New Bioactive Synthetic Fibres Developed in the Institute of Chemical Fibres

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Abstract
We discuss the development of bioactive fibres mainly destined for everyday uses and medical service. We present a survey of anti-bacterial, anti-fungal and anti-mite fibres which are presently available on the market. The results are described of research in the field of manufacturing and marketing anti-microbial fibres conducted at the Institute of Chemical Fibres in Łódź.

Key words: *anti-bacterial fibres, anti-fungal fibres, anti-mite fibres, melt spinning.*

Ongoing Progress in Commodity Textile Development Based on the General Drive to Better Living Standards

The health protective and hygiene properties conferred upon textiles not only improve their wearing value, but are also harmless to the natural environment, as they inhibit the growth of pathogenic microflora and mites, and also contribute to the limiting or elimination of sources of a number of diseases, such as mycosis and allergies; one a number of increasingly common health hazards is the range of allergies caused by mildew and allergens of home dust mites, among other sources [1].

Bioactive fibres which can inhibit the growth of home dust mites and pathogenic microorganisms which often account for mycosis and allergia, will have the desired impact in the fields of human existence and activity. If not properly protected, textiles readily provide an abode for the growth of microorganisms. Excessive growth of microorganisms on textiles raises mould, stains, discolouring and odour, thus greatly harming the functions and value of fabrics. In laboratory tests, *Bacillus subtilis* and *Aspergillus niger* survived almost perfectly on fibrous material, while *Micrococus luteus* and *Escherichia coli* lost 70-90% and 5-70% of their viability in one hour respectively, and up to 99% and 99.9% in a five-day exposure to air flow [2,3].

The modification of fibrous materials with anti-microbial agents can be accomplished in two basic ways:

- by chemical finishing of fibres and textiles, and
- during the forming of chemical fibres, by introducing bioactive agents to the spun polymer.

Amongst the anti-microbial additives for textile finishing which are best known in Europe are Sanitized® and Actigard®, produced by Clariant, and Tinosan offered by Ciba (4).

The process of textile finishing with the use of anti-microbial agents has the disadvantage of creating additional charges in effluents from the wet finishing processes, and also poor laundry and wear durability, whereas the addition of the anti-microbial agent to a spun polymer, whether in solution or melt, provides a slow release of the agent resulting in a long-lasting action. Several companies are presently producing modified chemical fibres containing biocides introduced to the fibre-forming polymer.

The ASOTA GmbH [5] offers an anti-microbial polypropylene (PP) fibre called Asota Sanitized which furthermore displays an anti-mite action. The fibre contains biocides manufactured by Sanitized AG under the trade-names of MBP 96-60 and MBE 97-65.

The Amicor plus, anti-microbial and anti-mite acrylic fibres (PAN) are offered by ACORDIS. In wear and laundry the additive is slow-released, and a simultaneous diffusion of the additive proceeds from the interior of the polymer matrix to the fibre surface [6].

Montefibre has in its production range a polyester fibre (PES) called Terital Saniwear, which contains an anti-microbial inorganic additive characterised by direct contact action. The low diffusion velocity of the agent produces a long-lasting effect that sustains many washings. It is a safe material, registered by FIFRA and approved by EPA, and the fibre has been granted an Oeko-Tex Certificate [7]. The renowned European PES fibres manufacturer Trevira sells Trevira Bioactive, a fibre in which bactericidal activity ensues from the use of silver ions deposited on a ceramic carrier [8].

Ciba Speciality Chemicals has put new anti-microbial agents on the market: Irgaguard B 5000 for PP and Iraguard B 7000 for PP, PA, and PES. These agents inhibit the growth of gram(-) and gram(+) bacteria, mildew and fungi. Reportedly, Irgaguard B 5000 is a silver/zinc zeolite, and Irgaguard B 7000 is a special powdered porous glass which slow-releases silver ions in a controlled way. Both materials sustain processing temperatures over 500°C [9].

New Bioactive Synthetic Fibres Prepared at the Institute of Chemical Fibres (IWCh)

In the IWCh, research is being conducted in the field of controlled slow-release and manufacture of bioactive chemical fibres, principally synthetic and melt-spunfibres. In the case of fibres which are modified during formation from a melt, the active substance deposited in the fibre exerts a direct action and is slow-released by diffusion from the interior of the fibrous matrix to the surface.

In the course of the research, a technology was prepared to produce anti-fungal polyamide (PA) filament fibres: Bionyl MI using clotrimazol, and its complex with ZnSo4 as additive and Bionyl MII with the addition of ketakonazol. The latter was designed mainly for special hosiery and socks used in the treatment of ringworm of the feet. The filament fibres were formed in both the classical way and as POY. Microbiological testing was carried out at the Medical University of Łódź, the Institute Textile de France and the Microbiological Laboratory of IWCh according to standard SN 195 921 in force in the European Union. The testing confirmed the effective anti-fungal action of the filament fibres and fabrics containing the filaments against such pathogenic fungi as *Candida albicans, Penicillium funiculosum, Penicillium mycetomagenum* and *Aspergillus niger*. In the testing conducted at the Institute of Drugs in Warsaw according to the ISO 10 993 standard, neither systemic toxicity nor irritating or sensitising action was found.

A technology was also prepared to produce a polyamide anti-bacterial filament Bionyl B. Anti-bacterial tests made in the Microbiological Laboratory of the IWCh according to the SN 195 920 and JIS L 1902:1998 standards presently in force in the European Union proved this filament's efficacy against *Escherichii coli*. Knitwear made from these fibres was tested in the Dermatology Department of the Medical University of Łódź. The absence of any systemic toxicity or irritant action was confirmed by the tests. Fabrics containing Bionyl MII and Bionyl B manifested durable anti-microbal activity even after numerous washings.

For PP fibres, a manufacturing know-how was elaborated and production was implemented in trial runs. Two fibre types were manufactured: Akfil G, containing the anti-fungal agent ketakonazol; and Akfil B, with bactericidal salts of silver. Both fibres are spun as POY yarn from the melt. In contrast to polyamide POY yarn with its anti-fungal outfit for the manufacture of socks, the bioactive PP yarn will find application in a broader range of applications in special hosiery and apparel [10,11,12]. The Institute of Chemical Fibres and the Gumitex company from Łowicz, Poland were jointly awarded a Gold Medal at the 48th World Exhibition of Innovation Research and New Technology "Eureka'99" in Brussels for 'Bioactive polypropylene yarn with anti-fungal and anti-bacterial properties'. In further developments, an additive of cavinon was used for the modification of melt-spun PP, PA, and PES fibres. Cavinon, offered by Toagosei Co., Japan, is a mixture of compounds including isothiazolin. The mechanical properties [13,14] of the fibres are presented in Table 1.

The microbiological activity of fibres was tested according to international standards [15,16], and is shown in Tables 2 and 3. The anti-bacterial activity was tested according to the Japanese JIS L 1902:1998

Table 1. *Mechanical properties of fibres modified with an additive of cavinon.*

Fibre	Amount of additive	Linear density	Tenacity	Elongation at break
	% wt	dtex	cN/tex	%
PP	0	47.4	42.6	53.5
	0.25	48.0	41.5	48.1
	0.75	48.6	40.4	40.7
PA	0	56.7	47.4	31.0
	0.25	56.9	42.9	24.1
	0.75	56.9	44.8	23.1
PES	0	52.5	38.1	26.6
	0.25	52.6	35.1	25.6
	0.50	53.0	32.8	22.9

Table 2. *Impact of the amount of cavinon on the activity of synthetic fibres against gram (-) Escherichia coli (according to Japanese Standard JIS L 1902:1988).*

Fibre	Amount of additive	Time	Amount of bacteria on sample	Bacteriostatic activity (S)	Bactericidal activity (L)
	% wt	h	units	-	-
PP standard	0	0	$2.9x10^4$	-	-
PP standard	0	24	$7.2x10^7$	-	-
PP	0.25	24	$1.0x10^3$	4.9	1.5
PP	0.75	24	<20	6.6	3.2
PA standard	0	0	$4.7x10^4$	-	-
PA standard	0	24	$1.8x10^7$	-	-
PA	0.25	24	<20	5.9	3.4
PA	0.75	24	<20	5.9	3.4
PES standard	0	0	$2.6x10^5$	-	-
PES standard	0	24	$<2.0x10^6$	-	-
PES	0.25	24	<20	6.3	4.0
PES	0.5	24	<20	6.3	4.0

standard. The amount of bacteria colonies was counted first on the initial sample, and next after 24 hours' incubation on control and tested samples. A positive S value stands for the ability to inhibit bacteria growth on a tested sample, meaning that after the same time the bacteria amount is smaller than on the control. A positive L value indicates the bacteriocidal capacity of the tested sample, and means that the bacteria amount is smaller than at the start of the test.
Microbiological testing confirmed very good bacteriostatic and bactericidal activity against gram(-) E*scherichia coli* of the PA, PP and PES fibres with cavinon additive. The antifungal activity against the tested fungi of PP fibres modified with cavinon addition within the range of 0.25-0.75% weight was positive.

For PA fibres, a larger amount of the additive is required; good activity against *Trichophyton mentagrophytes* (which causes ringworm of the feet) was only attained with up to 1% of cavinon. It can be concluded from the tests carried out for biological activity that cavinon is best suited to work as an anti-bacterial and anti-fungal agent providing bi-functional biological activity for the modified PP and PA fibres.

Table 3. *Antifungal activity of PP and PA fibres with cavinon additive (according to SN 195921 standard).*

Amount of additive	Control fungi	Kind of fibre			
		PP		PA	
		Inhibition zone	Estimation	Inhibition zone	Estimation
%	-	mm	-	mm	-
0	Trichophyton mentagrophytes	0	insufficient	0	insufficient
0.25		0	good	0	insufficient
0.75		0	good	0	insufficient
1.0		5	good	0	good
0	Candida albicans	0	insufficient	0	insufficient
0.25		0	good	4	good
0.75		6.9	good	6	good
0	Scopulariopsis brevicaulis	0	insufficient	0	insufficient
0.25		0	insufficient	0	insufficient
0.75		0	good	0	good
0	Aspergillus repens	0	insufficient	0	insufficient
0.25		1.5	good	4.5	good
0.75		10.5	good	10.8	good

Table 4. *Mechanical properties of fibres modified with bioactive Irgaguard B 7000.*

Fibre	Amount of additive	Linear density	Tenacity	Elongation at break
	% wt	dtex	cN/tex	%
PP	0	48.5	44.1	58.0
	1.0	46.5	44.3	46.5
PA	0	59.5	46.2	45.7
	1.0	61.4	35.5	32.3
PES	0	46.0	54.9	12.3
	1.0	47.5	43.7	10.0

Table 5. *Impact of Irgaguard B 7000 additive on bioactivity of modified PP, PA and PES fibres against gram (-) Escherichia coli (according to Japanese Standard JIS L 1902:988).*

Fibre	Amount of additive	Time	Amount of bacteria on sample	Bacteriostatic activity (S)	Bactericidal activity (L)
	% wt	h	units	-	-
PP standard	0	0	5.3×10^4	-	-
PP standard	0	24	3.1×10^7	-	-
PP	1.0	24	$<2.0\times10^1$	6.2	3.4
PA standard	0	0	7.5×10^4	-	-
PA standard	0	24	2×10^7	-	-
PA	1.0	24	9.4×10^3	3.3	0.9
PES standard	0	0	8.5×10^4	-	-
PES standard	0	24	2.1×10^7	-	-
PES	1.0	24	$<4.0\times10^1$	5.7	3.3

In further work aimed at obtaining antimicrobial fibres, a product of Ciba Speciality Chemicals called Irgaguard B 7000 was used to modify PP, PA and PES fibres in the melt-spun technique. The mechanical properties [13,14] of the fibres with the additive appear in Table 4.

In the case of PA and PES fibres with 1% of Irgaguard B 7000, the tenacity dropped by approximately 20% compared to standard fibres. For PP fibres with the same amount of Irgaguard B 7000, the tenacity did not change, while elongation was lower by approximately 20% compared to unmodified fibres. In further developments, it is advisable to use either auxiliary agents to facilitate the dispersion of the bioactive agents or their master batches. Such a modification of the manufacturing procedure may contribute to improving the mechanical properties of the fibres. The microbiological properties were estimated in the Microbiological Laboratory of the Institute of Chemical Fibres according to respective international standards [15,16]. The results of the anti-bacterial activity tests are shown in Table 5.

Microbiological tests of PP, PA and PES fibres with 1.0% of Irgaguard B 7000 on a polymer mass manifested excellent bacteriostatic and bactericidal activity against gram(-) *Escherichia coli*, and an absence of activity against the fungi *Candida albicans* and *Trichophyton mentagrophytes*.

The Institute's research was recently focused on elaborating modified PP and PA fibres that could be implemented in the commercial production of anti-mite textiles. A special device was prepared for testing flat textile fabrics for anti-mite activity according to the NF 639-011 French standard. Test results confirmed the effective action of modified bioactive fibres containing biological substances from the acaricide family. The results of that research will be the subject of a separate publication.

Summary

- The use of materials which inhibit the growth of microorganisms such as bacteria, fungi and house dust mites is called for in ever more areas, mainly in medical service (infection, allergies).
- Research works into fibres are being conducted at the Institute of Chemical Fibres, Łódź, Poland, with the aim of manufacturing melt-spun synthetic fibres such as PA, PP, PES with additi-

ves of bioactive substances that inhibit the growth of bacteria fungi and house dust mites.
- The work conducted hitherto at the Institute has produced a know-how for the manufacture of bioactive PA and PP fibres which is being successively implemented in practical use.

Acknowledoment

The problem will be presented at the 3rd Central European Conference „Fibre-Grade Polymers, Chemical Fibres and Special Textiles", Portorose, Slovenia, 10-12, September, 2003.

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