Antoni Niekraszewicz,
Jolanta Lebioda,
Jerzy Hoffman*,
Kazimierz Ruszkowski*,
Henryk Struszczyk

Institute of Chemical Fibres, Lodz
ul. Skłodowskiej-Curie 19/27,
90-570 Łódź, Poland
e-mail: biomater@iwch.lodz.pl,
iwch@iwch.lodz.pl

*Institute for Terotechnology,
Textile Machinery Branch
ul.Hipoteczna 6, 91-335 Łódź, Poland
e-mail: instytut@itee.radom.pl

Anti-mite Modified Polypropylene Fibres and Bedding Inserts Containing Such Fibres

Abstract
Research has been conducted in the Institute of Chemical Fibres with the aim of preparing synthetic fibres which can inhibit the growth of house dust mites thus limiting or eliminating a cause of allergy. The physical-mechanical properties of anti-mite polypropylene fibres and needle-punched nonwovens containing such fibres are presented. The anti-mite activity was tested according to the French standard NF G 39-011. A nonwoven containing modified polypropylene staple fibres was used to prepare bedding inserts, which were then tested with regard to their anti-allergic usefulness. It was found that the material causes a very distinct reduction in mite guanine concentration, and the bedding insert largely contributes to a much more comfortable feeling for the patients. The anti-mite nonwoven in the form of bedding inserts was approved by the Office of Registration for Medicinal Products, Medical Devices and Biocidal Products, as well as by the Ministry of Health.

Key words: *house- dust- mites, allergy, anti-mite fibres, non-woven, bedding inserts.*

Introduction

Allergic pathological states such as rhinitis and asthma bronchiales, particularly in the upper airways, are an ever-increasing problem for humans today. House dust is the most common inhalatory allergen [1]. About 100 million people world-wide are estimated to suffer from house dust mite atopy [2]. The mite's secretion constitutes the main allergen. Although the mites themselves are harmless to humans, their excrement, in tiny nubs of 10-40 microns in size, contain antigens which may trigger an allergic reaction when inhaled to the airways. Small, mucus-covered excrement particles stick easily to various home textiles. Therefore, upholstery furniture, carpets and bedclothes foster the accumulation of the allergen. It is assumed that living in houses in which the concentration of the mite antigen exceeds 2 μg/g of the dust (equivalent to 100 single mites in 1 gram of dust) essentially increases the risk of various allergy-related diseases of the airways.

When contemplating the causes of allergy, it may be concluded that the main threat comes from mites that have their abode in dust, upholstery furniture and, in particular, bedding. The most frequent mite species that appear in houses are *Dermatophagides pteronyssinus Dp* and *Dermatoiphgoides farinae Df*, and, in rooms at lower temperatures, *Acarus siro*, *Tyrophagus putrescentiae* (Figure 1) and *Glycyphagus domesticus* [3].

Most patients suffering from bronchitis, rhinitis and dermatitis react to house dust [4]. Changing ways of life and modern house interiors may also contribute to increased mite and fungi population and enhanced allergenic action, notably unnatural microclimates such as increased air humidity and lack of natural ventilation.

Well-known means to prevent the growth of mites are barrier textiles such as coverlets, mattress and pillowcases impenetrable to mites, their excrements and allergenic particles [5]. However, barrier textiles are insufficient protection against mites and allergens, as they can only be used in bedclothes. Quite a number of other materials, such as floor coverings, carpets, upholstery and decorative fabrics also constitute an abode for these pests.

The growth process of house dust mites, its impact upon asthmatic ailments, and the role which anti-microbial fibres may play in these phenomena have been investigated at Nottingham University and the Entomology Department at Cambridge University. Exfoliated skin cells cannot serve as a medium for the mites, as they are usually too dry and contain much fat. Under certain conditions, exfoliated skin can be degraded by the action of *Aspergilus repens* fungi, and thus serve as nourishment for the mites [6-8].

Figure 1. *Tyrophagus putrescentiae.*

The use of a proper biocidic agent as an additive to fibres extinguishes Aspergilus repens, and in consequence inhibits the growth of mites.

Acordis Co (UK) has put two such fibres on the market: Amicor Plus, an anti-microbial, polyacrylonitrile fibre, and an anti-mite fibre called Amicor Pure [9]. The acaracide is introduced into the spinning bath during the manufacture of the fibre. The acaracide is steadily extricated during the laundering and use of the fabrics containing the Amicor fibres, and replenished by its migration from the interior to the fibre surface [6].

The polyvinylchloride anti-mite fibre Rhovyl AS, containing benzyl benzoate as the acaracide, is produced by the French company Rhovyl [10].

The Austrian Asota GmbH manufactures the anti-microbe polypropylene fibre called Asota Sanitized, designed for blending with other synthetic and natural fibres. Another fibre made by the same company is the anti-mite Asota AM Plus, which bears biocides under the trade-names of MB P 96-60 and MB E 97-65 [11].

Another idea for inhibiting the growth of mites is proposed by the Sanitized company, which offers its Actigard AM 87-12 for use in the modification of textile surfaces by coating, dipping or spraying [12]. The disadvantage of such finishing is a certain instability and decreasing biological activity during the use of the textiles.

In the pursuit of methods to defeat pests, interest has risen in the possibility of disturbing chitin accretion. Protocuticule, a constituent of arthropod cuticule, is built up from tiny chitin fibres deposited in a protein matrix. It was found that synthetic derivatives of asymmetric benzarylureas are capable of effectively disturbing chitin accretion [13]. Substances that inhibit chitin synthesis are well known and used in plant protection. The Colorado beetle insecticides may be shown as a typical example. They usually appear in the form of chitin synthesis inhibitors under various trade-names like Andalin 250 DC, Ekos 100 EC, Mat 050 EC, Nomolt 150 EC [14]. It may be concluded that such compounds are able to limit the mite population effectively, particularly at their early procreation stage. However, application examples of typical insect chitin inhibitors used in the modification of chemical fibres are as yet unknown.

In the Institute of Chemical Fibres, investigations have been under way for many years to select substances and prepare fibres for slow-release actions using natural and synthetic carriers. Research has been focused on preparing antifungal and antibacterial polyamide [15] and polypropylene [16] fibres, and recently, also on synthetic fibres modified with anti-mite additives [17, 18]. The biologically active substance deposited in the synthetic fibres prepared by the Institute is control-released in sufficient quantities to sustain optimal anti-microbial activity. In case of the anti-mite fibres, the extricated biologically active substances inhibit the growth of house dust mites by direct action on the mites or their host, i e. *Aspergilus repens*. The following substances have been used as fibre-modifying active agents [19]:

- fungicides from the family of imidazol and triazol derivatives approved for use in contact with humans and animals. These inhibit the growth of Aspergilus repens, which constitutes a bridge in the mites' feed chain, and
- acaracides, for example from the group of organic and inorganic acids that display direct action on the mites.

In the Institute, we prepared bioactive polypropylene fibres that inhibit the growth of house dust mites and so limit or eliminate the cause of allergies [19, 20]. In the technology as elaborated, the acaricide is introduced into the fibre in the course of melt spinning. Textiles made of such fibres as air filters, carpets, floor covering, bedclothes, upholstery and decorative fabrics constitute protection against house dust mite allergens throughout the life of the fabrics.

Based on the manufactured amount of modified polypropylene staple fibres and polyester filling fibres, a prototype charge of nonwoven, suitable for bed linen, has been devised and produced [21]. The nonwoven was made by needle-punching. Inserts for pillows, quilts and bed sheets were made from the nonwoven. The inserts are interposed between the pillow and case, quilt and case, sheet and mattress. In such uses, they must meet certain requirements of strength and usability. The prepared sets of the bed-clothes were tested in respect of strength and anti-mite & anti-allergic action. It is expected that the prepared inserts will be used by patients suffering from house dust mite allergy.

Experimental

Raw materials

Polypropylene:

- Daplen RT 581 made by Borealis Belgium, melt flow index =35g/10 min,
- Malen P S 702 made by PKN Orlen Poland, melt flow index = 11-16g/10 min.

The melt flow index was measured at 230 °C and a load of 2.16 kg, with a spinneret of 2.09 mm in diameter.

Spin finish: Fasavin 2830 – 8% emulsion, manufactured by Zschimmer and Schwarz.

Anti-mite agent: The commercial product AM 92223 made by Wells Plastics UK was used as the anti-mite agent. It is a blend (concentrate) of polypropylene and the active substance Ceramite™ in 50/50 proportions. The concentrate resists temperatures up to 350 °C, is odourless, does not contain neurotoxins and is harmless to humans and the environment. Ceramite™ is an inorganic compound encapsulated in a ceramic coat.

Polyester filling fibre: cut length 38 mm, titre 3.3 dtx, made by Elana SA, Poland.

Enforcing cotton net: symbol BTG, mesh 10×5 mm, surface density ~ 40g/m^2 made by PPH Pabianitex of Pabianice, Poland.

Equipment

Extruder spinning plant Barmag, extruder [diameter 20 mm]. installed at the Institute of Chemical Fibres.

Draw-twister Barmag type SZ-16, installed at the Institute of Chemical Fibres.

Industrial staple fibre line composed of a feeding system, extruder [diameter 120 mm], spinning head with 8 spinnerets, drawing system, stabilisation-relaxation chamber, crimper, cutter and baler: installed at Viola-Multitex Co.

Industrial nonwoven pilot plant composed of a blender-opener, volumetric feeder, roller card, fleece laying machine and needling machine: installed in the Institute for Terotechnology.

Analytical Methods

The physical-mechanical properties were measured according to the following standards:

- Linear density: PN-ISO 1973;1997
- Breaking force and elongation of staple fibres: PN-EN ISO 5079;1999
- Fibre thickness: PN-EN ISO 9073-2;2002
- Breaking force and elongation of nonwoven: PN-EN 29073-1
- The anti-mite activity was tested according to the French standard NF G 39-011

The research and development works devoted to the preparation of anti-mite nonwoven products were carried out in three stages:

1. Preparation of anti-mite polypropylene staple fibres;
2. Preparation of the anti-mite needle-punched polypropylene/polyester nonwoven;
3. Confectioning of the bedding inserts.

Preparation of anti-mite polypropylene staple fibres

The method prepared for manufacturing the polypropylene (PP) fibres active against house dust mites consists in adding an active agent to the polymer melt and depositing it in the structure of the spun fibres. Based on earlier investigations [20], the concentrate AM 92223 was selected for the modification of fibres.

The investigation focused on finding a concentration of the biomodifying agent in the PP fibres that would provide anti-mite activity in both the fibres and textile products containing modified and other fibres. It was necessary to ensure that the additive used did not cause any disturbance in either the fibre-forming or fibre-drawing processes. It was also essential to attain physical-mechanical parameters of the fibres that would guarantee the useful properties of the final products.

Table 1. *Impact of Ceramite™ content upon the PP fibres activity against house-dust-mite activity.*

Content of active substance, % wt	Decrease of mite population, %
0	0
0,25	3
0,50	2
0,75	100
1,00	100
1,50	100

The spinning conditions resembled those applied in the forming of standard PP fibres. The active substance [a.s.]. content in the modified PP fibres was varied in the range of 0.25 to 2.5% wt. A reference trial without the agent was also made.

The formed fibres with varying Ceramite™ content were tested for biological activity. The testing was carried out in the Institute's Acarology Laboratory according to the French standard NF G 39-011. The testing results are presented in Table 1.

Up to 0.5% wt content of the active substance, the modified PP fibres do not manifest any anti-acaracide activity. In the range of 0.75 to 1.5% wt content, the decrease of the mite population was 100%. Based on the results, the amount of 1.0% wt active substance (equivalent to 2.0% of the AM 02223 concentrate) was assumed to be the optimum. This level content imposes sufficient anti-mite activity not only upon the fibres themselves but also on blends of modified and unmodified fibres (Figures 2 and 3).

The SEM inspection of the appearance of the Ceramite™-modified fibres shows that the biomodificator particles are quite uniformly distributed over the entire cross-section of the fibre, and fairly well on its surface.

Modified staple PP fibres with 1.0% wt content of active Ceramite™ were prepared for the manufacture of a nonwoven to be tested in respect of anti-allergy usefulness.

PP fibres with titre 4.6-5.0 dtex and a cut length of 32 mm were manufactured at the Viola-Multitex company on the spinning line (see Equipment).

Malen P type S-702 granulate from Orlen Co was used as raw material.

The fibres obtained met the requirements of the processing into nonwovens designed for the preparation of bedding inserts (Table 2).

Preparation of needle-punched anti-mite polypropylene/ polyester nonwovens

The anti-mite nonwoven was manufactured in the Institute of Terotechnology using the needle-punch technique. The PP fibres made in the Viola company were used as the active component, and staple polyester (PES) fibres with 38 mm cut length and 3.3 dtex staple as filling fibres. The latter manifest a higher moisture absorbency and elasticity in comparison to PP fibres. In the blend, they provide for softness and fluffiness of the products; they also ease the manufacturing of the nonwoven. The nonwoven designed for inserts under bed sheets was additionally enforced with a cotton net (BT6-100). In optimising the proportions of the raw materials, the nonwovens were made with contents of 12.5%, 25% and 50% of the modified PP fibres, with a surface density in the range of 160 to 200 g/m^2. PES fibres were the remaining component (87.5, 75.0, 50.0%).

The nonwovens were analysed in respect to their physical-mechanical and anti-mite activity (see Table 3).

Amongst the tested nonwovens, the material containing 50% PP fibresmanifested good anti-mite activity, completely extinguishing the mite population, while with lower PP fibre contents, the activity was either lacking (12.5% of PP fibres) or insufficient (70% at 25% PP content).

Bedding inserts made of nonwoven

Based on the results obtained, we decided to select nonwovens with 150-200g/m^2 surface density, containing 50% of staple PP fibre with the addition of 1.0% wt of Ceramite™, for the preparation of bedclothes inserts [21]. At the Institute for Terotechnology in Łódź, a trial batch of the nonwoven was made which was used for sewing bed-clothes inserts. These were also tested for anti-mite activity according to standard NF 6.39-011. The products have shown the ability to entirely inhibit the growth of house dust mites.

In Table 4 some properties of the anti-mite nonwoven are compiled.

Thanks to the use of rather short bioactive fibres, the nonwoven is characterised by fluffiness and good tear and deformation resistance; thus it responds well to the quality requirements of bedclothes.

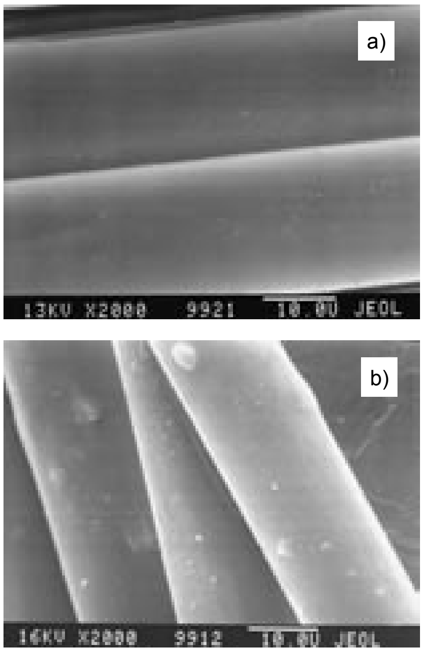

Figure 2. *SEM surface of standard PP and 1 % wt a.s. Ceramite- modified fibres. Magnification 2000×; a) PP standard, b) PP 1% wt a.s. Ceramite.*

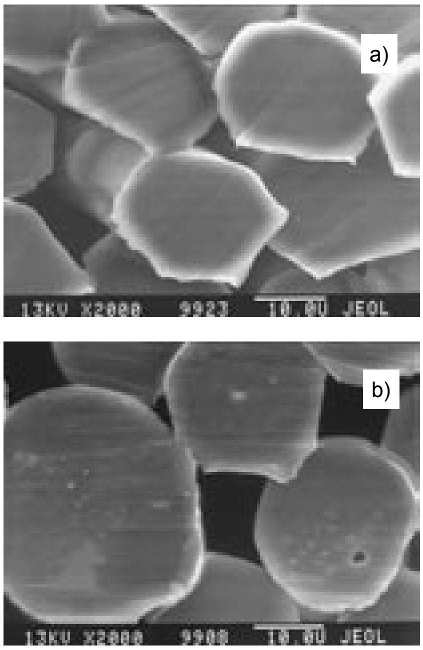

Figure 3. *SEM – cross-section of standard PP and 1 % wt a.s. Ceramite- modified fibres Magnification – 2000×; a) PP standard, b) PP 1% wt a.s. Ceramite.*

The bedclothes inserts were sewn as follows:
- for bed sheets, 2000 × 1400 mm
- for quilts, 2000 × 1400 mm
- for pillows, 700 × 800 mm

Table 2. Physical-mechanical properties and activity against house-dust-mites of Ceramite™ - modified PP fibres produced on industrial pilot scale.

Type of trial	Content of active substance, % wt	Ant-mite activity	Physical-mechanical properties			
		decrease of mite population, %	Cut length, mm	Linear density, dtex	Tenacity, cN/tex	Elongation, %
Standard	0	0	32,0	4,65	38,6	160
Modified	1	100	32,0	5,03	26,1	168

Table 3. Physical-mechanical properties and anti-mite activity of non-wovens containing anti-mite fibres.

Content of modified PP fibres, %	Anti-mite activity	Physical-mechanical properties					
	Decrease of mite population, %	Surface density, g/m^2	Thick-ness, mm	Average breaking force, N	Specifie breaking force, N/m	Tenacity conditioned, MPa	Elongation conditioned, %
12,5	0	194	3,39	84,8	1697	0,50	139
25,0	70	219	3,51	81,2	1611	0,46	127
50,0	100	168	3,09	77,5	1550	0,50	122

Table 4. Physical-mechanical properties of the anti-mite non-woven.

Parametr	Without net	With net
Surface density, g/m^2	158	213
Thickness, mm	1.74	2.19
Specific breaking force, along N/m	4040	4420
Tenacity, along MPa	2.32	2.02
Specific breaking force, across N/m	854	3600
Tenacity, across MPa	0.491	1.65
Elongation at break, along %	42	44.8
Elongation at break, across %	145	18.3

The anti-mite bed inserts were positively evaluated by the Office of Registration for Medicinal Products, Medical Devices and Biocidal Products (Poland), and approved for sale by the Polish Ministry of Health (approval no. 217/05).

Assessment of the inserts' anti-allergy usefulness

The inserts with the bioactive polypropylene fibre content were given to medical institutions for testing. Inserts without the bioactive components were also handed over as reference. The objectives of the testing were to assess the inserts' anti-mite action and their ability to soothe allergic reaction. The testing was carried out on patients in the Department of Allergology and Respiration Rehabilitation of the Medical University, Łódź and the Centre for Allergology in Łódź. For the tested material, the certificate of approval no. RNN/277/04/KB was issued by the Commission of Bioethics of the Medical University, Łódź.

The tests in both medical units revealed that the bedding inserts cause a remarkable statistical decrease in mite guanine concentration, and largely contribute to the patients' feeling much better.

Summary

1. Technological conditions were elaborated for manufacturing polypropylene staple fibres with anti-mite properties.
2. The optimal content of the biomodifying substance was established, based on biological testing in accordance with standard NF G 39-11.
3. Inserts were prepared from needle-punched nonwoven anti-mite bedclothes which met the usefulness requirements.
4. Medical testing confirmed that the inserts cause a remarkable decrease of mite guanine concentration, and soothe patients' allergic reactions.
5. The anti-mite nonwoven in the form of bedclothes inserts, were positively assessed by the Administration of Medical Devices, Drugs and Biocidal Materials, and given approval for sale by the Polish Ministry of Health.

Acknowledgments

- *The authors would like to express their thanks to the allergology team headed by Professor Krzysztof Buczyłko PhD., DSc. for their help in performing this project.*
- *This work has been carried out as part of the Task Project 'Implementing the production of an anti-allergic nonwoven' No. 6T082003 C/06102, co-financed by the Ministry of Science and Information Technology.*

References

1. *Fain A., Guerin B., Hart B.J. 1990. Mites and allergic disease, B. Guerin ed., Allerbio, Varennes-en-Argonne, 1990.*
2. *Bronswijk J. Van E.M.H.., Schober G. 1991. 'Management of mite development in the home', eds. W Schuster R. H., Murphy P.W. The Acari: reproduction, development and life-history strategies. Chapman and Hall: London, 507-516, 1991.*
3. *Samoliński B. 'Roztocze w niszy ekologicznej człowieka', XII Ogólnopolskie Sympozjum i Warsztaty Alergologiczne, Dobieszków 2003.*
4. *Kowalski Marek L. 'Alergia atopowa - epidemia XX wieku?' Służba Zdrowia, no. 65-68 2958-2961; 2000.*
5. *Brzeziński S., Ornat M., Malinowska, 'G.: Textile Barrier Materials for Special Applications.' Fibres & Textiles in Eastern Europe 4.[3/4]., pp 124-125 [1996].*
6. *Service D. [Courtaulds Fibres]. Amicor-Antimicrobial Fibres, Dornbirn, Chemical Fibres Conference, September, 1998.*
7. *Pat. WO 99/21421*
8. *Pat. USA 5746959*
9. *Jackowski T., Czekalski J., Cyniak D. 'Blended Yarns with a Content of Biological Active Fibres', Fibres & Textiles in Eastern Europe vol. 12, No 1 [45]., pp 19-23, [2004].*
10. *Bohringer A., Rupp J., Yonenaga A. 'Antimicrobial textiles', International Textile Bulletin 5/2000, 12.*
11. *Schobesberger C.P. [Asota GmbH]., Chemical Fibers International, vol. 48: 394-396, 1998.*
12. *Schmidt O., BU Textilchemikalien Clariant, seminar materials, Mikorzyn, 2000.*
13. *Sobótka W., 'Inhibitory biosyntezy chityny owadów', Postęp w chemii i zastosowaniu chityny i jej pochodnych, volume I, 180, Polskie Towarzystwo Chitynowe, Łódź, 1995.*
14. *Wachowiak H., Mrówczyński M., Widerski K., 1997. 'Stonka ziemniaczana – zalecenia zwalczania.' Ochrona Roślin, 6: 4-6, 1997.*
15. *Polish Pat. Appl. P-332396*
16. *Polish Pat. Appl. P-332398*
17. *Struszczyk H., Niekraszewicz A., Lebioda J., Brzoza K. 'Bioactive Synthetic Fibres', Vlákna a Textil 8[2]. 176-177 [2001].*
18. *Struszczyk H., Lebioda J., Twarowska-Schmidt K., Niekraszewicz A., 'New Bioactive Synthetic Fibres Developed in the Institute of Chemical Fibres', Fibres & Textiles in Eastern Europe vol. 11, No 2 [41]., pp 96-99[2003].*
19. *Struszczyk H., Research Project nr. 7 T09B 00620*
20. *Hoffman J., Niekraszewicz A., Lebioda J., Struszczyk H., 'Antiallergic nonwovens' Przegląd Włókienniczy, nr 9, pp. 41 – 44, 2005.*
21. *Task Project 'Implementation of the production of anti-allergic nonwovens', No. 6T082003 C/06102.*

Received 06.09.2005 Reviewed 24.10.2005