cotton	B. subtilis ATCC 6633 Proteus ATCC 33420	15 mm 15,2 mm	Disk diffusion method	[77]
Acidic ChSN solution	Viscose	S. aureus E. coli Candida glabrata (fungi)	97 % 94 % 85 %	ASTM E 2149-01	[78]
Chitosan/propolis Composite	Wool	S. aureus Pseudomonas aeruginosa Aspergillus niger	90 % 80 % 78 %	Plate count method	[79]
ChSN/Cu nanoparticles	Polyester/Cotton (50 %/50 %)	S.aureus E. coli	3 mm 3 mm	Disk diffusion method AATCC 100–1999	[80]

Table 4. Chitosan based textile materials and antiviral activity efficiency

Type of chitosan	Substrate	Application method	Virus type	Efficiency	Reference
ChSN/Carboxymethyl-cellulose composite	Polyamide fabric	Layer by Layer coating	Coronavirus MHV-3	99,99 %	[85]
hydroxypropyl chitosan / O-carboxymethyl-N, N, N-trimethyl ammonium chloride chitosan	Cotton fabric	press-rolling process	Ebola hepatitis	99 % 99 %	[86]
ChSN Layer	Polypropylene face mask	Middle Layer	Enterovirus 71 (EV71)	97.95 ± 0.61%	[87]
ChSN solution	Poly(lactic acid) face mask	Coating	HCoVOC43	97.9 %	[88]
ChSN/Citric acid solution	Cotton fabric	Impregnation	Herpes simplex virus1 (HSV-1)	99.9 ± 0.50 %	[89]
ChSN/ Sialyllactose	Fibers	Wet spinning	influenza virus (H1N1)	99.6 %	[90]

For ease of application and continuous production, antiviral application onto the fabric is preferable. For fabrics like cotton, wool, silk, and other manmade fibers, ChSN antiviral treatment is done by surface treatments, like the exhaust method, the pad-dry-cure method, and the coating technique, alone or in combination, depending on the antiviral composition and the fabric quality. Chitosan biopolymer can also be incorporated in manmade fibers before the fibre extrusion (Figure 11). The exhaust method is the most common and popular method of chitosan finishing of textile materials. This method is also well suited for the antiviral finishing of natural fibres and polyamide fabrics. The process is very similar to the dipping technique and application is carried out below the boiling temperature. For polyester fabric, the high-temperature exhaust method is preferable. The process is very similar to disperse dyeing and the application is carried out at 120-130 °C. The pad-dry-cure method is another way of applying ChSN onto the textile material. The fabric is padded with the ChSN composition in an aqueous medium along with a suitable binder, followed by drying and curing for proper fixation.

Several research works reported the use of chitosan as an antiviral agent in textile materials. Examples of these studies are highlighted in Table 4.

Nevertheless, it is well known that various chemical and physical procedures are used in the preparation of chitosan from chitin. This processing significantly affects the final chemistry of the chitosan and the product quality. The variability of ChSN sources and processes of preparation has led to production of wide range of chitosan polymers with different physicochemical properties, such as differences in degree of deacetylation, molecular weight, crystallinity, and residual ash and protein contents. Such variability in chitosan physicochemical properties could lead to inconsistent and conflicting reports regarding its antiviral performance [91].

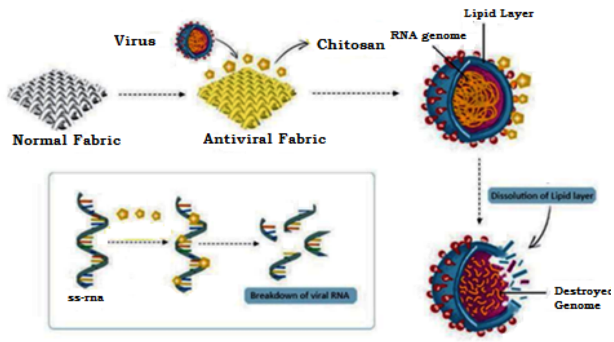

Figure 10. Antiviral mechanism through virus destruction on ChSN treated textile fabric [83]

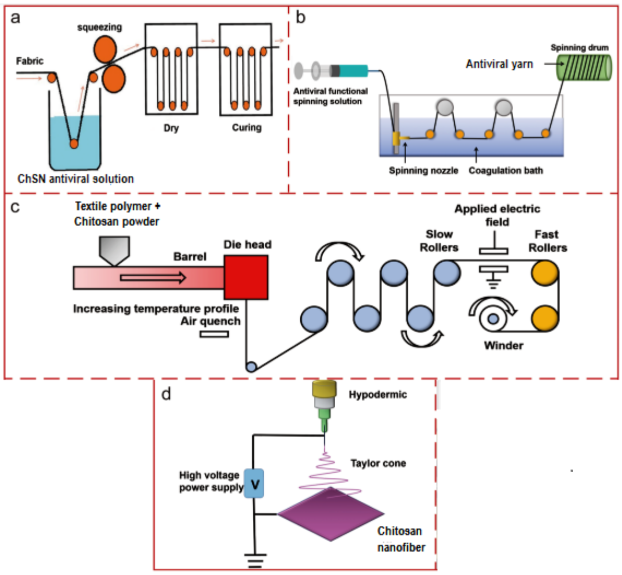

Figure 11. Methods of processing chitosan based antiviral textiles: (a) Antivirus textile soaking and rolling process, (b) Preparation of antiviral yarns by wet spinning, (c) Antiviral ChSN textiles prepared by melt spinning, (d) Equipment for electrostatic spinning of ChSN nanofibers [84].]

ECO-FRIENDLY DYEING WITH CHITOSAN

The dyeing process is a major step in fabric processing, especially for consumer esthetic test [92]. All dyeing methods require quite high energy, large amount of water and salts until the dye molecules distribute and diffuse uniformly. In addition, these processes release a high amount of complex effluents containing all chemicals together [93]. Therefore, the loss of untreated dye and salt and highly efficient effluent treatment all have very high equivalent cost. Moreover, the drawbacks also impact on aquatic environment-related health. The use of chitosan or modified chitosan has beneficial effects on dyeing process which reduces the amount of untreated dye in the bath without using any salt. As a result, a simple effluent treatment would be enough to process released effluent from dye house [94]. Chitosan contains a high proportion of amino groups which provide more dye sites for anionic (reactive, acid and direct) dyes to be absorbed by textile fibers and fabrics through Van Der Waals forces and electrostatic attraction. Therefore, ChSN treatment can improve tinctorial properties of textiles such as affinity to anionic dyes, color strength and fastness [95-96] in salt free dyeing baths [97].

Cotton fibers are extensively used in fabric production because of their exceptional characteristics of comfortability, air permeability, biodegradability, no static electricity build up and excellent hygroscopicity. Reactive dyes are usually used to dye cotton fibers owing to their brightness, diversity of colors, good wet fastness and easier applicability [98]. When applied to a cotton fabric in an alkaline environment, the dye reactive group forms a bond linking dye molecule and that of the fiber. Therefore, the dye form part of the fiber and will be less prone to removal by washing as compared to other dyestuffs which stick to the fabric by adsorption [99]. Conventional dyeing process of cotton fabric with reactive dyes requires the use of large amount of electrolyte as exhausting agent [100]. These electrolytes lead to enormous environmental problems because they are neither exhausted nor destroyed thus remaining in the discharged dye liquor [101]. To reduce the use of electrolytes in dyeing, different options have been explored. These options include surface modification of cellulose fabrics by reacting with compounds having cationic groups or managing dye and salt addition during the exhaustion process [102]. The surface of cotton fiber can be modified to increase dye-fiber interactions by introducing cationic sites either by aminization or cationization. This will overcome the lack of affinity of reactive dye to cotton fiber, therefore providing the possibility of salt free dyeing [103]. One such approach is cationization of cotton with –NH2 natural amino groups of chitosan (Figure 12).

Ashenafi et al. [105] modified the cotton fabric surface with chitosan through cationization reaction. Then, chitosan modified textile was dyed with Reactive red-31 dye without salt and compared with the conventional dyed cotton. Chitosan modified cotton showed 13.1 % improvement in dye exhaustion, 10.6 % in dye fixation and 21.5 % in the total dye utilization as compared to the conventional sample. Also, the color strength of the modified cotton fabric was better than that of conventional sample which is 18.88 and 18.02 respectively. In addition, both the dyeing time and temperature were reduced by 10˚C and 20 minutes, respectively in the cationized cotton dyeing technique. Compared with untreated cotton dyed with a conventional dyeing procedure, the chitosan modified cotton fabrics dyed without electrolytes have adequate and quite comparable colorfastness to

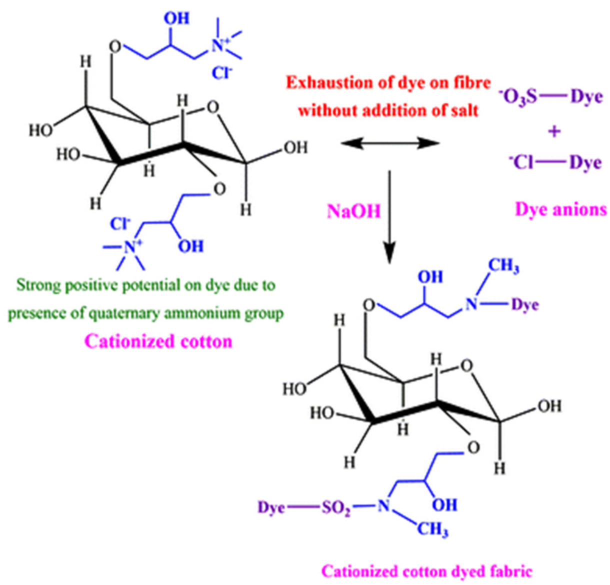

Figure 12. Dyeing mechanism of reactive dye on cationized cotton [104].

washing, dry rubbing and wet rubbing fastness but slightly reduced light fastness. Besides, the chitosan modified dyeing process greatly reduced the amount of water usage and time required to adequately rinse and remove hydrolyzed reactive dye. Similar results were recently obtained by Rehman et al. [106] when they dyed chitosan treated cotton with five ultimate reactive dyes: Drimarene Blue, Drimarene Red, Drimarene Yellow, Drimarene Lemon and Drimarene Fuschia. Their results showed an increase in the shade depth (measured by color stregth K/S) of chitosan treated samples as compared to untreated samples. Color fastness properties like washing fastness and rubbing fastness were also improved because of greater dye fixation. But, light fastness was not significantly affected because it depends upon the inherent dye structure hence it remained almost the same.

In another work, Karthikeyan and Ramachandran [107] carried out salt-free reactive dyeing of cotton fabrics pretreated with emulsions of chitosan nanoparticles. Nano-emulsions with different chitosan concentrations: 0.01 %, 0.05 %, 0.1 %, 0.3 % and 0.5 % (w/v) were used for cotton fabrics padding at a pick up weight of around 80 %. Then, nanochitosan treated cotton samples were dyed in a dye bath containing 3 % of CI Reactive Red 6. They concluded that when the nanochitosan concentration increases, the dye uptake also increases and the cotton fabric treated with 0.5 (w/v) chitosan nanoparticles had higher K/S values. Moreover, the crocking and washing fastness values of all such dyed samples are quite satisfactory and slightly superior to those of conventional dyed sample. This was probably due to the fact that cotton fabrics coated with nanochitosan have uniform depth of shade after dyeing because chitosan can cover the neps formed in immature cotton fibers.

According to Aitova [108], the surface characteristics of wool fabric depend on the various types of treatments, such as plasma, enzymatic and chitosan treatments. All these processes induce high dyeing efficiency and shrink-resistance in wool fabric. For example, the plasma, enzyme and ChSN combination give the best K/S values compared to untreated dyed fabric. Since plasma pretreatment modifies the surface, enzymatic treatment can remove the hydrophobic layer of wool more efficiently, which makes dye migration higher after the application of chitosan.

Polyester fibers show a hydrophobic character and swell to a very small extent in water making access by dyestuff molecules to the fiber difficult. This together with the absence of active chemical groups makes it difficult to dye polyester with dyestuffs other than disperse dyes. In an attempt to dye polyester with reactive dye, Najafzadeh et al. [109] coated alkali treated polyester samples with nano-chitosan. Then surface modified fabrics were dyed with Bezactive green S-4B reactive dye. They affirmed that increasing nano-chitosan content resulted in higher dye adsorption. Dyed polyester fabrics showed good dry-rubbing and washing fastness and moderate wet-rubbing fastness. According to these results, reactive dyeability of polyester at low temperatures in the absence of a carrier provides a more environmentally friendly alternative to traditional polyester dyeing methods.

Several other studies reported the use of chitosan and its derivatives to improve the dyeability of textile fabrics with anionic dyes. These interesting research works are summarized on Table 5.

However, in general synthetic dyes are allergic, carcinogenic and detrimental to human health [120]. In addition, synthetic dyeing processes involve the use of huge quantities of hazardous chemicals. For these reasons, the interest in use of non-allergic, non-toxic and eco-friendly natural dyes (such as Roselle, Lawsonia inermis L, Cochineal, Curcuma and so others) for textile applications is growing these last years as a result of the stringent environmental standard imposed in many countries. But, it is well known that the majority of natural dyes generally show very low affinity toward textile fibers and possess poor color fastness properties [121]. To overcome these problems, chitosan biopolymer can replace the salts such as ferrous sulphate, sodium sulphate, sodium carbonate and sodium chloride which have been widely used for dyeing of textiles with natural dyes to improve the fastness properties and dye absorption rate. Textile dyeing with natural dyes using biocompatible and biodegradable modification agents such as chitosan is the cost effective environmental friendly approach in the field of dyeing industry and emphasized that the modification of the fabric is one of the best routes to improve the affinity between dye and fabric [122].

In the recent work of Verma et al. [123], chitosan coated cotton fabric was dyed with the natural dye Marigold. They found that ChSN treated samples exhibited high percent dye absorption (50.25 %), good colour strength (10.51) and acceptable wash fastness grade (4). In another work, Mansour et al. [124] investigated the use of chitosan to improve the dyeability of cotton fabrics with Hibiscus sabdariffa L. (Roselle). The results of this study highlighted that cotton fabrics treated with ChSN have better depth of shade (K/S = 11) than those untreated fabrics (K/S = 4) dyed with Roselle. The cotton fabrics treated with chitosan not only provide better depth of shade but also give better wash and light fastness than those of the untreated fabrics dyed with Roselle.

In order to dye cotton fabric with natural dye sodium copper chlorophyllin (SCC), Zhao et al. [125] used ChSN as a double-layered fabric coating to serve as bio-mordant. They found that the maximum qe (adsorption amount) of SCC calculated from the Langmuir isothterm model was raised from 4.5 g/kg to 19.8 g/kg. The dye uptake of the treated fabric was improved from 22.7 % to 96.4 % at 1 % dye concentration. By a second chitosan layer cured on the dyed fabric via the cross-linking method the wash fastness of the cotton fabric dyed with SCC can be improved from 3 to 5.

In another research, Ke et al. [126] investigated the application of Cochineal natural dye on cotton fabrics treated with chitosan. Their experimental results showed that treating cotton with 15 g/L ChSN and baking at 130 °C offered the higher Cochineal adsorption. Dyeing kinetics curves indicated that with the increase of the dyeing temperature, dye diffusion coefficient increased and half dyeing time decreased. The washing and rubbing fastness of the treated cotton fabrics were all improved and rated above grade 3. Cochineal was also used by Safapour et al. [127] to dye wool yarns using chitosan-cyanuric chloride (ChSN-Cy). Results showed that ChSN-Cy (15 % on weight) treatment of wool had several beneficial effects which brought about remarkable improvement in dye uptake, decrease in optimum dyeing time and temperature, elimination of metal mordant from dyeing process due to bio-mordant role of ChSN-Cy, and development of antibacterial finish against pathogenic gram negative E. coli and gram positive S. aureus bacteria which was durable up to 20 washing cycles.

In an interesting previous study, Bhuiyan et al. [128] investigated the multifunctional treatment of jute fibers with chitosan and its effect on dyeing with the extract of the leaves of henna, commonly known as Lawsonia inermis L., and antibacterial characteristics of obtained jute fibers. The detailed study has demonstrated the double effects of ChSN on jute fiber. The treatment of jute with chitosan can appreciably enhance the uptake of dye by the fiber. Moreover, the color fastness property of dyed fabrics against washing and rubbing also exhibits within the acceptable range of good to excellent. On the other hand, the antimicrobial activities of jute fabric increase significantly due to the combined effect of natural dye henna and ChSN.

TEXTILE WASTEWATER TREATMENT BY CHITOSAN AND ITS DERIVATIVES

Textile wet processing operations (mainly dyeing and printing) produces high volumes of effluent wastewater often containing residual amounts of dyes. These dyes are extremely poisonous and potentially toxic together with a wide range of industrial polluting agents and they are linked to environmental contamination and fatal diseases. Raw or modified chitosan and their blends/composites have gained the focus of modern research for dyeing removal due to their excellent biosorbent properties, such as cationic and macromolecular structure with high adsorption capacity. Several dyes degradation methodologies using chitosan and its derivatives have been

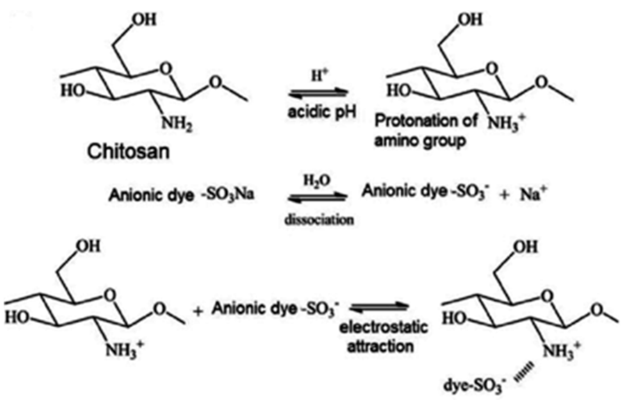

Figure 13. Adsorption mechanism of anionic dyes onto chitosan surface.

investigated including physicochemical (such as adsorption, coagulation-flocculation and separation/filtration) and biochemical (like bioremediation and bacterial degradation) processes [141]. These techniques were based on different adsorption mechanisms such as ion-exchange, complexation, coordination/ chelation, electrostatic interactions, acid-base interactions, hydrogen bonding, hydrophobic interactions, physical adsorption and precipitation [129].

The literature survey has indicated that raw chitosan was used in different physical forms in dyes removal, such as powder (particles and nanoparticles), hydrogels, beads, films and non-woven mats. Table 6 is a summary of interesting studies on dyes removal from textile effluents by different forms of chitosan and obtained maximal adsorption capacity (Qm).

As we can see on table 6, the order of dye adsorption capacity by chitosan is acid > direct > reactive > basic> disperse dyes. In fact, it is well confirmed that chitosan is very effective for the adsorption of anionic dyes, especially in an acidic environment, following the ion exchange mechanism illustrated on Figure 13. However, the low adsorption capacity achieved in the case of basic and disperse dyes is attributable to unfavourable electrostatic interactions between the positively charged chitosan and positively charged dye molecules.

Although chitosan exhibits great potential as a dye adsorbent, it suffers from several limitations, such as high crystallinity and low hydrophilicity [138]. Chemical modification of chitosan molecules by crosslinking reactions (uniting the macromolecular chains with each other) or grafting (inserting functional groups) leads to the formation of chitosan derivatives with superior properties (enhancement of adsorption capacity and resistance in extreme medium conditions, respectively) [139].

The grafting of carboxyl amine and sulfur groups to ChSN has been regarded as an interesting method for improving some of the important specifications for enhanced dye adsorption, e.g. improving mechanical strength and its stability in acidic medium and increasing porosity as well as increasing surface area

[140-142]. The grafting of various functional groups onto the hydrogel network or the chitosan backbone can also improve chitosan's removal performance and selectivity for dye molecules and also used for controlling diffusion properties. The presence of new functional groups on the surface of the materials results in an increase of surface polarity and hydrophilicity and this enhances the biosorption of polar sorbates and improves the biosorption selectivity for the target dyes. Several cross-linking agents, e.g. epichlorohydrin ECH [143], sodium tripolyphosphate TPP [144] and glutaraldehyde GLA [145] revealed better results in preparing chitosan beads. Other cross linkers were also used to modify chitosan such as ionic liquids [146]. However, the adsorption capacity of this class of biosorbents remains not broad-spectrum: the amine and hydroxyl groups of ChSN indeed act as active sites for trapping mainly anionic pollutants while the effectiveness towards cationic dyes is rather scarce due to adverse electrostatic interactions. To overcome this problem, de Luna et al. [147] recently developed new composite chitosan-based hydrogels containing hyper-cross-linked polymer (HCLP) particles. HCLP particles were prepared by a modified Davankov procedure, consisting in the radical bulk polymerization of the poly[divinylbenzene (DVB)-vinylbenzyl chloride (VBC)] precursor followed by hyper-crosslinking of the obtained product by Friedel-Crafts reaction. Then, ChSN/HCLP hydrogels were obtained by phase inversion method in order to efficiently combine the dye biosorption ability of chitosan and the capacity of the porous particles of trapping dye molecules. Batch biosorption experiments revealed a synergistic effect between chitosan and hydrogels and the samples are able to remove both anionic and cationic dyes.

Results in terms of maximum adsorption capacities Qm (in mg/g) for dyes removal obtained on different cross-linked chitosan are compiled on Table 7.

In last few years, a new generation of chitosan hybrid materials (composites and nanocomposites) have been synthesized and achieved improvement in adsorption properties. Chitosan was blended with other particles such as clay, graphene, dioxide titanium (TiO_2), halloysite, zeolites, magnetite, Zinc oxide (ZnO) and obtained composites gave excellent adsorption properties. Notably, the materials listed above are also well known adsorbents for removing wide range of hazardous compounds including dyes.

Therefore, composites of these materials with chitosan have often resulted in improved mechanical and chemical stability with large surface area which made them desirable adsorbents for large-scale dyes removal treatment.

In another work [162], Zhang et al. prepared zirconium-based chitosan microcomposite (Zr-ChSN) and employed as an efficient adsorbent for the removal of Orange II dye from aqueous solution. Equilibrium isotherms showed a good fit with the Langmuir isotherm and the maximum adsorption capacity was calculated as 926 mg/g indicating that the Zr-ChSN microcomposite exhibited excellent efficiency for the removal of Orange II dye. The mechanisms of adsorption were attributed to electrostatic attraction and exchange reaction between Zr-ChSN and dye $-SO_3$ anions.

It is observed that the adsorption properties of chitosan are drastically improved when it is made composites with metal oxides.For example, $Fe(OH)_3$-loaded chitosan beads were developed for removal of anionic Congo red and methyl orange dyes from the solution [163].

Table 5. Some applications of chitosan in anionic dyeing of textile materials.

Textiles	Dyes	Improved dyeing properties	References
Wool	Reactive : Thioxo-4-thiazolidinone	dyeuptake Fastness (light, rubbing and perspiration)	[110]
Viscose	Acid dyes : Red N-HFS and Blue N-HFS	Dye absorption Color pick up %	[111]
Cotton/Nylon 50:50 wt. %	Acid : Red 138	Shade depth, Color strength	[112]
Polypropylene	Acid : CI acid red 151	Dye absorption	[113]
Cotton	Reactive: C.I. Reactive red-31	Color strength Dye exhaustion Fastness (light, wash, rub)	[114]
Viscose	Acid Orange 7 and Methyl Red	Color strength Fastness to light, rubbing And perspiration	[115]
Silk	Reactive: Cibacron Blue FN-G	Color fixing rate Dyeing depth Fastness (wash, rub)	[116]
Jute	Reactive : Novacron Red FN2	Dyebath exhaustion Color strength	[117]
Polyamide 6	Reactives : CI Red 198 and CI Black 5	Dye uptake Fastness (wash, rub)	[118]
Polyeser/cotton 50:50 wt %	Reactive : CI Red 198	Color intensity Perspiration fastness	[119]

Table 6. Application of chitosan as adsorbent for textile dyes.

ChSN form	Dyes	Qm [mg/g]	References
Particles	Astrazon GTLN Red: Basic Telon B Red: Acid Remazol Yellow RR: Reactiv Scarlet Red 23: Direct	58.8 144.9 98 142.8	[130]
Powder	Acid Blue 9	210	[131]
Nanoparticles	Direct Blue-86 C.I. Reactive Blue 21	1097±55 302±18	[132]
Film	Tartrazine Azo Amaranth Azo	413.8 278.3	[133]
Hydrogel	C.I. Reactive Black 5 C.I. Disperse Orange 3	122 40	[134]
Powder	Indigo	6.9	[135]
Suspension	Malachite Green: Cationic Crystal Violet: Cationic Sunset Yellow: Anionic Acid Yellow 17: Anionic Direct Blue 7: Anionic	14.2 16.2 160 176 1172	[136]
Powder	Dianix orange: Disperse	50	[137]

Table 7. Adsorption capacities for dye removal with different modified chitosans.

Modified chitosan	Dyes	Qm [mg/g]	Reference
Cyclodextrin-ChSN	Methylene Blue	2780	[148]
Epichlorohydrin- ChSN	Reactive Blue 2 Reactive Yellow 86	2498 1911	[149]
Edetate- ChSN	Reactive Yellow 84 Reactive Black 5	1883.6 1296.6	[150]
Urea amonium tartrate- ChSN	Congo Red	1597	[151]
Tripolyphosphate- ChSN	Reactive Black 5	1125.7	[152]
Glutaraldehyde- ChSN	Reactive Black 5	846.9	[153]
Quaternary ChSN	Reactive Orange	1060	[154]
Polyacrylic acid- ChSN	Methylene Blue	990	[155]
Aerogel ChSN	Methylene Blue	785	[156]
Network ChSN	Methyl Violet Congo Red	411 621	[157]
Fe- ChSN	Acid Red 73	206	[158]
Hyper cross linked gydrogels - ChSN	Indigo Carmine Rhodamine 6G	118 78	[159]
N-maleyl- ChSN	Methylene Blue Crystal Violet	66.89 64.56	[160]
Acrylamide- ChSN	Astrazone Blue	47	[161]

The adsorption capacities were 445.32 and 314.45 mg/g for Congo red and methyl orange, respectively at a pH 3. Similarly, Magnetic chitosan-graphene oxide MCGO nanocomposite was prepared in the work of Jiang et al. [164] as a multi-functional nanomaterial for Methyl Orange (MO) dye removal. The effect of the experimental parameters including adsorbent mass, pH value, contact time and concentration of MO on the adsorption capacity was investigated. The maximum adsorption capacity of MCGO for Methyl Orange dye was 398.08 mg/g.

Nanocomposites of chitosan and ZnO or Zeolite offer also very interesting dye removal results. In the study of Abul et al. [165], Chitosan Zinc Oxide Nano composite was used as an adsorbent for removal of sample that contains two reactive dyes: Reactive Black HN and Reactive Magenta HB from textile dying industry effluent. They found that by using 2 gm of composite per liter of effluent at ambient temperature and 60 minutes time of contact, it may be possible to remove 99 % of the original colors of the effluent. Later on, the adsorption of Methylene Blue dye (MBD) from aqueous solutions was investigated by Dehghani et al. [166] using a new composite made up of shrimp waste chitosan and zeolite as adsorbent. They found that the Freundlich isotherm model exhibited better fitting (R2 =0.999) with experimental equilibrium data than the Langmuir one (R2 =0.956). According to Freundlich isotherm model, maximum adsorption capacity of the composite was 24.5 mg/g.

Integration of chitosan with clay material led to the development of more efficient dyes adsorbent system. Ngwabebhoh et al. [167] investigated the adsorption of nitrazine yellow dye by chitosan/montmorillonite (ChSN-MMT) composite as biosorbent. Box–Behnken methodology was applied to optimize the adsorption experiments. Maximum adsorption values were determined as 144.41 mg/g at pH 5. Recently, Kafil et al. [168] synthetised chitosan/carbon nanoflowers as a novel nanocomposite for Acid Black1 (AB1) and Congo red CR azo dyes removal. Maximum adsorption capacities of AB1 and CR were found to be 259.13 and 553.12 mg/g, respectively (according to Langmuir model under initial dye concentration of 400 mg/L at pH = 6.75).

CONCLUSION AND PERSPECTIVES

Textile is one of the most usable consumer products in our daily life although industrial processes are mostly hazardous. Along textile production chain the used finishing agents and chemicals are often toxic and non-biodegradable. According to investigated research works, the use of chitosan natural polymer could offer an opportunity to develop sustainability and eco-friendly textile finishing processes. Interestingly, ChSN and its derivatives offer a myriad of opportunities as an antimicrobial, anti-pollution and antiviral agent in textile products and processes.

Nevertheless, the main problem that arises is that the majority of manufactured chitosan has different physical properties including color, viscosity, and density. In addition, purity of the product differs from one manufacturer to another and produced chitosan is marketed under various grades including industrial, medical, pharmaceutical and food.

The global market for chitin and ChSN reached a volume of $ 4.2 billion by 2021 [169], with a compound annual growth rate of 15.4 %, intensifying the need for a search of other sources to satisfy the growing market. In fact, the raw materials for bulk production of chitosan are usually from marine sources because of the abundance of the raw materials in the form of shellfish waste from the seafood industry. The production cost for the traditional crustaceans based chitosan is cheap (10 US dollar per kg to 1000 US dollar per kg) compared with fungal based ChSN [170]. In addition, marine sources may have seasonal variations in availability, and the heavily mineralized exoskeletons make for an arduous extraction process. Therefore, deep research investigations together within industrial efforts on ChSN alternative sources, such as insect biomass, mushroom and fungal bodies and microbial biomass, and their production processes may tackle such limitations.

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TRAVELLER CLEARER GAUGE CONSEQUENCE ON YARN QUALITY

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ABSTRACT

Traveller clearer is an important part of the ring frame machine because, without it, fiber flying in the traveller cannot be cleaned. As a result, fiber congests travellers which may lead to a rise in end breakage rate as well as declination of quality of yarn. Six ring spun yarns of count 85's tex were produced by using different traveller clearer settings and Burkina Faso cotton fiber was used as a raw material. Both High Volume Instrument (HVI) along with Advanced Fiber Information System (AFIS) was used for recognizing the fiber properties. The ring-spun yarn was produced from the roving count of 985 tex and spindle speed was kept at 7000 R.P.M. with Twist Per Meter (TPM) 492. Evenness properties, as well as strength of yarns, were measured with Uster Tester-6 and Titan Single Yarn Strength Tester respectively, and end breakage rate was studied. One-way ANOVA test was accomplished for all properties of yarn by using Microsoft Excel 2019. Traveller clearer gauge with 3.10 mm shows the best result among the other samples. Yarn properties such as imperfection index, hairiness, Sh (-), tenacity, and processing performance like end breakage rate express the best values. ANOVA result shows a significant difference for all properties except elongation.

KEYWORDS

Traveller clearer; Hairiness; End breakage rate; Ring frame; ANOVA.

INTRODUCTION

The ring spinning system is the most popular spinning system among all though it is a traditional spinning system. The reason behind its popularity of this is that it is not complex and easy to operate, can produce material with suitable characteristics, and any material along with any count can be smoothly spun on it. One limitation of this spinning system is that the production rate is low due to the addition of travellers with rings and yarn [1]. Both twisting and winding mechanisms in a ring spinning system cannot be imagined without the combined work of ring and traveller. Although it is a very tiny part it plays the most significant role in this spinning [2]. The speed of the traveller can be increased but there are possibilities to melt the traveller itself due to the heat generation of the contact point between ring and traveller, damage to the ring, and increased end breakage rate of the spinning system [1]. Traveller generates heat up to 300°C due to running at a surface speed of 110–170 km/hour [3]. Several benefits such as upgrading hairiness, decreasing end breakage rate, and wear as well as bringing afterward financial profits can be possible by using a nickel-coated ring and traveller surface [4].

It was invented by Messrs in the USA in 1829 to guide the yarn onto the package [5]. The main task of a traveller is to insert twist, maintain spinning tension along with wind the yarn onto the bobbin. Higher traveller speed can be achieved by decreasing the balloon. During spinning, multiple breakages can be occurred due to the too lightweight of the traveller. Traveller clearer and traveller settings have an impact on traveller fly, if the setting is closer it generates a hit to the traveller and finally, this creates fly [6].

Traveller clearer is used to clean the fly from the outer side of the traveller. If the traveller is not cleaned properly that may lead to promote the end breakage rate, along with yarn quality deterioration [7]. One of the performances measuring factors of ring spinning and twisting devices are actuated by the act of ring and traveller. To remain the flange traveller, fly free it is essential to fine-tune the traveller cleaner accurately. Ring and traveller do not correct the quality of the sliver produced from the drawing process, but the appropriate selection of them affects yarn properties, especially yarn hairiness. The

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Received August 2, 2022; accepted October 12, 2022

surface condition and eccentricity of the ring also creates problem in yarn. Academically the speed of the traveller fluctuates significantly even eccentricity of the ring at 0.3mm which leads to the traveller humming as a resulting rise in hairiness in yarn. Traveller cleaner is used in a short-staple spinning mill to keep the traveller away from gathering fibers. Loose settings of cleaner to a traveller may lead to end breakage as well as deterioration yarn quality due to the congestion of fibers in travellers creating a jam [8].

Tension forces developed from the thread balloon on the yarn are subjected to the traveller. Practically tension on yarn on the ring frame is not measured rather than it is assumed from the balloon shape. Traveller has an impact on the balancing of balloon shape during the processing of yarn [9]. The eccentricity of several parts of the ring frame creates yarn tension variation that leads to hairiness on yarn [10]. Traveller weight has a significant effect on the hairiness properties of the yarn. Hairiness affects the fabric properties and creates a problem, especially in the case of warp yarn which may break during processing along with reducing the efficiency of the process. One of the reasons for fabric pilling is yarn hairiness which affects the appearance of the fabric [11].

MATERIALS AND METHODS

Materials

Burkina Faso cotton fiber-Burkina Faso, Africa's top cotton producer- was used as a raw material to produce 85 tex card woven yarn. The cotton fiber properties were tested under standard atmospheric conditions (20±2° C and 65% RH) on a High-Volume Instrument (HVI) and Advanced Fibre Information System (AFIS). The average properties of those tests are given in Table 1.

Table 1. Fibre properties.

HVI		AFIS	
Properties	**Values**	**Properties**	**Values**
SCI	126	NEP [Cnt/g]	340
Moisture [%]	6	NEP Size [um]	699
Mic Value	4.52	SCN [Cnt/g]	21
Maturity Ratio	0.88	SCN [um]	1195
UHML [mm]	29.64	SFC [%]	10.2
UI [%]	81.25	UQL [mm]	30.6
SF [%]	10.10	5% [mm]	35.30
Strength [GPT]	31.2	Fineness [mtex]	180
Elongation [%]	4.6	IFC [%]	8.6

Methods

Initially, cotton fibre was passed through blow room line and carding machine both of which were from the Trutzschlar brand for opening and cleaning purposes. The delivery speed of the carding machine was 263 m/min to produce slivers of 6.03ktex. Next, eight card slivers were fed to the breaker drawing machine, and a drawn sliver of 6.03ktex was produced at a delivery rate of 650 m/min. Then, eight ends of the breaker drawn sliver were fed to the finisher drawing machine to get a 6.03ktex sliver at a delivery rate of 650 m/min. After that, roving of 985 tex was produced at a flyer speed of 1100 rpm, and a twist level of 43 per meter. Finally, ring staple yarn of count 85's tex was manufactured with a spindle speed of 7000rpm with a twist level of 492 /meter, along with 6 gauge settings including 2.5 mm, 2.8 mm, 2.9 mm, 3.0 mm, 3.1 mm, and 3.2 mm.

Quality parameters such as mass irregularity, yarn faults in terms of imperfection index, and yarn hairiness were measured using a Uster Tester-6 with a test number 8. The single strength and elongation of yarn were measured using a Titan Single Yarn Strength Tester with 10 samples under standard atmospheric conditions (20±2°C and 65% RH). The confidence interval attached to each figure was calculated by using the following formula as the low number of repeated measurements was used.

$$\bar{x} \pm t\frac{s}{\sqrt{n}}, \qquad (1)$$

where, $\bar{x}$ = arithmetic mean, t = statistical factor, s = standard deviation, and n = number of observations, t value for 8 and 10 samples is 2.365 as well as 2.262 respectively.

RESULTS AND DISCUSSION

Results

The results of measurements of yarn irregularity, imperfection index, hairiness, and tensile behavior of 85's tex carded ring spun woven yarn using the experimental design are given in Table 2.

Table 2. Yarn properties.

Traveller Gauge [mm]	2.50	2.80	2.90	3.00	3.10	3.20
CVm [%]	12.71	11.72	11.94	11.62	11.77	11.52
Imperfection Index [-]	42	28	23	18	16	31
Hairiness [-]	9.23	8.97	9.42	9.13	8.81	10.7
Sh [-]	1.86	1.84	1.99	1.97	1.8	2.01
Tenacity [cN/tex]	15.22	16.08	14.95	15.82	16.11	15.28
Elongation [%]	8.12	8.21	8.26	8.25	7.81	8.03
End Breakage Rate/100 Spindle-Hr.	32	40	20	37	17	21

Discussion

Yarn Unevenness

Yarn unevenness is normally expressed in two terms named unevenness percentage of mass and coefficient of variation of mass. The coefficient of variation of mass is more universe that unevenness percentage of mass. It is seen from figure 1 that gauge 3.2 mm performs well whereas the 2.5 mm gauge shows the opposite result. The result of gauge 3.2 mm is the best due to the sufficient gap for a traveller to clean up. Also observed in figure 1 is that there is no statistically significant difference among all samples except 2.5 mm.

Imperfection Index

Imperfection is a frequently occurring fault in yarn and without imperfection, it is completely unimaginable to produce yarn. It is the summation of three faults thin place (-50%)/km, thick place (+50%)/km, and neps (+200%)/km. From figure 2, it is observed that gauges 2.5mm and 3.1mm show the highest and the lowest value and they are 42 and 16, respectively. Setting 3.2 mm details 31, followed by 2.8 mm at 28, after that 2.9 mm with 23, and lastly 3.00 mm at 18. 3.1mm gauge represents the best result while 2.5mm is the reverse. It is assumed that the probable reason behind this is that in 3.1 mm gauge better fiber is incorporated into the yarn. A statistically significant difference is shown between 2.5 mm and 3.0 mm and 2.5 mm and 3.1 mm settings in Figure 2.

Hairiness

Hairiness is an important yarn parameter that depends on not only the fiber properties but also the process parameters, along with machine parts. It is such a parameter that relates to the comfortability of end products, especially for apparel. According to figure 3, the highest hairiness value of 10.7 is seen in the case of the 3.2 mm setting and the lowest one is 8.81 for the 3.1 mm gauge. 3.1 mm gauge shows the good quality of yarn because it is assumed that this gauge is optimum for traveller cleaning. Figure 4 shows that the 3.1 mm scale denotes the best result, however, 3.2 mm demonstrates the worst result. No significant difference is seen in Figure 3 except 3.2 mm gauge and Figure 4.

Tensile Strength

The tensile strength of the yarn is important for further processing. It has a great impact on the processing performance of fabric either in weaning or knitting. It is observed from figure 5 that 3.1 mm represents the highest value at 16.11 cN/tex while 2.9 mm displays the lowest value at 14.95 cN/tex. This is because it is presumed that in the 3.1 mm gauge setting, fibres are orientated straighter and more parallel. There is a statistically significant difference between 2.9 mm and 3.1 mm.

Elongation

Elongation is significant yarn property that is necessary for further end products. As can be seen from Figure 6, the bottommost figure belongs to 3.1 mm settings but the highest digit goes to 2.9 mm. The assumption behind this may be that in 2.9 mm gauge settings fibers are not incorporated in parallel into the yarn body properly. No significant difference is seen in Figure 6.

End Breakage Rate

End breakage in the ring frame creates faults in yarn as well as produces a huge amount of wastage. One of the factors that affect productivity in spinning is the end breakage rate. It also affects the speed and performance of the ring frame [7]. Figure 7 represents the highest rate in the 2.8 mm measure and the lowest rate in the 3.1 mm gauge. It is assumed that at a lower gauge setting there is a possibility to create tension on the yarn which may cause breakage while at a 3.1 mm setting, assumed optimum settings where tension on yarn is less cause a low breakage rate. There is a statistically significant difference observed in Figure 7 among all samples.

Statistical Analysis

One-way ANOVA test was completed for almost all yarn properties by using Microsoft Excel 2019. The tests were carried out at alpha level 0.05. P-values of all tests are given below.

Table 3. P-value of ANOVA test of yarn properties.

Yarn Properties Name	***P-value***
CV_m [%]	0.00*
Imperfection Index [-]	0.00*
Hairiness [-]	0.00*
Tenacity [cN/tex]	0.01*
Elongation [%]	0.55
End Breakage Rate/100 Spindle-Hr.	0.01*

Statistically, a significant difference is noticed in the case of all properties excluding elongation from the above table as the P-value is less than 0.05.

Post-Hoc Analysis

The alpha level used for comparison was 0.003 (Bonferroni correction) and the pairwise comparison number was 15. The results are given in Table 4.. There is a statistically significant difference among five pairs (Marked in star) in the event that co-efficient of variation, six pairs (Marked in star) in case of hairiness along with imperfection index, and one pair (Marked in star) in end breakage rate as well as tenacity because their value is less than Bonferroni correction factor.

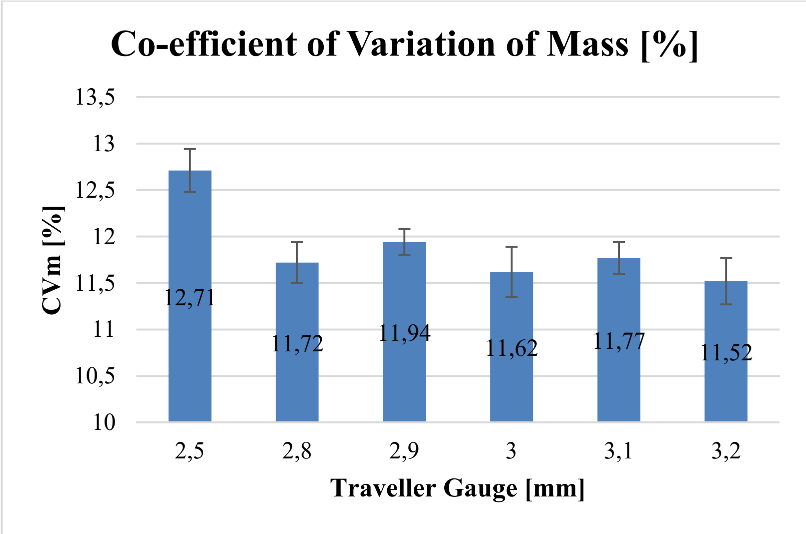

Figure 1. CV_m percentage of yarn.

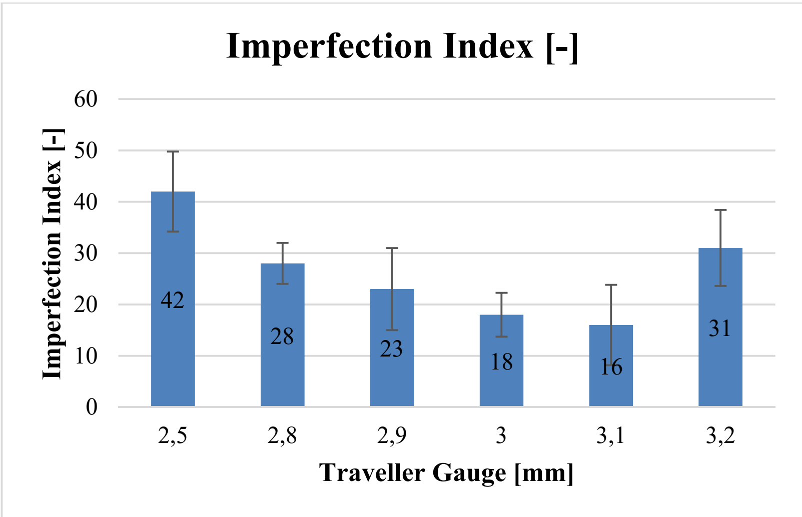

Figure 2. Imperfection of yarn.

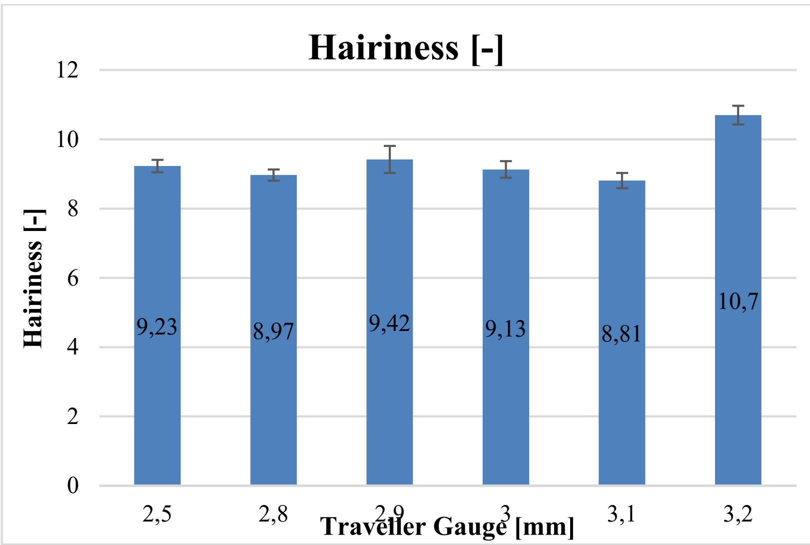

Figure 3. Hairiness of yarn.

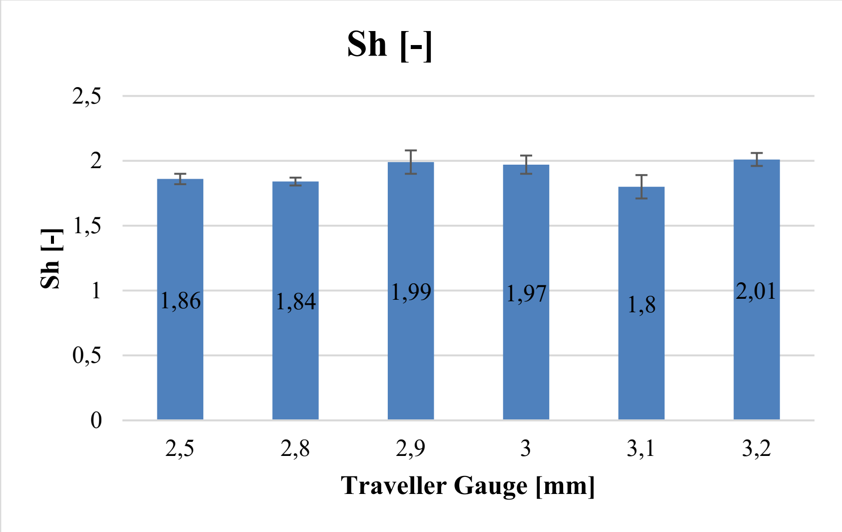

Figure 4. The standard deviation of hairiness of yarn with a cut length of 1 cm.

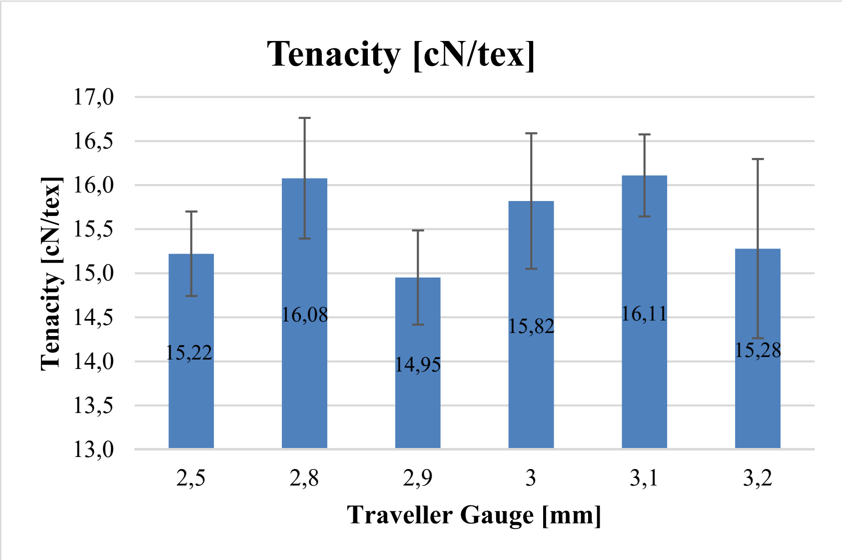

Figure 5. Tenacity of yarn.

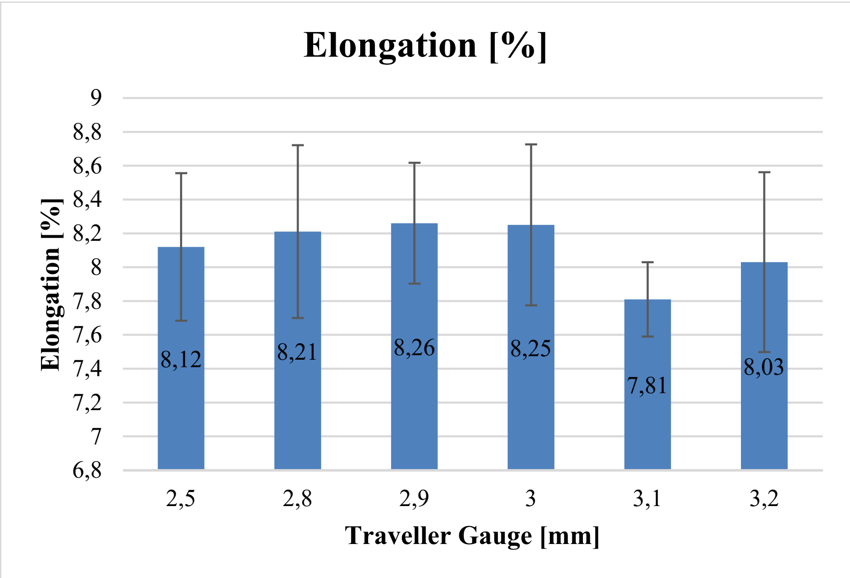

Figure 6. Elongation of yarn.

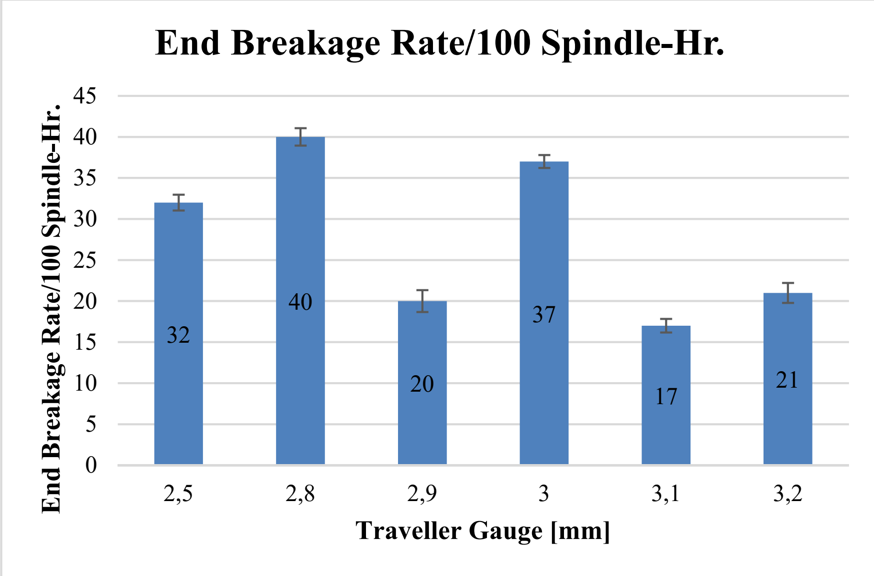

Figure 7. End breakage rate at ring frame.

Table 4. *t*-test: Two-Sample Assuming Equal Variances.

Yarn Properties	Paired Groups Names (mm)	Values of P(T<=t) two-tail	Yarn Property/Processing Parameter	Paired Groups Names (mm)	Values of P(T<=t) two-tail	Yarn Property	Paired Groups Names (mm)	Values of P(T<=t) two-tail
	2.5 & 2.8	0.000*		2.5 & 2.8	0.029		2.5 & 2.8	0.032
	2.5 & 2.9	0.000*		2.5 & 2.9	0.326		2.5 & 2.9	0.406
	2.5 & 3.0	0.000*		2.5 & 3.0	0.434		2.5 & 3.0	0.153
	2.5 & 3.1	0.000*		2.5 & 3.1	0.002*		2.5 & 3.1	0.048
	2.5 & 3.2	0.000*		2.5 & 3.2	0.000*		2.5 & 3.2	0.910
	2.8 & 2.9	0.138		2.8 & 2.9	0.023		2.8 & 2.9	0.009
	2.8 & 3.0	0.597		2.8 & 3.0	0.216		2.8 & 3.0	0.575
CVm [%]	2.8 & 3.1	0.529	**Hairiness [-]**	2.8 & 3.1	0.135	**Tenacity [cN/tex]**	2.8 & 3.1	0.001*
	2.8 & 3.2	0.282		2.8 & 3.2	0.000*		2.8 & 3.2	0.157
	2.9 & 3.0	0.073		2.9 & 3.0	0.149		2.9 & 3.0	0.051
	2.9 & 3.1	0.400		2.9 & 3.1	0.004		2.9 & 3.1	0.247
	2.9 & 3.2	0.018		2.9 & 3.2	0.000*		2.9 & 3.2	0.528
	3.0 & 3.1	0.307		3.0 & 3.1	0.025		3.0 & 3.1	0.007
	3.0 & 3.2	0.626		3.0 & 3.2	0.000*		3.0 & 3.2	0.351
	3.1 & 3.2	0.122		3.1 & 3.2	0.000*		3.1 & 3.2	0.170
	2.5 & 2.8	0.002*		2.5 & 2.8	0.342			
	2.5 & 2.9	0.001*		2.5 & 2.9	0.137			
	2.5 & 3.0	0.000*		2.5 & 3.0	0.550			
	2.5 & 3.1	0.000*		2.5 & 3.1	0.074			
	2.5 & 3.2	0.025		2.5 & 3.2	0.248			
	2.8 & 2.9	0.196		2.8 & 2.9	0.004			
	2.8 & 3.0	0.002*		2.8 & 3.0	0.660			
Imperfection Index [-]	2.8 & 3.1	0.001*	**End Breakage Rate**	2.8 & 3.1	0.002*			
	2.8 & 3.2	0.473		2.8 & 3.2	0.027			
	2.9 & 3.0	0.273		2.9 & 3.0	0.012			
	2.9 & 3.1	0.093		2.9 & 3.1	0.609			
	2.9 & 3.2	0.115		2.9 & 3.2	0.895			
	3.0 & 3.1	0.228		3.0 & 3.1	0.005			
	3.0 & 3.2	0.005		3.0 & 3.2	0.058			
	3.1 & 3.2	0.003		3.1 & 3.2	0.608			

CONCLUSIONS

Overall, it can be said that 2.9 mm, 3.0 mm, and 3.1 mm settings perform similar results and there is no statistically significant difference found from the confidence interval attached in each figure except end breakage rate along with tenacity between 2.9 mm and 3.1 mm, and Post-Hoc Analysis test. There is a statistically significant difference found from Post-Hoc Analysis between pair 2.8 mm and 3.1mm just in case of imperfection index, end breakage rate, and tenacity. Although 2.9 mm, 3.0 mm, and 3.1 mm gauges can be used, settings 3.1 mm is much preferred due to the imperfection index, hairiness, Sh(-), tenacity, and end breakage rate representing good results. Other properties such as evenness, and elongation are also considerable. It may be assumed that the possible reason behind this result of this sample is fibers get optimum space for cleaning of traveller which contributes to a cleaner yarn body, as well as tension on the yarn, is also proper. On the other hand, the remaining samples such as 2.5 mm as well as 3.2 mm demonstrate comparatively worst results in the case of all properties. This happened due to the much closer or wider settings of travellers clearer. The amount of breakage is observed higher in below 3.1 mm settings due to the closed position of the clearer near the traveller triggering a huge amount of tension on the yarn which may lead to more breakage.

It can be seen from the ANOVA analysis that, there is a significant difference for all samples without elongation. However, t-Test: Two-Sample Assuming Equal Variances confirms that statistically significant differences exist in five pairs, six pairs, and one pair in the case of CVm%, imperfection index as well as hairiness, and tenacity along with end breakage rate accordingly. Finally, it can be thought that a 3.1 mm gauge is suitable for better processing of fibres.

Acknowledgement: *The authors thank are due to the Bangladesh University of Textiles for providing facilities for work.*

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EFFECT OF DIFFERENT CRIMP METHOD OF JUTE FIBRE ON STRENGTH AND ELONGATION PROPERTIES OF JUTE YARN AND WOVEN FABRIC

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ABSTRACT

Yarn and fabric strength is one of the most important parameters to predict the uses of the end product. Fabric strength mostly depends on yarn strength and yarn strength is prejudiced by fibre strength or fibre properties. Crimp is one of the essential parameter that influences the fibre properties. In this research, crimp box and gear crimp methods were used to introduce crimp into jute fibre. It was found that crimps were irregular in size, shape and number produced from crimp box method. On the other hand, crimps produced from gear crimp method were comparatively regular in size, shape and number. Yarn and fabric strength tests were carried out according to testing standard. It was revealed that yarn strength and elongation at break of gear crimp method were higher than that of crimp box method. Apart from this, fabric strength and elongation were also improved for a regular and increased number of crimps for gear crimp method.

KEYWORDS

Fibre crimp; Mechanical crimp; Crimp box method (CBM); Gear crimp method (GCM); Woven fabric; Tensile strength and elongation.

INTRODUCTION

Jute fibres are environmentally friendly, non-biodegradable, cheap and available natural fibres. They exhibit better physical, mechanical and thermal properties compared to other natural jute allied fibres like hemp, kenaf and banana fibres and the end product made of jute fibres also exhibit higher performance for the mentioned properties[1]. Jute fibre is a natural fibre having no crimp. Crimp is the waviness of a fibre. Crimp is defined as the condition in which the axis of a fibre proceeds from a straight line and tracks a simple or a complex or an irregular wavy path in the same phase [2]. Crimp plays an important role to increase the cohesion between fibres and also helps to spin them. So, mechanical crimp has to be imparted into jute sliver to make it suitable for spinning. This crimp influences yarn properties as well as fabric properties. It was found that jute yarn properties like yarn hairiness, irregularities were improved and yarn strength was increased due to the increased number of imparted crimp into jute sliver during drawing in the draw frame machine [3].The main mechanical properties of a woven fabric are its strength and elasticity. The breaking force and elongation at break are the most common characteristics of the mentioned fabric properties. These breaking force of yarns and woven fabrics are interrelated and increased when the elongation at break increases[4]. The tensile strength of fabric also deals with the required force to break a large amount of yarns simultaneously in either warp or weft direction. The force at which the yarn breaks is directly proportional to cross-section or diameter of the yarn. The tensile force verified at the moment of rupture is termed as the tensile strength at break [5]. The breaking strength and elongation are the two prime quality aspects of any spun yarn. The tensile strength and elongation of a yarn are essential to the process ability of the yarn in the subsequent processing and operational life of the end product made of the yarn. The strength of any staple yarn is determined by different fibre properties, yarn structural geometry, spinning process and parameters. It is revealed that yarn strength increases with the increase of crimp in the fibre, as fibre to fibre interconnectionimproves the fibre bonding [3, 6]. It was also revealed that warp and weft yarn parameters influence the fabric'sbreaking force. Various properties of yarn such as raw material, lineardensity, and structure influence the character of the stress–strain curves and the breaking force of fabric in the warpand weft directions [7, 8].The breaking force and elongation at break of fabric were

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Received April 25, 2022; accepted October 18, 2022

depended on the breaking force and elongation of yarn [9]. Crimp and as well as fabric structure also help to extend the yarn and fabric more [10]. It was also obtained that the fibre properties, the type and parameters of spinning affect the yarn properties such as strength, while the fabric properties are affected by warp and weft density, count of the warp and weft yarn of the woven fabrics and weave structure. The mechanical properties of fabrics are also influenced by the weaving conditions such as weaving speed, warp insertion rate, weft beat-up force, the way of shed opening, warp preparation for weaving, warp and weft tension, number of threads in reed dent etc. The properties of raw fabrics consequently also depend on the construction and technological parameters of spinning and weaving [11]. Azeem et al. [12] evaluated the effect of spinning technologies and weave on the fabric's mechanical and surface properties. Ring spun (combed, carded) and open-end techniques were used to manufacture yarns. Plain, twill, and satin weaves were used for the fabrics. Once the fabric stiffness increases, elongation at break also increases. A significant effect of the spinning technique and weave on these properties was established. Kumpikaitė and Sviderskytė [13] attained the dependencies of breaking force and elongation at break for different weave factors. They showed that there is no correlation between breaking force and elongation at break of fabric, but elongation at break depends on the weave factors of fabric, i.e., if the fabric stiffness increases, elongation at break will also increases. Dependencies of breaking force and elongation at break on the weft setting were recognized as well. The results show that with the increases of weft setting, the breaking force slowly decreases and the elongation at break increases. Another paper [14] described that twist multiplier and woven structure are largely responsible for the strength of woven fabrics in greige and as well as finished fabrics. They worked on blended raw materials and different weave structure and showed its effect on fabric strength and elongation. It is also explored that the influence of different compositions of different cotton fiber blends on the tensile properties of yarns from these blended yarns. It was recognized that the composition of the cotton blend influences the properties of yarn [15].

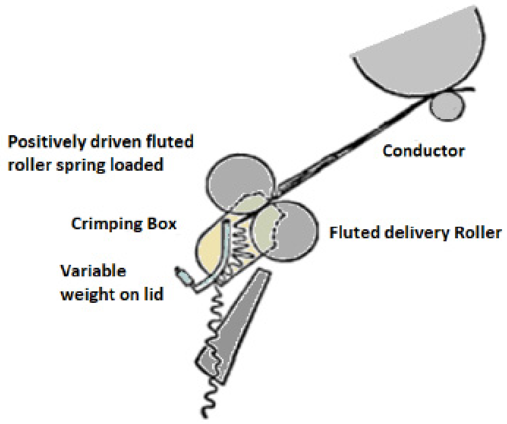
Therefore, after the literature analysis, it was concluded that the breaking force and the elongation at break were previously analyzed for yarns and woven fabrics of different raw materials, yarn densities, and blended materials with different material ratios; but the effect of regular crimp on the properties of yarn and fabrics were not analyzed. Therefore, the aim of this research was to find the effect of fibre crimp on the breaking force and elongation of yarns and woven fabrics.

MECHANISM OF CRIMP METHODS

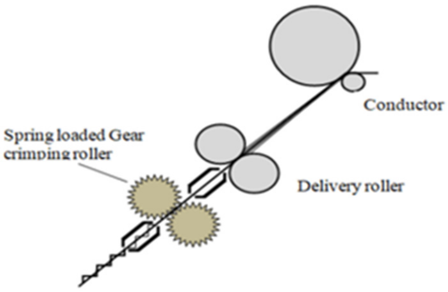
The crimp box method (CBM) is regularly used to introduce mechanical crimp into jute fibre during the drawing process. In this research work, the newly developed gear crimp method (GCM) for jute fibres is also used to impart mechanical crimp into jute sliver.

In the CBM, in Figure 1(a), the sliver leaves the nip of the drafting rollers and passes the sliver plate into the nip of a pair of fluted delivery rollers, the upper roller of the pair is spring-loaded and positively driven. A lid is needed in the crimping box to impart crimp into the sliver. Some weight is applied to the lid and it generates a pressure or load on the sliver in the crimp box. As a result, fibre is compressed or compacted under pressure and irregular crimp is produced into jute sliver. The length of time on any particular place of sliver remains in the crimp box can be controlled by means of different weights which can be added to the lid. Due to the use of different weight on the lid, the crimp produced into sliver also gets changed. A heavyweight causes a greater mass of sliver in the box for lifting it up and develops more crimp in the jute sliver [16]. This crimp causes inter-fibre cohesion which is very important for jute processing and also for subsequent processing. In CBM, produced crimps are irregular in size and shape. Therefore, the number of crimps per inch also becomes irregular. On the other hand, for GCM, in Figure 1(b), two crimping rollers are responsible to impart crimp into sliver. In this machine, there are two feed rollers, two guide rollers, two retaining rollers, one jockey roller, two pinned rollers, one drawing roller, one pressing roller, two fluted delivery rollers and two crimping rollers. Four pairs of crimp gears with different number of teeth were also developed to impart crimp into sliver. The slivers enter into the machine by passing over two feed rollers and two guide rollers. Then they pass between the retaining rollers and a self-weighted jockey roller and then meet the pins of the pinning rollers. After that the sliver passes between two fluted delivery roller, they work as guide roller as well as anti-friction roller to reduce the slippage of sliver. Afterward passing the nip of the drafting rollers, it passes over the sliver plate into the nip of a pair of fluted delivery roller, after that, it passes between the nips of the gear crimp rollers, and then crimp is formed in the sliver which is regular in size and shape. The lower crimp roller is positively driven and the upper crimp roller is spring-loaded. The pair of crimp rollers should be changed to change the number of crimps in per unit length [17].

The advantages of GCM are: regular crimp in size and shape and equal length of the fibre in unit length. But the limitation of this method is: maximum five numbers of crimps per inch (5 crimps / inch) can be imparted into sliver.



(a)



(b)

Figure 1. (a) CBM [16] and 1(b) GCM [17].

MATERIALS AND METHODS

Materials used: Bangla White B grade jute fibre was used to produce jute yarns. It is also known as Tossa jute. Reed length of jute fibre was 360 cm and technical length of jute fibre was measured after breaking card operation and it was 27.94 cm. In this research work, CBM and GCM were used for imposing mechanical crimp into jute sliver. Yarns were produced by using the slivers having regular and irregular crimps. Jute woven fabrics were produced by the yarns with $\frac{1}{1}$ plain weave structure in CCI loom. Sample details are given in the Table1, 2 and 3. Figure 2 shows the weave plan and drafting plan of the sample fabrics.

Apron draft spinning frame was used for spinning. The spinning machine was worked with flyer leading principle. Process parameters are in Table 2.

Methods used: Yarn strength and elongation, fabric strength and elongation were measured to accomplish this research work. Test methods and equipment are given below in Table 4.

X		X		X
	X		X	
X		X		X
	X		X	
X		X		X

(a)

			X	
	X			
		X		
X				X

(b)

Figure 2. (a) Weave plan and (b) drafting plan for plain weave.

EXPERIMENTATION

Experimentation of yarn strength test

Yarn strength was measured by using the Universal Tensile Strength Tester machine, James Heal. ASTM D 2256-10, single strand method was used to measure the yarn strength. The tests were carried out with a Machine speed of 300 mm/min, break detection 20%, jaw scheme 5, and jaw separation 250 mm. A sample of 250 mm yarn was gripped between the two jaws. The upper jaw was fixed and the lower jaw was movable. This machine is worked on the constant rate of extension (CRE) principle. The lower jaw moved at constant a rate and the yarn was extended and an increasing tension was developed until the yarn broke down. The load at which yarn breaks down and the elongation percentages were taken from the machine. Time taken for a test was 20 sec. Five samples were tested to measure the yarn strength.

Factors affecting the yarn strength and elongation:

The factors that affect the prediction of yarn strength include fibre properties such as fibre length, length uniformity, strength and elongation, yarn properties such as count and twist. Yarn factors that affect the yarn breaking elongation are the spindle speed, traveler mass, machine draft, yarn count and twist [18].

Table 1. Properties of raw jute fibre.

Statistics		Reed length of jute fibre [cm]	Technical Length of jute fibre [cm]	Fibre Fineness [micron]	Breaking load [kg]	Tenacity [gm/tex]
Mean		360	30.2	51.64	4.52	45.306
Standard Deviation		3.36	1.92	3.28	1.15	12.27
Confidence Interval	Upper Limit	363.35	31.89	53.67	5.53	56.06
	Lower Limit	357.45	28.51	49.60	3.51	34.55

Table 2. Main parameters of spinning frame.

Parameters	Spinning frame
Spindle speed	3200 rpm
Draft	11.30
Drafting system	Apron draft
Yarn per twist (TPI)	5

Table 3. Sample details for different crimping method.

Crimping method	No. of crimps per unit length [inch or 2.54 cm]	Yarn count [tex]	Fabric thickness [mm]	Structure of fabric	Thread density [EPI x PPI]
Crimp box	2.5	210	1.454	$\frac{1}{1}$ Plain weave	16 x 12
	3.5	214	1.606		
	5.0	298	1.616		
Gear crimping	3.0	218	1.622		
	4.0	258	1.634		
	5.0	311	1.688		

Table 4. Test methods for yarn and fabric tensile strength.

Name of the test	Machine used	Test method
Yarn strength and elongation	Universal Strength Tester	ASTM D 2256-10
Fabric strength and elongation	Universal Strength Tester	EN ISO 13934-1:2013

Experimentation of fabric strength test

Jute woven fabrics were tested to measure the fabric strength by using the standard test method EN ISO 13934-1:2013, part-1, determination of maximum force and elongation at maximum force using the strip method. The tests were carried out with a Machine speed of 100 mm/min, break detection 10%, jaw scheme T27, and jaw separation 200 mm. A sample of 50.8 mm width and 200 mm was gripped between the two jaws. The upper jaw was fixed and the lower jaw was movable. This machine is worked on the CRE principle. The lower jaw moved at a constant rate and the yarn was extended and an increasing tension was developed until the sample broke down. The load at which the sample breaks down and the elongation percentages were taken from the machine. Five samples were tested to measure the fabric strength.

Factors affecting the fabric strength and extension:

Factors that are important for fabric strength and elongation are type of fibres or blend use, twist amount and twist direction of yarn, yarn count, yarn setting, weave design and float length [19, 20].

RESULTS AND DISSCUSION

The main parameters of tensile tests for yarns and fabrics are the breaking force and elongation at break or extension %. Maximum force, yarn tenacity or strength and the extension% of yarns are given below in table 5 and fabric strength and extension % is given in table 6 and 7. Standard deviation and confidence intervals for 95% are also shown in the table with upper and lower limits.

Yarn strength

Strength is a very important property of yarns. Yarn strength is the force required to break a strand of a single yarn. It is expressed in N. The strength of yarn gives an idea that how much load can be applied to it and it is very important for different processes of yarns such as weaving and knitting. It is established that the tensile strength of a fabric depends not only on the strength of the component yarn, but also on the yarn structure, yarn bending performance, fabric geometry, tensile properties such as tensile force and tensile elongation of used yarns [21]. The breaking tenacity of yarns was also calculated. From Figure 3, it is found that yarn strength is increasing with the increasing number of crimps per inch. As crimp increases, the yarn becomes bulk, more regular and more quantity of fibres accumulates in the unit length of yarn, as a result, the strength increases. Strength increases in every stage of increasing crimp. It is also found that yarn strength is higher for GCM compared to CBM.

Table 5. Different parameters of yarn for various crimp method.

Crimp method	No. of crimps per unit length (2.54 cm)	Max. Force [N]	Yarn Strength				Yarn Elongation			
			Tenacity [cN/tex]	Standard Deviation	Confidence Intervals		Elongation [%]	Standard Deviation	Confidence Intervals	
					Upper Limit	Lower Limit			Upper Limit	Lower Limit
Crimp box method	2.5	23.07	111.42	26.50	134.67	88.21	1.25	0.28	1.57	1.07
	3.5	24.63	117.20	26.63	140.47	93.78	1.49	0.30	2.38	1.85
	5.0	40.39	130.80	17.02	145.75	115.92	1.94	0.26	3.26	2..80
Gear crimp method	3.0	25.86	120.46	2.96	123.60	117.87	1.44	0.32	2.41	1.84
	4.0	32.71	128.74	3.21	131.56	125.93	1.51	0.38	3.51	2.83
	5.0	45.75	149.56	3.11	152.29	146.84	2.06	0.23	4.02	3.62

Table 6. Fabric strength for various crimp methods.

Crimp method	No. of crimps per unit length	Fabric Strength Max. Force [N]		Standard Deviation		Confidence Intervals		Confidence Intervals	
						Upper Limit	Lower Limit	Upper Limit	Lower Limit
		Warp	Weft	Warp	Weft	Warp		Weft	
Crimp box method	2.5	865.79	593.71	9.17	2.43	889.02	842.56	616.94	570.48
	3.5	1038.93	740.77	35.43	21.74	1062.16	1015.69	763.99	717.53
	5.0	1232.24	914.38	6.29	8.43	1255.47	1209.01	939.41	892.95
Gear crimp method	3.0	1112.31	814.42	7.41	9.89	1135.54	1089.08	837.65	791.19
	4.0	1278.01	988.04	7.06	9.20	1301.24	1254.78	1011.27	964.81
	5.0	1342.88	1151.29	8.59	8.06	1366.11	1319.64	1174.52	1128.06

Table 7. Fabric elongation for various crimp methods.

Crimp method	No. of crimps per unit length	Fabric Elongation [%]		Standard Deviation		Confidence Intervals		Confidence Intervals	
						Upper Limit	Upper Limit	Upper Limit	Lower Limit
		Warp	Weft	Warp	Weft	Warp		Weft	
Crimp box method	2.5	1.72	2.85	0.105	0.176	1.824	1.639	2.994	2.685
	3.5	3.01	4.38	0.133	0.324	3.151	2.917	4.602	4.033
	5.0	6.54	7.21	0.259	0.259	6.705	6.250	7.783	7.328
Gear crimp method	3.0	3.93	4.97	0.605	0.436	4.450	3.389	5.372	4.607
	4.0	5.35	6.09	0.527	0.488	5.882	4.957	6.873	6.018
	5.0	7.33	8.59	0.259	0.259	7.281	6.826	8.669	8.214

Yarn extension

Elongation at break is the amount of stretch of a yarn that can take before it breaks and the breaking extension is the extension of the yarn at the breaking point expressed as a percentage. It is found in Figure 4 and 5 that yarn extension is slightly more for the yarn produced from gear crimp method. It is also clear that yarn extension% is increased due to the increased number of crimps of yarns. This is due to the strength of the yarn, as strength is more, it takes more load and more time to break. As a result, extension is more.

Fabric strength

Tensile strength and extension % are important parameters of the woven fabric that determines the durability of the textile material. Fabric strength in warp way is mostly influenced by weave structure and yarn density [22]. It is established from Figure 6 and 7 that fabric strength in both warp and weft way is higher for more number of crimps and it is also clear that GCM shows better strength than that of CBM. This is due to regular crimp formation and the length of fibre in the unit length is equal to the GCM.

Fabric elongation

Fabric strength and extension % are the most important characteristics of woven fabrics. Fabric extension at break depends on yarn evenness, strength and also on fabric strength. It is seen from the Figure 8 (a), (b), 9 and 10 that extension% of fabrics in both warp and weft way produced from GCM is more than that of CBM, because the yarns are more regular and even due to regular crimp and fabric strength for is also higher for GCM. It is also found that a higher number of crimp also affect the strength of yarn and as well as fabric strength and extension at break [23].

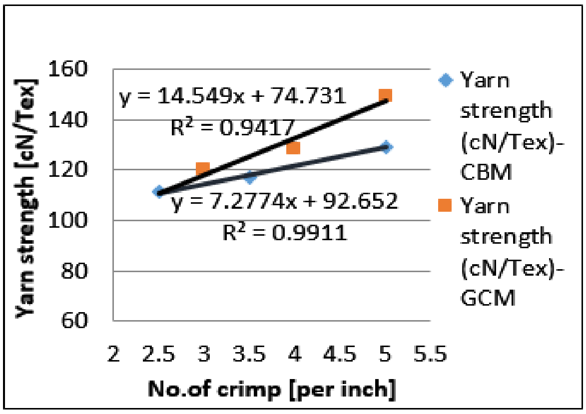


Figure 3. Yarn strength vs number of crimps for CBM and GCM.

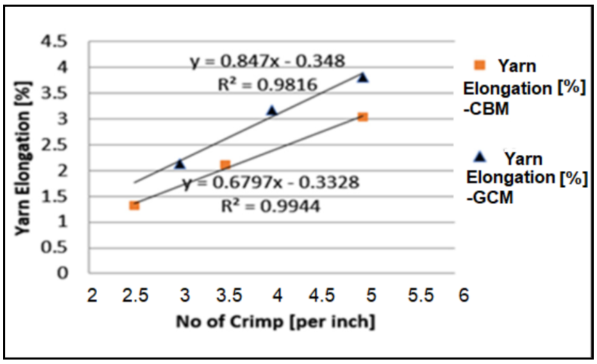


Figure 4. Yarn elongation % vs number of crimps for CBM and GCM.

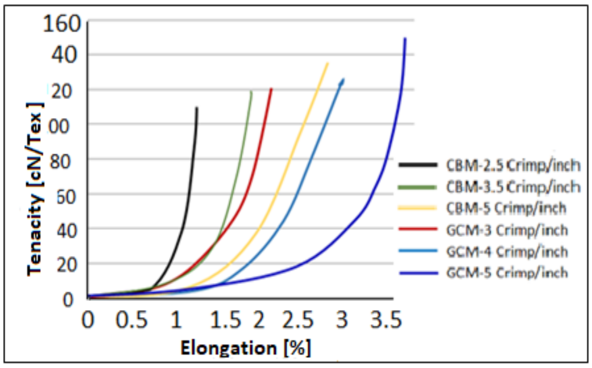


Figure 5. Tenacity – Elongation curve for CBM and GCM.

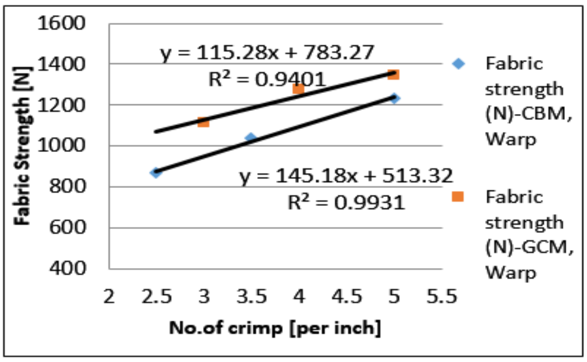


Figure 6. Warp way Fabric Strength vs Number of crimp of different crimp method.

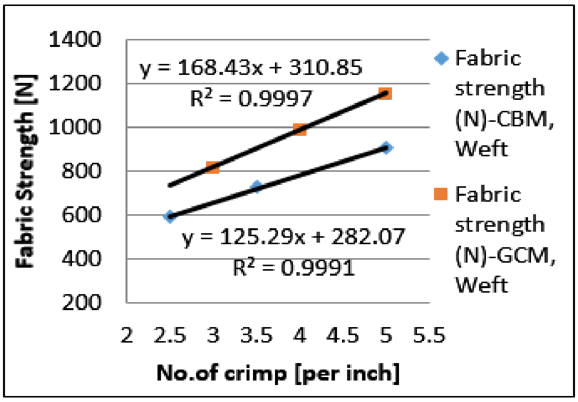
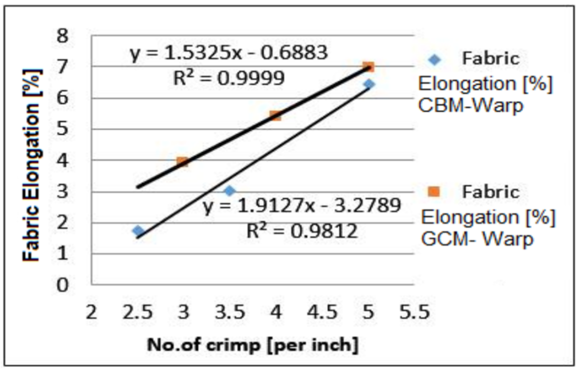
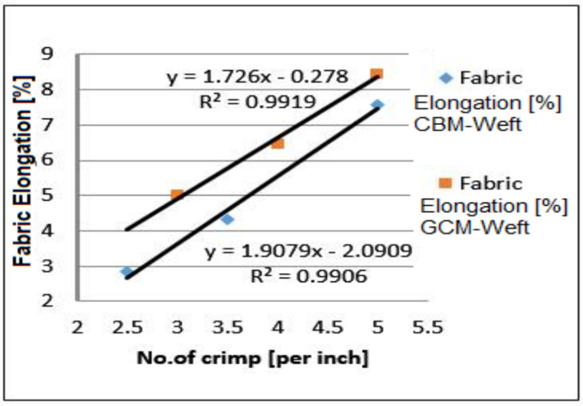


Figure 7. Weft way Fabric Strength vs Number of Crimp of different crimp method.



(a)



(b)

Figure 8. Fabric Elongation vs Number of crimps for CBM and GCM at (a) warp and (b) weft direction.

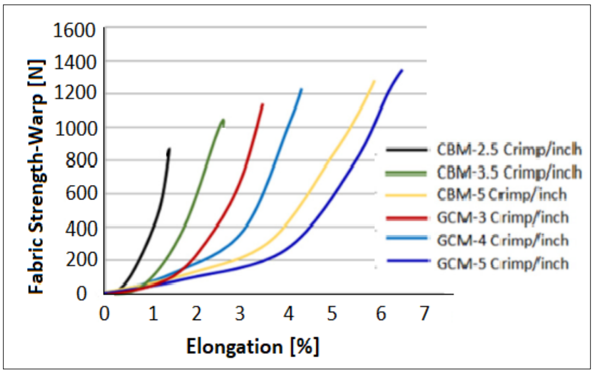


Figure 9. Fabric strength (warp) – elongation curve for CBM and GCM.

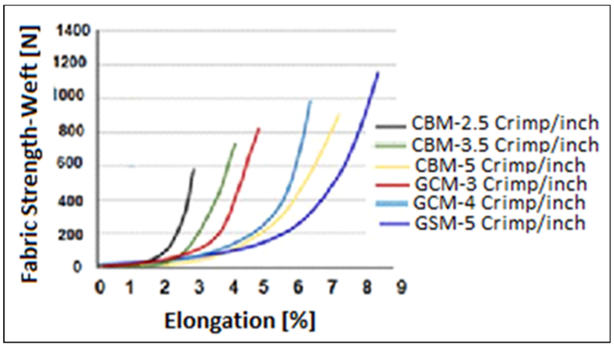


Figure 10. Fabric strength (weft) – elongation curve for CBM and GCM.

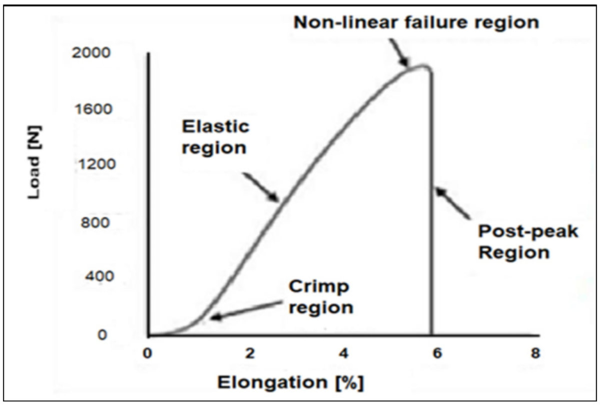


Figure 11. Load-elongation curve.

When a woven fabric is tested and exposed for tensile testing, then it goes over the four regions in a load-elongation curve, which has been enlightened here in Figure 11. The viscoelastic nature of the materials can be observed here as a low slope in the starting phase which is the first region also called the crimp region. It is also observed in first region that the crimp is decreased in one set of yarn during tensioning while it increases in another set of yarn and it is known as the crimp interchange. Therefore, a large increase in elongation at a low load level in the crimp region can also be observed in the load-elongation curve. In the second region of the curve, it rises steeply and when more force is applied to the fabric, more extension is occurred, as the extensions in fibers as well as in the yarns also start. The slope of curve in comparison to previous region increases as the straightened yarns bear more load and it is termed as elastic region. The third region of the load elongation curve is non-linear part and it can be seen before tensile strength is reached. It is due to the random breakage of fibres present in the yarns which are also prior to their localized failure. The last stage is the post-peak region, a rapid decrease in the load beyond the tensile strength can be observed that relates to the increasing yarn failure [15].

CONCLUSION

From the research study and results, it can be seen how different methods and number of crimps or crimp variations of fibres influence the mechanical properties of yarns and fabrics. Yarn strength is higher for GCM. The maximum breaking force in warp and weft direction is exhibited in the fabrics with the highest tensile elongation for higher number of crimps and also for GCM. As it is revealed in the study that the tensile properties of yarn and fabric are higher for the newly developed GCM. So the yarns produced from the GCM can be used to make ropes or braids for load-bearing applications and ship anchoring. Again the fabrics with higher strength can be used as technical textiles as mobil tech for boat hull, geo-textiles where mechanical properties are required and agro textiles for load-bearing application. So, this method can be a new era for producing jute yarns and woven fabrics along with greater tensile properties.

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EVALUATION OF THE COMPATIBILITY OF POLYORGANYLSILOXANES AND HIGH-MOLECULAR POLYMERS USED AS EMULSIFIERS IN FINISHING WORKS

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ABSTRACT

The compatibility of polyorganylsiloxanes and high-molecular polymers used as emulsifiers was evaluated. The surface and bulk properties of the studied compounds were evaluated using the solubility parameters (δ). It is shown that the copolymers of acrylic acid compound – polyacrylamide and hydrolyzed polyacrylamide, as well as polyvinyl alcohol without residual acetate groups in the macromolecule have the highest degree of incompatibility with polyorganylsiloxanes. It was established that the presence of residual acetate groups in the macromolecule of polyvinyl alcohol leads to an increase in the degree of compatibility of polymers. The calculated data on the fractions of solubility parameters and cohesive energy of polyorganylsiloxanes and emulsifying polymers are presented. The contributions of the components of polymers cohesive energy due to the fractions of dispersion interaction α_d, dipole-dipole interaction α_{dd}, and hydrogen bonding α_h, as well as their influence on the degree of solubility of the polymer – emulsifier system, are shown. The choice of polyvinyl alcohol with residual acetate groups as an emulsifier for polyorganylsiloxanes is theoretically substantiated based on the concept of the solubility parameter as a measure of the affinity of the system components. The developed approach to assessing the compatibility of the polymer – emulsifier system is of practical importance for the creation of polymer compositions in the finishing works.

KEYWORDS

Polyorganylsiloxanes; High-molecular polymers; Emulsions; Compatibility Solubility parameters.

INTRODUCTION

Polyorganylsiloxanes (organosilicon polymers) are widely used in the finishing of textile materials. Due to their unique properties, these compounds are used in the creation of hydrophobic, superhydrophobic and flame retardant textile materials, increase the biocidal properties of fabrics, and change their surface energy. Due to the use of polyorganylsiloxanes, anti-adhesion properties are obtained, which contributes to self-cleaning of fabrics. Polyorganylsiloxanes are often used as crosslinking agents in the implementation of finishing technologies based on the use of polymers, as well as to impart softness, drape, silkiness to textile materials, depending on their purpose.

The choice of polymer components for the preparation of finishing compositions, the method of mixing them, the degree of compatibility (mutual solubility) is dictated by a set of properties that the composition should have, the structure, the properties of components themselves, the real capabilities of technological equipment for finishing work.

Most organosilicon compounds are insoluble in water, as a result of which they are either pre-dissolved in organic solvents or used in the form of emulsions. The use of organic solvents from the point of view of environmental safety is difficult, since they are not only toxic, but also flammable compounds. Organosilicon emulsions based on surfactants or macromolecular compounds (usually water-soluble polymers) are not always stable over time.

The use of such water-soluble polymers as polyvinyl alcohol and polyacrylamide for the formation of emulsions does not cause any particular environmental hazard due to their low toxicity. The use of these compounds as emulsifiers for the preparation of polyorganylsiloxane emulsions is also justified by the fact that the polymers used are film-forming substances that increase the strength (fixation) of composite film on the surface of textile material during the finishing processes.

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Received July 7, 2022; accepted October 10, 2022

The unbound emulsifier migrates as a result of leaching from the polymer film, which leads to a decrease in transparency, an increase in crispness, and a deterioration in the adhesion of the film to the substrate. In the applied coating, this process leads to a deterioration in water resistance and aesthetic defects, the so-called "snail trails". The issues of assessing the compatibility of polymers are relevant for the purposeful selection of components that provide the system with operational compatibility. When creating polymer compositions, as well as for mixtures of polymers and little used polymers, for which there are no data on the degree of solubility, the calculation method for estimating the mutual solubility of polymers is effective.

In the world, there are several theoretical methods for calculating the solubility parameters δ, as well as experimental methods for assessing the compatibility of polymers or a polymer with a solvent [1-3], namely Hansen, Hildebrand-Sketchard, Van Crevelen, Hoftizer-Van Crevelen, Hoy, Small, Panayot, Flory-Huggins, as well as computer programs HSPiP и HSPStudio [4].

The solubility parameter δ is originally based on cohesive energy and is used to evaluate the ability of polymers to dissolve in a solvent, and it is also a measure of the ability of any two kinds of components to mix. In practice, two main theories of polymer solutions are most often used: Hildebrand-Sketchard and Hansen in the form of the concepts of a three-dimensional solubility parameter and Flory-Huggins. The Flory-Huggins theory is mainly used in the study of polymer systems to evaluate the thermodynamic affinity of a polymer and a solvent using the Flory-Huggins constant. The presence of several theories indicates that all of them are not without flaws and have a number of limitations.

The article [5] provides an assessment of the compatibility of hydrophobic polydimethylsiloxane with hydrolyzed polyvinyl acetate (with 0%, 86% and 100% degree of hydrolysis) for mixtures in various ratios, their surface and bulk properties are determined, based on the calculation of the Flory-Huggins interaction parameter (χ) the compatibility of mixtures and phase transitions are evaluated using atomistic molecular dynamics.

In the study [6] the physical affinity between the epoxy matrix and the carbon fibers was evaluated using Hansen Solubility Parameters (HSP), high physical compatibility of the polymers was found because their respective HSPs are close.

In [7], the authors announced the development of a new approach using the solubility parameters (δ) calculated by the group contribution method as an indicator of the extraction of additives from plastic.

Considering the process from a thermodynamic point of view, it can be noted that there is practically no information in the literature on the use of solubility parameters for evaluating the interaction of polyorganylsiloxanes and high molecular weight emulsifiers. Almost all publications refer to the description of emulsions as colloidal systems created from immiscible liquids and do not take into account the degree of affinity between them.

In this regard, the issues of assessing compatibility are relevant for the targeted selection of the most effective emulsifier that provides a stable structure and operational properties of the emulsion.

The goal of the study is to theoretically substantiate the choice of the most effective high-molecular emulsifier for creating polyorganylsiloxane emulsions, based on the assessment of the thermodynamic parameters of polymers and the calculation of the thermodynamic compatibility criterion as a measure of the affinity of the components.

MATERIALS AND METHODS

The following polyorganylsiloxanes were studied in the work: polyethylhydrosiloxane with degree of polymerization n=8, n=15, n=20 (PEHS), polymethylhydrosiloxane (PMHS), polydimethylsiloxane (PDMS).

The high-molecular surfactants were studied as emulsifiers for organosilicon polymers: polyvinyl alcohol (PVA), polyvinyl alcohol with residual acetate groups ($PVA_{ac.gr.}$), polyacrylamide (PAM) and hydrolyzed polyacrylamide (HPAM).

Emulsifiers, including high-molecular ones, which include the above, being adsorbed on the surface of droplets, reduce the surface tension at the “droplet – dispersion medium” interface due to the adsorption-solvation factor and give the system stability.

The compatibility of polymers, their surface and bulk properties were calculated from the solubility parameters (δ). The determination of the solubility parameter δ of polymers was carried out using the increment method, which consists in choosing repeating units of the polymer and finding the increments of the cohesive energy $\Delta E_0 = \Sigma\Delta E_i$, and the increments of Van der Waals volumes $\Delta V = \Sigma\Delta V_i$ of individual atoms and groups. The volume of each atom depends on its environment, i.e. on the type of atoms that are chemically bonded to it. The values ΔE_i and ΔV_i known for many groups of atoms, atomic groupings, and intermolecular interactions were used in the calculation. To calculate the solubility parameters, we used the data by increments given in [8, 9] and extended to polar substances as well. In Table 1 presents not only the cohesive energy $\Sigma\Delta E_i^*$ as an additive sum, but also the molar volumes $\Sigma\Delta V_i$ calculated for each atom and various atomic groups.

The values of the solubility parameter δ for the polymers under study were determined by calculation using an equation (1) that allowing to calculate the cohesive energy and its fractions:

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} = \frac{\sum_i (\Delta E_i^*)_d + \sum_i (\Delta E_i^*)_{dd} + \sum_i (\Delta E_i^*)_h}{N_A \sum_i \Delta V_i}, \quad (1)$$

where δ is the Hildebrand solubility parameter for the polymer; $\Sigma\Delta E_i^*$ is the contribution of each atom and type of intermolecular interaction to the cohesive energy, reduced as many times as the Van der Waals volume of the molecule is less than the molar volume, and is an additive value; $\Sigma\Delta V_i$ is the occupied (Van der Waals) volume of molecules, which consists of the Van der Waals volumes of individual atoms; N_A is Avogadro's number.

The fractions of cohesive energy due to dispersion interaction αd, dipole-dipole interaction α_{dd} and hydrogen bonding α_h were calculated from relations (2)–(4), respectively:

$$\alpha_d = \frac{\sum_i (\Delta E_i^*)_d}{\sum_i \Delta E_i^*}; \quad (2)$$

$$\alpha_{dd} = \frac{\sum_i (\Delta E_i^*)_{dd}}{\sum_i \Delta E_i^*}; \quad (3)$$

$$\alpha_h = \frac{\sum_i (\Delta E_i^*)_h}{\sum_i \Delta E_i^*}. \quad (4)$$

In this case, the sum of the fractions of the cohesive energy is equal to 1 (5):

$$\alpha_d + \alpha_{dd} + \alpha_h = 1. \quad (5)$$

RESULTS AND DISCUSSION

Since emulsions are heterogeneous systems, they are thermodynamically unstable. The lack of thermodynamic compatibility of polymers leads to the formation of a two-phase structure; their mixtures are dispersions of particles of one polymer in another. However, the thermodynamic incompatibility of polymers is not an obstacle, and vice versa, in some cases, it is thanks to the incompatibility of polymers that it is possible to obtain a unique structure. The solubility parameters, sometimes referred to as the cohesion energy parameters, are responsible for the value of the cohesive energy. As mentioned above, the solubility parameters are three initial molecular forces that control the dissolving activity of polymers: dispersion force αd, polarity αh and hydrogen bonding, dipole-dipole interaction energy αdd. – i.e. forces that hold the molecule together and therefore control the interaction between polymers.

The values of the Van der Waals volumes of the studied polymers calculated from the volume increments ΔVi of all atoms in the repeating polymer unit, as well as the value of the cohesive energy and its fractions, the solubility parameter and surface tension of the polymers are presented in Table 1.

To improve the compatibility of polymer blends, the value of the dipole-dipole interaction and hydrogen bonds should be sufficient to cover the contribution of dispersion interactions.

Let us consider the change in the structural and thermodynamic parameters of polyorganylsiloxanes and polymers used as emulsifiers: polyacrylamide and hydrolyzed polyacrylamide. With a practically insignificant change in the proportions of dipole-dipole, dispersion interactions, and hydrogen bonds, the cohesive energy doubled from 54000 kJ/mol to 101000 kJ/mol for hydrolyzed polyacrylamide. The values of the structural parameters of hydrolyzed polyacrylamide changed, namely, the Van der Waals volume increased significantly from 0.0643 nm^3 to 0.1240 nm^3.

A somewhat different situation develops with the values of the structural and thermodynamic parameters of polyvinyl alcohol and polyvinyl alcohol with residual acetate groups. With regard to the structural parameters of polymers, it can be noted that the presence of residual acetate groups in the molecular chain of polyvinyl alcohol, compared with polyvinyl alcohol without acetate groups, is accompanied by an increase in the Van der Waals volume by more than 2 times: from 0.0415 nm^3 to 0.1210 nm^3.

With regard to thermodynamic parameters, the cohesive energy of polyvinyl alcohol compared to polyvinyl alcohol with the presence of acetate groups increases by almost 100%. The change in the cohesive energy is due to a change in the values of the fractions of its components: dipole-dipole, dispersion interaction and hydrogen bonds. As can be seen, in polyvinyl alcohol without residual acetate groups, the greatest contribution to the cohesive energy is made by hydrogen bonds. In the presence of residual acetate groups in the macromolecule of polyvinyl alcohol, a significant influence is made by the dispersion component, the high value of which 0.431 compared to 0.267 characterizes the weakening of the bond between electrons and the nucleus, i.e. promotes better solubility. The fraction of hydrogen bonds decreases from 0.733 to 0.403.

Table 1. Structural and thermodynamic parameters of polymers.

Polymer	Solubility parameter, δ [J/cm^3]$^{1/2}$	Surface tension [mN/m]	Van der Waals volume, $\Sigma_i \Delta V_i$ [nm^3]	Cohesive energy, ΔE^* [kJ/mol]	Fractions of the cohesive energy		
					α_d	α_h	α_{dd}
Emulsifier polymers							
PVA	30.0	46.6	0.0415	33000	0.267	0.733	0.000
$PVA_{ac.gr.}$	23.7	38.4	0.1210	60000	0.431	0.403	0.166
PAM	30.8	50.7	0.0643	54000	0.368	0.447	0.185
HPAM	30.3	63.6	0.1240	101000	0.326	0.477	0.197
Polyorganylsiloxanes							
$PEHS_{(n=8)}$	14.2	19.4	0.620	137000	1.000	0.0000	0.000
$PEHS_{(n=15)}$	15.0	26.3	1.140	262000	0.893	0.1070	0.000
$PEHS_{(n=20)}$	14.8	28.2	1.510	339000	0.917	0.0826	0.000
PMHS	13.7	16.7	0.501	103000	1.000	0.0000	0.000
PDMS	14.6	20.2	0.612	142000	1.000	0.0000	0.000

Table 2. The values of the components of the solubility parameter of polyorganylsiloxanes and emulsifiers and the degree of their compatibility.

Pairs of polymers under study	β value	Indicators				
		Φ value	Constant 2ρ	α value	Interfacial tension γ [dyn/cm^2]	Solubility condition $\mu=2\rho\beta$
PAM + $PEHS_{(n=8)}$	0.07	0.85	1.374	0.88	16.99	4.70>0.09
PAM + $PEHS_{(n=15)}$	0.14	0.78	1.374	0.75	19.79	4.22>0.19
PAM + $PEHS_{(n=20)}$	0.12	0.75	1.374	0.79	22.28	4.33>0.16
PAM + PMHS	0.00	0.87	1.374	1.00	16.78	5.05>0.003
PAM + PDMS	0.09	0.85	1.374	0.82	16.61	4.45>0.13
HPAM + $PEHS_{(n=8)}$	0.02	0.91	1.374	0.97	18.84	4.55>0.02
HPAM + $PEHS_{(n=15)}$	0.14	0.86	1.374	0.75	19.60	4.08>0.19
HPAM + $PEHS_{(n=20)}$	0.13	0.83	1.374	0.77	21.65	4.19>0.18
HPAM + PMHS	-0.08	0.93	1.374	1.17	19.57	4.89>-0.11
HPAM + PDMS	0.05	0.91	1.374	0.90	18.24	4.31>0.07
PVA + $PEHS_{(n=8)}$	0.03	0.80	1.374	0.93	18.11	4.46>0.05
PVA + $PEHS_{(n=15)}$	0.09	0.73	1.374	0.83	21.85	4.00>0.13
PVA + $PEHS_{(n=20)}$	0.07	0.69	1.374	0.87	24.54	4.11>0.10
PVA + PMHS	-0.02	0.82	1.374	1.05	17.46	4.79>0.03
PVA + PDMS	0.06	0.80	1.374	0.88	17.84	4.22>0.08
$PVA_{ac.gr.}$ + $PEHS_{(n=8)}$	0.38	0.91	1.374	0.42	8.08	2.79>0.52
$PVA_{ac.gr.}$ + $PEHS_{(n=15)}$	0.43	0.86	1.374	0.39	10.26	2.50>0.59
$PVA_{ac.gr.}$ + $PEHS_{(n=20)}$	0.40	0.83	1.374	0.44	12.30	2.56>0.55
$PVA_{ac.gr.}$ + PMHS	0.32	0.93	1.374	0.48	8.03	2.99>0.44
$PVA_{ac.gr.}$ + PDMS	0.41	0.91	1.374	0.39	7.80	2.64>0.56

A contribution to the cohesive energy of the dipole-dipole interaction appears, the value of which is 0.166, which is absent in polyvinyl alcohol without acetate groups.

The change in the ratio of the contributions of the components to the cohesive energy of the studied polymers affects the change in the value of the solubility parameter of polyvinyl alcohol with residual acetate groups and is 23.7 (J/cm^3)$^{1/2}$ in comparison with the value of the solubility parameter of polyvinyl alcohol 30 (J/cm^3)$^{1/2}$. The surface tension of polyvinyl alcohol also significantly decreased from 46.6 mN/m to 38.4 mN/m for polyvinyl alcohol with residual acetate groups in the macromolecule.

Thus, we can conclude that the main bonds that determine the cohesive strength of polyvinyl alcohol are hydrogen bonds. In the macromolecule of polyvinyl alcohol with residual acetate groups, the number of hydroxyl groups is less, and therefore the probability of formation of intermolecular hydrogen bonds is also reduced. The presence of acetate groups in the macromolecule contributes to the appearance of weaker hydrophobic interactions that arise between the nonpolar parts of the molecules, which also contribute to the formation of the interfacial layer.

As for the thermodynamic parameters of polyorganylsiloxanes, the greatest contribution to the cohesive energy is made by the dispersion component, which is equal to unity for PEHS with degree of polymerization *n*=8, PMHS and PDMS. Thus, of the three initial molecular forces that control the dissolving activity of polymers in a macromolecule, only the dispersion component is present. With an increase in the degree of polymerization of PEHS to *n*=15 and *n*=20, i.e. as a result of elongation of the polymer macromolecular chain, the dispersion component weakens, and the value of the hydrogen interaction component begins to affect the cohesive energy. Of the structural parameters, an increase in the Van der Waals volume by more than 2 times for PEHS with degree of polymerization of *n*=15 and *n*=20 can be noted as a result of the growth of the macromolecular chain of polymers.

Changes in the structural and thermodynamic parameters greatly affect the formation and stability of the emulsion. Using these data, the values of the solubility parameters for each polymer were calculated. To assess the degree of compatibility, an improved solubility criterion μ was used, which takes into account the dependence of solubility on the degree of polymerization and the nature of polymer supramolecular structure.

The solubility condition was determined as follows (6) [10]:

$$\mu \leq 2\rho\Phi\left(\frac{\gamma_p}{\gamma_s}\right)^{\frac{1}{2}}, \quad (6)$$

where $\mu = \frac{\delta_p^2}{\delta_s^2}$; δ_p, δ_s – Hildebrand parameters for polymer and solvent, respectively; ρ – constant equal to 0.686; γ_p, γ_s – surface tension of the polymer and solvent, respectively. The value of Φ is calculated as follows (7):

$$\Phi = \frac{4(V_s V_p)^{\frac{1}{3}}}{\left(V_s^{\frac{1}{3}} + V_p^{\frac{1}{3}}\right)^2}, \quad (7)$$

where V_s, V_p – the molar volumes of the solvent and polymer, respectively (per unit).

The calculation of the compatibility of the studied polymers and emulsifiers was carried out according to the following relations (8) – (10):

$$\mu < 2\rho\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right), \quad (8)$$

where

$$a_1 = \frac{\gamma_{p_1 p_2}}{\gamma_{p_2}}; a_2 = \frac{\gamma_{p_1 p_2}}{\gamma_{p_1}} \quad (9)$$

The interfacial tension was calculated from the relation (10):

$$\gamma_{p_1 p_2} = \gamma_{p_1} + \gamma_{p_2} - 2\Phi(\gamma_{p_1} \cdot \gamma_{p_2})^{\frac{1}{2}}, \quad (10)$$

where γ_{p1}, γ_{p2} – surface energies of polymers 1 and 2, respectively.

According to the criterion μ, solubility will be observed if the calculated values $2\rho\Phi(\Phi - \sqrt{\Phi^2 - 1 + a})$ are greater than or equal to the value of $\mu = \frac{\delta_{p_1}^2}{\delta_{p_2}^2}$. By introducing the notation (11), the solubility criterion μ can be estimated from relation (12):

$$\beta = \Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right). \quad (11)$$

$$\mu < 2\rho\beta. \quad (12)$$

The Table 2 shows the results of the evaluation of the compatibility parameters of emulsifier polymers and polyorganylsiloxanes based on a theoretical calculation of the solubility parameters δ.

According to the data on the solubility of compounds obtained by the calculation method (Table 2), it can be seen that in all cases the left side of the criterion μ is much larger than its right side, i.e. there is an incompatibility of the studied emulsifiers and polyorganylsiloxanes. According to the calculation results, it can be concluded that the copolymers of acrylic acid compound, polyacrylamide and hydrolyzed polyacrylamide, have the highest degree of incompatibility with polyorganylsiloxanes. Polyvinyl alcohol without residual acetate groups in the macromolecule is also characterized by a high degree of incompatibility.

The presence of residual acetate groups in the macromolecule of polyvinyl alcohol significantly affects the decrease in the value of the hydrogen interaction component from 0.733 to 0.403, at the same time, the effect of dispersion interaction increases from 0.267 to 0.431, as a result of which the degree of compatibility of polymers increases almost 2 times.

Considering that emulsions are based on mixtures of incompatible polymers, the improvement in the compatibility of polyorganylsiloxanes and polyvinyl alcohol with residual acetate groups in the macromolecule is accompanied by an increase in the mutual diffusion of their macromolecules at the interface between the contacting phases. As a consequence, a layer of segmental solubility is formed. The formation of an interfacial layer of segmental solubility is an equilibrium phenomenon, due not to kinetic, but to thermodynamic laws [11]. The interfacial layer will be the wider, the more compatible the polymers.

CONCLUSIONS

Based on the concept of the solubility parameter as a measure of the affinity of the system components, the choice of polyvinyl alcohol with residual acetate groups as a high-molecular emulsifier capable of forming a layer of segmental solubility with polyorganylsiloxanes on the phase interface is theoretically substantiated, which ensures the stability of the emulsion due to the structural-mechanical factor.

The developed approach to assessing the thermodynamic compatibility of the polymer – emulsifier system is of practical importance for predicting the stability of an emulsion over time and its operational compatibility in the process of creating finishing compositions.

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AIMS AND SCOPES

“Vlakna a Textil” is a peer-reviewed scientific journal serving the fields of fibers, textile structures and fiber-based products including research, production, processing, and applications.

The birth of this journal is connected with three institutions, Research Institute for Man-Made Fibers, Svit (VÚCHV), Research Institute of Chemistry of Textiles (VÚTCH) in Žilina and Department of Fibers and Textiles at the Faculty of Chemical Technology, Slovak Technical University in Bratislava, having a joint intention to provide, utilize and deposit results obtained through the research, development and production activities dealing with the aforementioned scopes. „Vlákna a Textil“ journal has been launched as a consequence of a joing of existing magazines „Chemické vládkna“ (VÚCHV) and „Textil a chémia“ (VÚTCH). Their tradition should provide a good framework for the new journal with the main aim to create a closer link between the basic element of the product - fibre and its fabric - textile.

Since its founding in 1994, the journal introduces new concepts, innovative technologies and better understanding of textile materials (physics and chemistry of fiber forming polymers), processes (technological, chemical and finishing), garment technology and its evaluation (analysis, testing and quality control) including non-traditional applications, such as technical textiles, composites, smart textiles or garment, and nano applications among others. The journal publishes original research papers and reviews. Original papers should present a significant advance in the understanding or application of materials and/or textile structures made of them.

VLÁKNA A TEXTIL
Volume 29, Issue 3, November 2022

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