

OVERVIEW ON FUNCTIONAL SOCKS AS EXAMPLES FOR TEXTILE PRODUCTS MADE IN EUROPE – WITH SPECIAL VIEW ON ANTI-INSECT FUNCTIONAL TEXTILE PRODUCTS

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Abstract: Socks are textile products quite often offered with additional functional properties. Such functional socks are often produced in Europe and still offered to affordable prices. The current paper gives an overview on several textile functionalization. It is especially dedicated to functional socks with anti-insect properties, there four commercially available products are taken as examples and discussed in detail. A discussion is made on the relation of dedicated application with the functional properties to fiber composition and functional agents. This overview paper supports for the reader a view on the range of typically used fiber materials, special fibers and functional agents.

Keywords: sock, function, functional textile, anti-insect, anti-microbial, IR spectroscopy.

PREGLED FUNKCIONALNIH ČARAPA KAO PRIMERA TEKSTILNIH PROIZVODA PROIZVEDENIH U EVROPI – SA POSEBNIM OSVRTOM NA FUNKCIONALNE TEKSTILNE PROIZVODE PROTIV INSEKATA

Apstrakt: Čarape su tekstilni proizvodi koji se često nude sa dodatnim funkcionalnim svojstvima. Takve funkcionalne čarape se često proizvode u Evropi i dalje se nude po pristupačnim cenama. Ovaj rad daje pregled nekoliko funkcionalizacija tekstila. Posebno je posvećen funkcionalnim čarapama sa svojstvima protiv insekata, gde su četiri komercijalno dostupna proizvoda uzeta kao primeri i detaljno razmotrena. Diskusija se odnosi na namenske primene sa funkcionalnim svojstvima prema sastavu vlakana i funkcionalnim sredstvima. Ovaj pregledni rad pruža čitaocu pogled na niz tipično korišćenih materijala od vlakana, specijalnih vlakana i funkcionalnih sredstava.

Ključne reči: čarapa, funkcija, funkcionalni tekstil, antiinsekticidno, antimikrobno, IC spektroskopija.

1. INTRODUCTION

Textiles are versatile and fascinating products used for manifold purposes. For consideration of special challenging applications many textile products are equipped with special functional properties [1, 2]. Probable for each type of cloth, different types

of functional textiles are offered for various demand. Prominent examples are found in work-wear with fire-retardant properties or medical textiles with antimicrobial properties for customers with atopic dermatitis [3-7]. Interesting products in the field of functional textiles are functional socks, because they are often built up by a composition of different fiber

types to optimize the properties of the whole product [8]. Functional socks usually use mixed materials to meet different requirements for comfort, durability and protection [9-11]. An overview on selected functional properties typically found in special socks is presented in Figure 1. There are socks with fluorescence effects to increase the visibility as a part of work safety [12]. However, fluorescence effects are also applied just for fashionable reasons to create neon-effect socks, as for example shown in Figure 2. Under illumination with UV light, these clothing items exhibit a bright color effect. More important functions for work safety are related to fire-retardant and anti-static properties [9, 13-15]. Socks with fire-retardant properties are often based on acrylic fibers which are built up by co-polymers containing chlorinated fire-retardant co-units. Those clothing items are often offered for persons working in fire-defense. [15, 16]. Antistatic functional socks should prevent accidentally ignition of gas or dust and protect also against painful electric shock [17]. For comfort reasons socks are also functionalized in direction of moisture management and heat regulation [9, 18, 19]. Finally, bioactive functions have to be mentioned, which modifying the interaction to living organism. Antimicrobial textiles act against microorganism like bacteria and fungi [19-21].

Antimicrobial socks are often dedicated to three different types of application – sport sector, atopic dermatitis and diabetes [22-25]. For the sport sector a task antimicrobial function is the avoiding and elimination of unwished bad odor. This odor is the result of bacterial decomposition of sweat [22]. People suffer-

ing under atopic dermatitis can get a support by antimicrobial textiles, because they prevent secondary infection, e.g. with yeast as *Candida* [23]. Finally, there are antimicrobial socks especially offered for people suffering under diabetes. Here, the antimicrobial socks help to prevent infections on the foot [24, 25].



Figure 2: Examples for functional socks with neon-fluorescence effect. Shown are socks of two different coloration placed on a UV lamp. This UV lamp emits black light with emission maximum around 380 nm. The non-visible UV light emitted by the lamp is impressing transformed to visible light by transmission through the fluorescent socks.

Additional to antimicrobial textiles, also textiles with anti-insect functionality can be named as bio-active clothing items. By these clothing items, insects are repelled or killed and by this action humans are protected. This anti-insect function is especially demanded for applications in the fields of outdoor sports, military clothes or for tropical regions [26]. A detailed view on anti-insect textiles is given in following section.

2. ANTI-INSECT BY TEXTILE PRODUCTS

Textile insect protection items can be categorized into two main areas of application: personal protection through special clothing, and room-specific protection through textile barriers such as insect nets on doors, windows, or as bed canopies [27, 28]. A further distinction can be made between mechanical and chemical insect protection [27-29]. Mechanical insect protection using knitted mesh is used in both clothing and spatial protection. The fineness of the mesh structure varies depending on the area of application, the prevailing environmental conditions, and the type

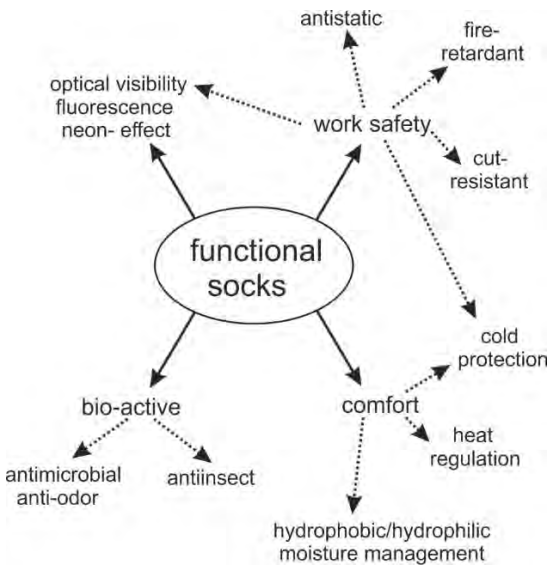


Figure 1: Overview on selected functional properties often realized on textile socks. A correlation of properties with applications is given.

of insect to be protected against [27]. Chemicals with anti-insect properties might be categorized into substances acting as repellent or as insecticide (Figure 3). The substances with repellent properties should be further sub-categorized into natural based substances or synthetic chemicals (Figure 3). Some of the most commonly used natural repellents are citronella, lemon eucalyptus oil or neem [30-32]. Neem is a plant-based active ingredient derived from the neem tree [32]. Synthetically produced insect repellents include substances such as picaridin or N,N-diethyl-m-toluamide (DEET) [33, 34]. The mechanisms of action of these substances are based either on an olfactory effect, which deters the insect via its sense of smell, or on a tactile effect, where the protective effect is achieved through direct contact. Insecticides are also used for protection of wool fibers against destruction from moths [35].

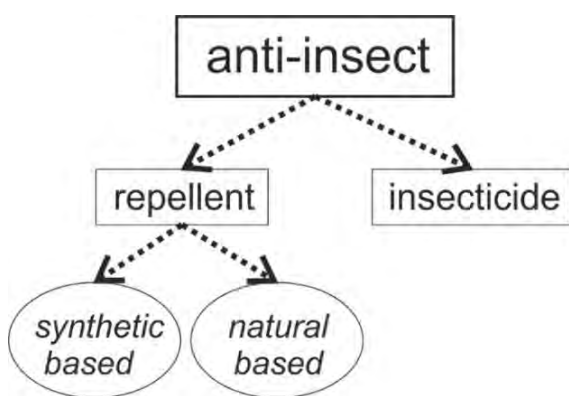


Figure 3: Schematic view on categories of anti-insect chemicals.

A very prominent synthetic repellent is diethyl toluamide which is abbreviated also as DEET or DETA (sum formula $C_{12}H_{17}NO$) [Feuser2020; Goodyer2018]. Compare the chemical structure of DEET in Figure 4. The synthetic active ingredient IR3535 (3-((N-n-butyl-n-acetyl)aminopropionic acid ethyl ester) ($C_{11}H_{21}NO_3$), also known as Insect Repellent

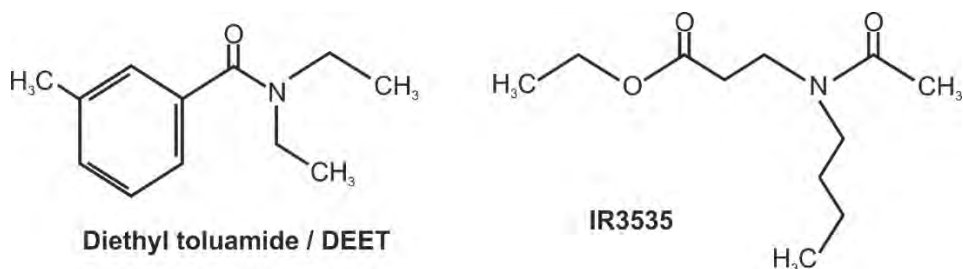


Figure 4: Chemical structures of the two synthetic repellent agents – Diethyltoluamide / DEET and IR3535.

3535, was developed by Merck in 1975. IR3535 acts on olfactory effects and is not lethal for insects [36]. It is structurally related to β -alanine – compare the chemical structure in Figure 4.

Alternatively, to the synthetic repellents, also bio-based repellents are used. Geraniol ($C_{10}H_{18}O$) is a monoterpene allyl alcohol and a component of essential oils obtained, e.g. from plants of the Lamiaceae, Poaceae, and Pinaceae families [37]. Compare the chemical structure of Geraniol in Figure 5. It is a major component of lemongrass (Citronella) and has olfactory properties. Geraniol and similar essential oils possess effective insect repellent properties, but their duration of action is limited due to the volatile nature of these substances, meaning they evaporate quickly and thus lose effectiveness. To extend the duration of action, encapsulation techniques such as microencapsulation are used to delay release and maintain protection on textiles for longer duration [38]. Lemon eucalyptus oil (from *Corymbia citriodora*) contains the active ingredient (+)-citronellal, which can be converted to p-menthane-3,8-diol (PMD) ($C_{10}H_{20}O_2$) through acid-catalyzed cyclization [39]. Compare the chemical structure of PMD in Figure 5. PMD acts olfactorily and masks human scents, severely impairing host recognition by insects.

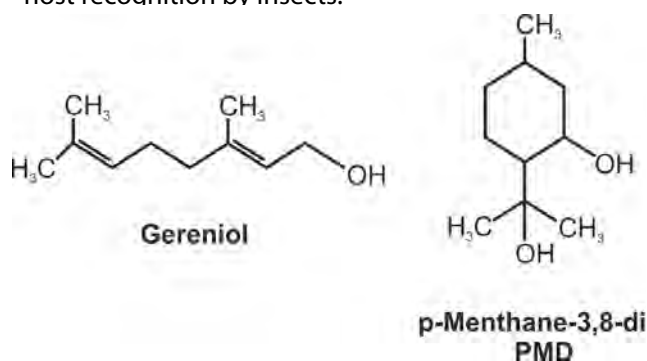


Figure 5: Chemical structures of the two bio-based repellent agents – Geraniol and p-Menthane-3,8-diol / PMD.

A prominent example for an insecticide used in textile applications is Permethrin (Figure 6). The action of this substance is based on a contact toxicity for insects [40, 41]. Permethrin can be applied on textiles using different methods, as e.g. sol-gel technology or encapsulation techniques [42, 43].

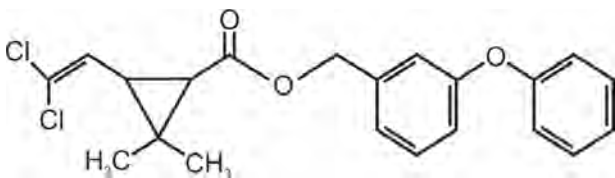


Figure 6: Chemical structure of the insecticide Permethrin (sum formula C₂₁H₂₀Cl₂O₃).

3. FUNCTIONAL SOCKS

3.1 Product description

For the current overview four different functional socks are chosen as product examples exhibiting different types of functional agents as anti-insect components. All four products are produced in European countries. The presentation and discussion of the products is done based on material composition, country of production, distribution platform and prices. The selected functional socks can be categorized into three primary areas of application: leisure, medical and workwear. Depending on the area of application, the functional properties, material composition, and distribution channel vary. Table 1 supports an overview on the 4 products, while in Table 2 details

on fiber composition and functional components are listed together with additionally claimed functional properties.

The products A and B are classified as leisure products for outdoor use. Both products are sold through online sportswear platforms. A direct comparison of the two models reveals a price difference of 8 Euro. This might be explained, by the fact that the product A is designed specifically for children, which is reflected in the design and smaller size. Looking at the online shops where the socks can be purchased, it is also noticeable that they can be distinguished into different price segments. Product A is sold through platforms such as Decathlon, a sports retailer that focuses on a wide range of products in low to mid-price ranges. In contrast, the product B is supplied by the company Craghoppers which primarily sells its own-brand products through its own online shop, which is positioned in the mid-price segment. The product A and product B sock models are among the most expensive products within the comparison examined. This could be due in particular to the use of organic cotton (bio-cotton) as the main material, which is reflected in the pricing. Product A contains 16% polypropylene fibers which is quite uncommon for clothing. Instead, polypropylene fibers are often used in technical applications as ropes or in the automotive sector [48, 49]. Polypropylene fibers are characterized by its low weight and hydrophobicity. These material properties are particularly advantageous for use in outdoor clothing to improve textile comfort. Further polypropylene is a quite cost competitive polymer material [50].

Table 1: Overview on discussed commercial product examples – for functional socks with anti-insect properties. The references are related to company web-pages with further supplier information.

Product	Name	Shop	Purpose	Country of production	Price [Euro]	References
A	Reima	Decathlon	Outdoor, leisurewear	Italy	15	[44]
B	Craghoppers	Craghoppers	Outdoor, leisurewear	Portugal	23	[45]
C	DeoMed Medical Products	Tiedtke Medical	Medical, diabetes	Poland	9	[46]
D	Runnex	BIG Arbeitsschutz	Workwear	Slovenia	13	[47]

Table 2: Overview on fiber composition and functional agents of considered product examples. Compositions and agents are mentioned as given by the supplying companies.

Product	Fiber composition	Functional agents	Additionally claimed functions
A	Cotton (bio) CO 74%, Polypropylene PP 16%, Polyamide PA 8%, Elastane 2%	Geraniol (from lemon grass extract)	---
B	Cotton (bio) CO 65%, Polyester PET 19%, Polyamide PA 15%, Elastane 1%	Noisilife (Eucalyptus citriodora oil, hydrated, cyclized)	---
C	Viscose (bamboo) 72%, Polyamide PA 25%, Elastane 3%	Permethrin, Tetradecyl (3-(trimethoxy silyl) propyl) ammonium chloride	Antimicrobial
D	Polyester PET (coolmax) 43%, Polyamide PA, 32% Cotton CO, 22%, Elastane 2%, Carbon-Fiber 1%	IR3535 3-((N-n-Butyl-n-acetyl) aminopropionic acid ethyl ester)	Antistatic

The product C is supplied by a company dedicated to diabetic socks as a preventative health product. They are sold through a specialized online shop focused on products for people with diabetes. In addition to integrated insect repellent, the socks exhibiting an antimicrobial finishing. This is listed as dimethyl tetradecyl(3-(trimethoxysilyl)propyl)ammonium chloride among the active ingredients. The chemical structure of Tetradecyl (3-(trimethoxy silyl) propyl) ammonium chloride (sum formula $C_{22}H_{50}NO_3SiCl$) is presented in Figure 7. Its antimicrobial action is related to the positively charged quaternary ammonium group in combination with a long alkyl chain. The trimethoxysilyl group is dedicated as anchor for the application on cellulose based fibers. In contrast, diabetes socks are often containing silver coated yarns to implement the antimicrobial effect [51]. However, due to the tremendous prize increase for silver in 2025 and 2026, the use of silver containing textiles might be decreasing in near future [52].

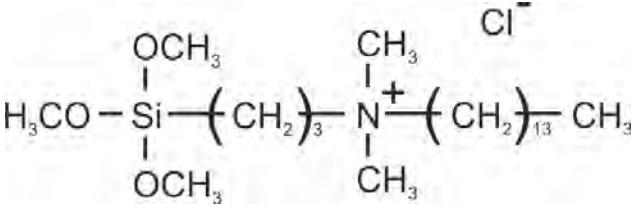


Figure 7: Chemical structure of the antimicrobial agent Tetradecyl (3-(trimethoxy silyl) propyl) ammonium chloride.

This antimicrobial finish is intended to reduce the development of sweat odor and promote a hygienic wearing experience. Furthermore, the finish helps inhibit the growth of fungi and bacteria, which is particularly relevant for the sensitive feet of diabetics. Especially to avoid serious infections leading to the diabetic feet syndrome [53]. The core material of product C is bamboo viscose, which is considered as moisture-regulating, and breathable due to its cellulosic composition.

Product D is specifically designed for use as workwear and are sold, among other places, through an online shop. Compared to products A to C, product D must meet significantly different standards. In addition to an integrated insect protection, achieved through impregnation with the active ingredient IR3535, for this product also antistatic properties are mentioned. These antistatic properties enable the controlled dissipation of electrostatic charges and help reduce the risk of sparks in potentially explosive work environments or when handling flammable materials. The product D contains 1% carbon fiber, which may contribute to increased material durability. This fiber increases the durability of the fabric and supports the longevity of the socks, especially under regular heavy use. Additionally, carbon fibers are electric conductive and for this might be placed in this product D to introduce also antistatic properties [54]. Compared to the other three products, the content of synthetic fibers with more than 65% is quite

high in product D, so the incorporation of conductive carbon fibers might be necessary to realize durable antistatic properties. Since work socks are often worn for extended periods and must maintain comfort during increased physical activity, COOLMAX® polyester is used as the main component. COOLMAX® polyester is used as the main component for the socks, which must be maintained during physical activity. This fiber, thanks to its increased surface area, can wick away moisture more quickly, keeping the wearer cool and dry [55, 56].

3.2 Product investigation

In this section some investigations on the four product examples are presented and discussed. The aim of the presented investigation is to support material information going beyond the information supported by the supplier of the products.

3.2.1 Microscopic analysis

Microscopic images of the product examples are realized by scanning electron microscopy SEM using a Tabletop 3000 microscope from Hitachi. The measured SEM figures are presented in Figure 8 in medium magnification. The fiber structure can be determined. Cotton fibers can be identified by their fiber shape for

products A and B. Uncommon structures or dirt are not detected by SEM.

3.2.2 IR spectroscopic measurements

For evaluating the fiber type composition of the four example products, IR spectra are recorded from the main part of the socks. By these spectroscopic measurements the supplier information on the fiber composition should be confirmed. These spectroscopic measurements are done using a FT-IR spectrometer IRTracer-100 (Shimadzu). The recorded IR-spectra are depicted and compared in Figure 9. The relations of main signals with the mentioned fiber types are marked. The IR spectrum of product A is mainly determined by signals related to the main fiber component cotton. Also signals related to the vibrations of polypropylene PP fibers can be identified [57, 58]. Nevertheless, these signals are also overlapping with some signals of cotton. The signals around 2900 cm^{-1} are assigned to C-H stretching vibrations of aliphatic units and are originated from both components cotton and polypropylene. The strong intensity of these signals for product A is probable caused especially by the presence of polypropylene. The fiber materials which are also mentioned by the supplier – polyamide PA and elastane – are not detected, probable because of smaller content.

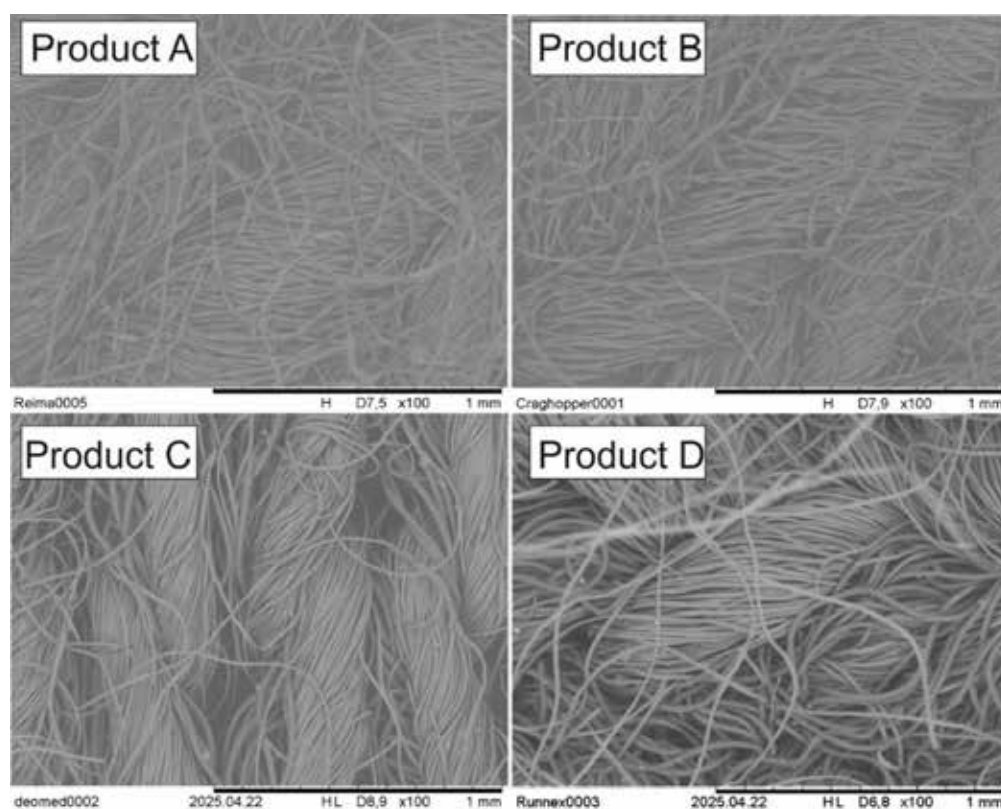


Figure 8: Microscopic images of the different product samples.

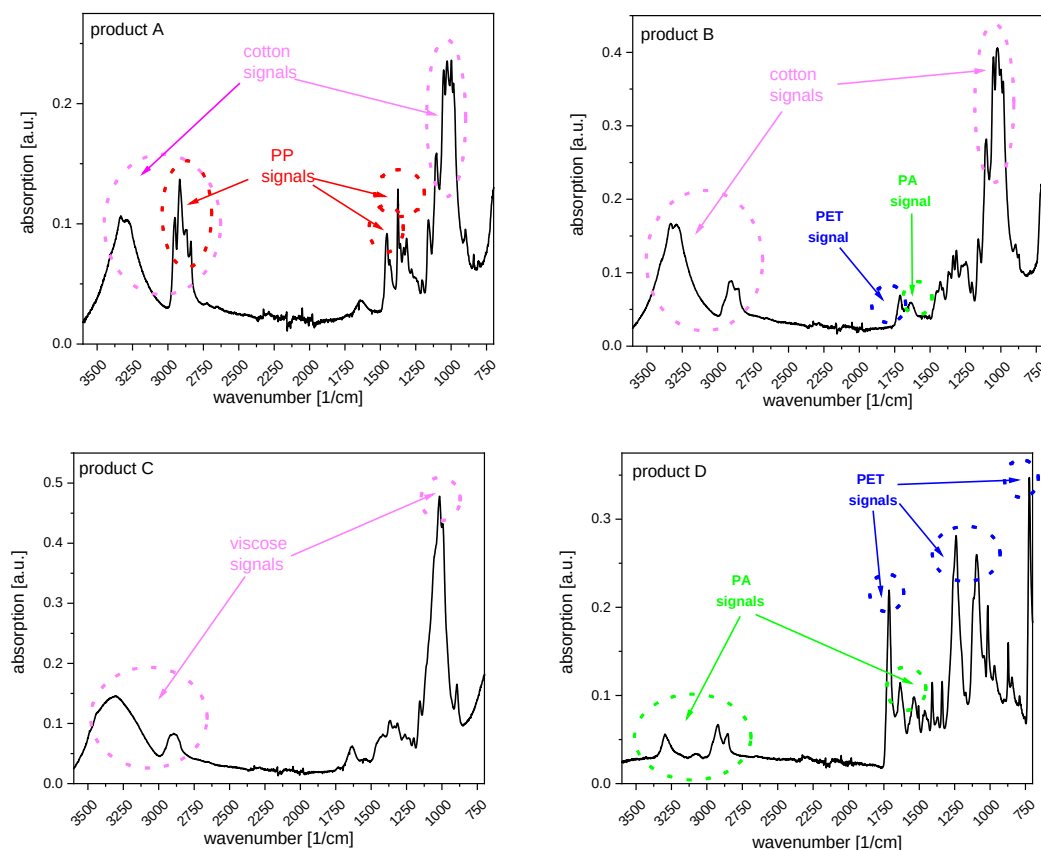


Figure 9: IR spectra of the different product samples.

For product B, the IR spectrum exhibits mainly signals from cotton as main component. For both by-component fibers PET and PA small signals can be determined at 1712 cm^{-1} and at 1639 cm^{-1} . These signals are related to $\text{C}=\text{O}$ stretching vibrations of the ester group from PET and the amide group from PA, respectively [58]. The IR spectrum of product C is determined mainly by the signals related to cellulose (viscose fibers). Only a small signal at 1634 cm^{-1} might be related to polyamide fibers which are present in smaller content but this signal could be also related to incorporated water in the cellulosic fiber, so the determination of polyamide in product C is not certain. The IR spectrum of product D is clearly dominated by signals of the main fiber component PET with strong signals at 1714 cm^{-1} , 1241 cm^{-1} , 1096 cm^{-1} and 723 cm^{-1} . For the present polyamide fibers also several clear but average signals can be identified at 3296 cm^{-1} , 3079 cm^{-1} , 1635 cm^{-1} and 1542 cm^{-1} . These signals are related to different vibrations of the amide group [59]. The other fiber components cotton, elastane and carbon fibers cannot be identified in this IR spectrum.

3.2.3 Sensorial evaluation

Sensorial evaluation is performed by smell tests on the products A and B containing olfactory agents. The

sensorial evaluation is done in accordance to standard ISO 1600-28. The aim was to assess any changes in odor due to wear and tear. The test measures the odor intensity (on a scale of 0-6, where 0 is low intensity and 6 is high intensity) and includes a qualitative description of the odor. The evaluation follows the test procedure – one smell of the textile sample, testing person takes a step back and evaluates the overall impression, eventually repeating of procedure for verification. The results of sensorial evaluations are listed in Table 3 on new purchased products and on products after storage or different performed fastness tests. A wash fastness test is done according to ISO 105-C06. Here the textile sample is placed in a steel vessel 150 mL liquid and 10 steel balls. An ECE washing agent and a washing device Labomat 30 is used. Washing duration is set to 30 minutes and washing temperature to 40°C . After washing rinsing with cold water for two minutes is done. Finally, line drying at room temperature is done. The sweat fastness test is done according to ISO 105-E04 with an alkaline solution ($\text{pH}=8$) and an acidic solution ($\text{pH}=5.5$). Afterwards drying of samples is performed at 60°C for 15 minutes.

For both new products an intensive smell is determined, which can be described as lemon like for

Table 3: Results for sensorial evaluation on product A and product B.

Sensorial results Product A		sample	
		Product B	
Description of smell		Lemon like, attractive	eucalyptus-lemon, significant
Intensity of smell	New product	5	5
	After storage for 2 weeks	2.5	3
	After wash test	0.5	1.5
	After sweat test, acidic	0.5	0.5
	After sweat test, alkaline	0	0.5

product A and eucalyptus-lemon like for product B. After placement out of the package and storage at normal atmosphere and room temperature for two weeks, the smell is still present on the products but the intensity is decreased. It can be assumed, that during the two weeks of storage, the active components evaporate and by this the intensity of smell effect decreases. However, after testing the products after washing or in contact with artificial sweat, the smell is significantly decreased or totally deleted. The fastness properties of the applied functional components are obviously low.

4. CONCLUSIONS

The functionalization of textile materials is an interesting field leading to a broad range of differently modified products. An important group of functional textiles are functional socks. These products are affordable to reasonable price, covering a broad range of different fiber types and functional applications.

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