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Permethrin Application on Polyamide and Polyamide-Polypropylene Knitted Fabrics

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Abstract
Innovative textile materials with insecticidal and repellent properties can be used in many areas of the textile industry (sportswear, children's thermoactive clothing, combat uniforms, tents, sleeping bags, mosquito nets, protective clothing for foresters and hunters etc.). In this study, the chemical treatment of polyamide (PA) and polyamide-polypropylene (PA/PP) knitwear with permethrin, a third generation insecticide from influenza synthetic pyrethroids, which is toxic to insects but harmless to humans, was undertaken (Sanitized AM®23-24 preparation was used). In addition to the active substance, the bath contained a cross-linking agent (Appretan®N92111) and softening agent (Solusoft®FE). The content of active substance in the textile product after the application process was examined in dependence on the concentration of the preparation in the bath. When using the right concentration of permethrin and auxiliaries, the fabrics after washing 20 times still showed an effective concentration of insecticide.

Key words: *permethrin, insecticides, repellents, insect repellent clothing, polyamide, polypropylene.*

Introduction

In recent years, the intensive development of functional technologies for textile products has been observed. Clothing is not only used to cover the body of users, but more and more often it performs additional functions: aesthetic, protective, and repelling insects.

Due to climate change, the range of insects from the tropical zone is expanding to the north, which means that the risk of diseases caused by these insects is increasing in Europe [1, 2]. In Poland, we most often encounter threats of insect bites (mosquitoes and gnats) and arachnids (ticks). Insect bites, especially ticks, in addition to discomfort, often have dangerous consequences (tick-borne encephalitis, Lyme disease, chronic atrophic dermatitis, granulocytic anaplasmosis, babesiosis) [3]. In Poland, the number of cases of tick-borne encephalitis reported in 2018 were 197 and in 2019-214 (as of November 15, 2019), and over 21.000 Lyme disease cases [4, 5]. There has been an increasing tendency of the incidence of Lyme disease in subsequent years and a high level of reported cases of tick-borne encephalitis. The main endemic regions of tick-borne encephalitis are located in north-eastern Poland. It is thought that there are many more cases, but they are not recognised and reported by doctors [6]. Insect and tick bites pose a threat in the form of the disease entities listed above. The need to protect against insect bites – especially for people exposed to such a threat in their daily work – requires the development of technology for finishing textile materials with active substances – insecticidal or repellent. The demand for textile products made of artificial fibres is increasing, which are now more functional [7]. The literature describes numerous ways of modifying fibres, knitted fabrics and products made from PA, PP and PES in order to give them appropriate functions or to examine properties. PA fibres and products were modified to give them antibacterial and antifungal properties by two-stage modification of polyamide products consisting in introducing carboxyl groups into the PA macromolecule by grafting vinyl monomers, and then attaching an appropriate drug to such modified fibres [8]. The ability of PA and PP fibres used in the production of textile floor coverings for the sorption of nicotine from air polluted by tobacco smoke and pure nicotine was also examined. Polypropylene fibres were modified with titanium dioxide coated with silver nanoparticles. Polypropylene fibres are more susceptible to nicotine sorption than polyamide fibres. The modification of titanium oxide coated with nanosilver significantly accelerates the photocatalytic decomposition of nicotine adsorbed by polypropylene fibres [9]. The electromagnetic shielding properties of composite yarns from blends containing acid-resistant steel wire, continuous polyamide and polyester fibres as well as chopped fibres made from regenerated cellulose from bamboo raw material were also investigated. The far infrared emissivity and anion density of knitted fabrics produced with different proportions of the components used were tested. In addition, the effectiveness of the electromagnetic protection of knitted fabrics was tested at various elongations. Increased elongation does not significantly affect the shielding properties; only the use of the lamination method increases the shielding effect [10].

There are also numerous literature reports on giving flat textiles insect repellent properties using permethrin, which is a third generation contact insecticide, harmless to mammals but lethal to ticks, mosquitoes and many other insects. It is a component of many insecticides, including shampoos against lice and fleas. It has no smell and can be applied to all known fabrics, even to delicate silk [11]. cotton knitwear and their mixtures with artificial fibres: polyester [12-15], polyamide [16] and polypropylene [13] were treated with permethrin. No insect repellent finish has been used on 100% PA or 100% PP knitwear.

Permethrin was applied as a solution or emulsion by surfacing, impregnation, coating or spraying on a textile material [12, 15-18]. Various auxiliaries were used in the padding bath: organic acids, wetting and anti-foaming agents. The disadvantage of permethrin finished textile materials is the poor durability of the permethrin finish during laundry. The release of permethrin during subsequent washes causes the loss of protective properties of the textile and its penetration into the ecosystem, which is harmful to aquatic

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organisms. In the technology of permethrin application on textiles, cross-linking agents are used, polyvinyl acetate or amylopectin [12, 17], in order to more permanently "bind" the active substance to the fibre. Finished textiles were also treated with permethrin [17].

A method was developed to provide PA and PA/PP fabrics with anti-lead properties by using permethrin as the active substance. In addition to the active substance, the padding bath included a cross-linking agent in the form of an aqueous dispersion of copolymers of acrylic acid esters and polyvinyl acetate, and a silicone emollient.

Characteristics of preparations for finishing knitted fabrics used in tests

Chemical tests of Sanitized® AM 23-24, Appretan® N 92111 and Solusoft®FE used in the anti-lead finish of knitted fabrics were performed.

The active ingredient of Sanitized®AM 23-24 anti-tick/anti-lead agent, used in the finishing process, is permethrin – CAS No.: 52645-53-1 ($C_{21}H_{20}Cl_2O_3$), classified as third generation insecticide (a substance from the pesticide group) and used as a crop protection agent against pests, in veterinary medicine and as a sanitary measure. Permethrin, like other pyrethroids based on the cyclopropane ring, is a mixture of cis and trans geometric isomers, each of which is a mixture of optical isomers – enantiomers (***Figure 1***).

According to the safety data sheet, Sanitized®AM 23-24 (Clarchem) contains 30-40% permethrin, 10-30% benzyl alcohol and 30-40% ethoxylated isotridecanol. Chromatographic analysis of the preparation intended for testing showed a 38.31% permethrin content of the 25/75 cis/trans composition. On the domestic commercial market, Sanitized®AM 23-24 is declared as a textile impregnation agent acting against mites, registered Office for Registration of Medicinal Products, Medical Devices and Biocidal Products [19, 20]. According to the manufacturer's data, materials treated with Sanitized®AM 23-24 meet the requirements of Class I-IV products in the Oeko-Tex Standard 100, EPA (US Environmental Protection Agency) [21] and OECD international certification system in the field of irritant/allergenic activity based on in vitro tests No. 406: Skin Sensitisation [22, 23].

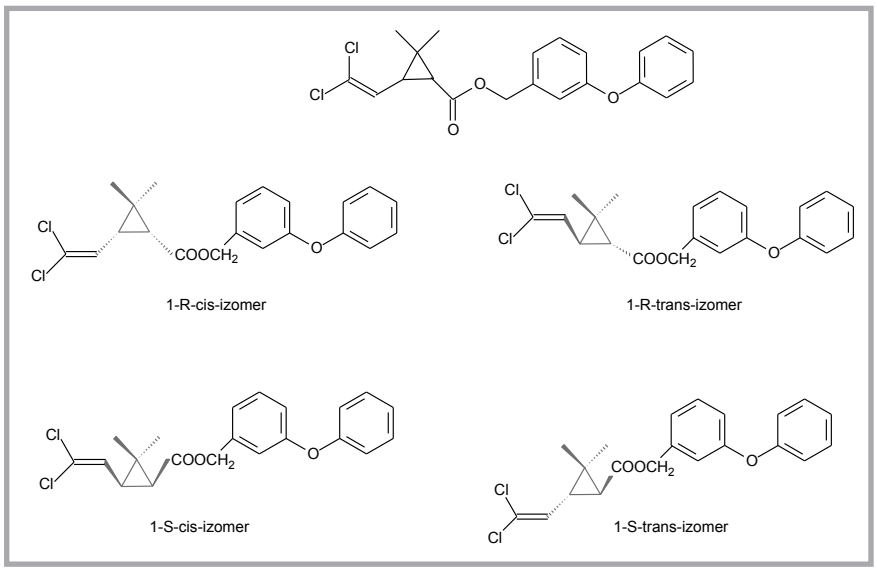

Figure 1. *Permethrin isomerism.*

The agent is indicated by the manufacturer for the finishing application of synthetic and cotton-containing textiles with the possibility of combining with other chemicals of special functions. According to the manufacturer's data, textiles provide an anti-lead/anti-tick function with a permethrin content of 1300 ± 300 mg/m^2 [24], determined by liquid chromatography (HPLC). The manufacturer of the agent (Sanitized AG) assessed the special utility functions of textiles intended for protective products against mosquitoes for the army, which was undertaken at the Swiss Tropical Institute [24-26].

Currently, there are only a few textiles on the market that have protective features against insect bites (Dutch manufacturer Rovince). Therefore, there are no standards that could specify a permethrin content sufficient to effectively repel insects. According to Khoobdel, the effective concentration of permethrin in products intended for soldiers is 1250 mg/m^2 [27, 28]. The sufficient content of this agent to repel insects was also found: for materials after 20 washing cycles: 600-700 mg/m^2, and after 50 washes: 200 mg/m^2 [13, 24].

In the finishing process of the textiles, an auxiliary binder was used, known under the trade name Appretan®N92111 (liq.), which is a substance identified as polyvinyl acetate (CAS No: 9003-20-7), known primarily as a component of adhesives and emulsion paints. For textile application, it is used in the aqueous dispersion of copolymers of acrylic acid esters with vinyl acetate, known, among others, as an insoluble substance in the gastrointestinal tract for pharmaceutical use in the production of sustained release drugs, drug carriers and gastro-resistant gelatine capsules [29]. As a softening agent, a si-

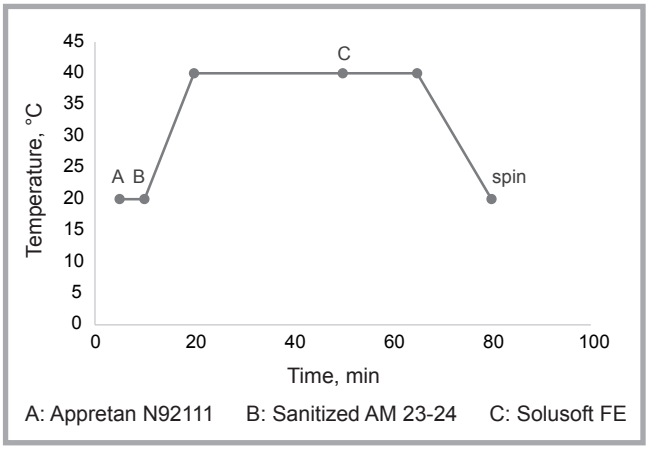

Figure 2. *Scheme of permethrin application on PA and PA/PP fibres.*

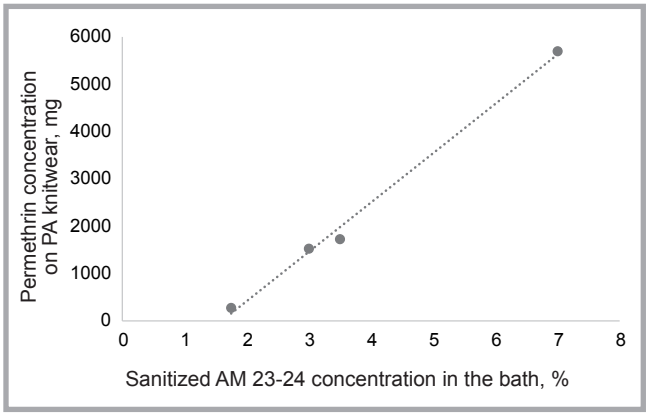

Figure 3. Dependence between the concentration of permethrin in PA knitwear and the Sanitized AM 23-24 concentration in the bath.

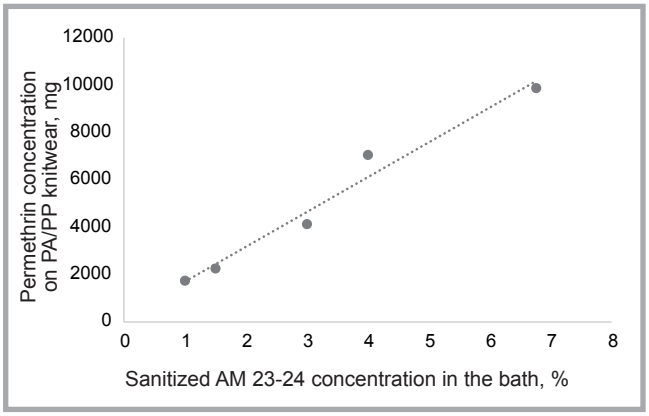

Figure 4. Dependence between the concentration of permethrin in PA/PP knitwear and the Sanitized AM 23-24 concentration in the bath.

licone preparation – Solusoft® FE (Clariant) was used.

Material and methods

For the application of active substances that provide protection against insects, a textile product was used, from which thermoactive underwear is manufactured at Active Pro.

The test included dyed polyamide (PA) fabric with a surface weight of 130 g/m^2 and knitted fabric consisting of a mixture of polypropylene-polyamide fibres (PP/PA) with a surface weight of 210 g/m^2, which have already been subjected to the standard washing process after staining in industrial conditions. Measurement of the surface mass was carried out in accordance with the methodology specified in the PN-EN 29073-1:1994 standard [30]. The application of permethrin on knitted fabrics was carried out in a bath with a pH of 4.5-5.0 containing Sanitized®AM 23-24, a cross-linking and softening agent, in Linitest Original Hanau dyeing apparatus, according to the scheme below (***Figure 2***).

The amounts of active and auxiliary substances used were determined experimentally, as well as process parameters such as padding temperature, bath times, the time and degree of cropping, and the drying temperature. After the process, the fabric was centrifuged at 800 rpm for 1 min. in a Ravanson washer-extractor, model: XPB72-LP. Cross-linking and drying of the sample was carried out in a laboratory dryer at 120 °C for 10 minutes. The durability of the application of the active substance on the test textile materials subjected to wet processing was evaluated after 20 washing cycles performed at 40 °C, in accordance with the conditions specified in the PN/EN 105C06: 2010A1M standard [31].

Assessment of the effectiveness of the knitwear modification consisted in carrying out tests determining the permethrin content before and after conducting the washing process 20 times. Quantitative studies of the permethrin content were carried out according to the method of high performance liquid chromatography with diode detection developed (HPLC/DAD), on a Perkin Elmer chromatograph.

Determination of the permethrin content on PA and PP/PA fibres was achieved by its extraction from fibres with an organic solvent (acetonitrile) and by chromatographic analysis of a solution containing the active substance extracted from the fibres.

When using preparations containing permethrin, it should be remembered that it has a long-term adverse effect on the aquatic environment [20, 21]; therefore wastewater after processes in which permethrin is used should be utilised. The manufacturer of Sanitized® AM 23-24 recommends adjusting the sewage pH to 13.5, next neutralising it, and only then passing it onto a treatment plant.

Table 1. *Permethrin content in PA knitted fabric as a function of its concentration in the bath before and after 20 washing cycles.*

Sample number	Sanitized AM 23-24 concetration in the bath, %	Permethrin content in knitted fabric, mg/m^2	Permethrin content in knitted fabric after 20 washing cycles, mg/m^2	Appretan N92111 cross-linker concentration, %
1	7.0	5698	–	4
2	3.5	1728	425	4
3	3.0	1527	–	4
4	1.75	276	–	4
5	3.5	2083	826	8

Table 2. *Permethrin content in PA/PP knitted fabric as a function of its concentration in the bath before and after 20 washing cycles.*

Sample number	Sanitized AM 23-24 concentration in bath, %	Permethrin content in knitted fabric, mg/m^2	Permethrin content in knitted fabric after 20 washing cycles, mg/m^2	Appretan N92111 cross-linker concentration, %
1	6.76	9879	–	4
2	4.0	7057	–	4
3	3.0	4133	–	4
4	1.5	2258	–	4
5	1.0	1743	1315	4

Results

An effective concentration of permethrin (1728 mg/m^2) in PA knitwear was obta-

ined at a concentration of 3.5% of Sanitized AM 23-24. After 20 washes, the concentration of permethrin decreased significantly (from 1728 to 425 mg/m^2). Increasing the amount of crosslinking agent Appretan N92111 improved the insect repellent finish (***Table 1***). In PA/PP knitwear, a concentration of 1743 mg/m^2 permethrin was obtained at a concentration of 1% Sanitized®AM and 4% crosslinker in the bath. However, the concentration of permethrin in PA/PP knitwear after repeated washing processes was at the appropriate level – 1315 mg/m^2 (***Table 2***). The relationship between the concentration of permethrin on PA and PA/PP knitwear and the concentration of Sanitized®AM 23-24 in the bath was developed experimentally (***Figure 3***, ***Figure 4***), which is linear with the correlation coefficient for PA knitwear – 0.997, and for knitwear PA/PP – 0.988.

Summary

Currently, there are few textile products on the market that have properties that protect against insect bites. These are products made of knitted and woven cotton fabrics as well as of mixtures of cotton and artificial fibres.

In this study, a method of finishing polyamide (PA) and polyamide-polypropylene (PA/PP) knitted fabrics with insect repellent properties, for which there is a market demand, was developed. The permethrin content in each case is sufficient for the knitting materials evaluated.

For PA knitwear, the concentration of permethrin was obtained after the application process – 2083 mg/m^2, using 3.5% preparation of Sanitized®AM 23-24 and 8% of Appretan®N92111 crosslinking agent. For knitwear PA/PP, a concentration of 1743 mg/m^2 permethrin was obtained using 1% of Sanitized®AM 23-24 and 4% of Appretan®N92111 crosslinker. Washing 20 times lowered the active substance content, while maintaining its concentration at a sufficient level, for PA – 826 mg/m^2, and for PA / PP – 1315 mg/m^2, which provides a insecticidal and repellent function.

The research presented is an introduction to the development of anti-lead and anti -tick finishing technology for textiles.

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