Polypropylene-based long-life insecticide-treated mosquito netting

by Prof Walter Focke and Dr Walter van Pareen

Malaria causes approximately one million deaths a year and more than 300 million cases of severe illness. The World Health Organization (WHO) regards insecticide-treated nets (ITNs) as an important component in its efforts to roll back malaria.

Extensive trials using insecticide-treated nets have established their efficacy to protect against a range of vector-borne diseases. Current efforts focus on making such nets widely available and to popularise their use.

The first mosquito nets were treated with insecticidal formulations by a dipping process. However, long-life nets, treated at factory level, are preferred. ITN programmes in Africa revealed low net retreatment rates because users do not perceive the need for it. The dipping procedure is not simple and the insecticides are either too expensive or not widely available. Treatment centres are not operational or are unsustainable. The treatment of nets at factory level would be restricted to professionals who are better able to control the environmental impact of the effluents.

Netting materials used so far include cotton, nylon, polyester, polyethylene and polypropylene. Multifilament netting has apparently performed better in ITN trials and is also more comfortable. In Africa, where transmission is intense, it has been shown that it is not so much the net, but rather the insecticide in the net that provides protection against malaria vectors. Thus, it is vital to make sure that the net is treated with an effective insecticide. Therefore, this study focused on nets with the insecticide incorporated into the fibre polymer. A key target for the WHO is a product that can resist more than 50 ISO normalised washes at 60°C.

Complex issues, such as safety, efficacy, life span and cost, affect insecticide selection, formulation design and dosage level determination. Synthetic pyrethroids are the only insecticides currently used for treated nets. The WHO sanctions the use of a selected set of insecticides. The pyrethroids are lipophilic compounds that easily pass through cell membranes. They are absorbed through the skin by inhalation or ingestion. Their toxicity is related to their affinity for receptors or targets in the sodium channels essential for nerve conduction. Fortunately, their rapid metabolism greatly lowers the magnitude of the resultant toxicity.

Pyrethroid pesticides combine broad-spectrum insecticidal activity with low mammalian toxicity. Their short persistence in the environmental is a desirable property. The pyrethroids were declared acceptable by the WHO, as the ITNs showed no teratogenic, carcinogenic or mutagenic effects in experimental toxicity studies. Low dosages are used for treatment. They bind strongly to fabrics and have a low volatility. The risk of oral and inhalation toxicity by the users of treated nets is therefore remote.

Developing polypropylene-based nets

Sasol and the University of Pretoria investigated the possibility of making a polypropylene-based net. The ultimate purpose of this project is the development of long-lasting, polypropylene-based mosquito netting, which conforms to WHO specifications.

Initial effectiveness against mosquitoes

Table 1 provides an overview of the efficacy testing results for unwashed insecticide-containing socks and nets. The WHO standards specify >95% knockdown after one hour and >80% mortality after 24 hours. Socks containing any of the six insecticides tested conformed to this requirement at ca. 0.2–0.4% loading.

Effect of washing on net performance

Additives are lost from the surface via sublimation/evaporation or

Table 1: Initial effectiveness against mosquitoes in WHO cone and cylinder tests

Active	Percentage	Knockdown 1 hour	Mortality 24 hours	Method	Format
Alphacypermethrin	0.29	100	100	Cone	Net
Alphacypermethrin	0.38	100	100	Both	Net
Bifenthrin	0.38	100	100	Cone	Net
Cyfluthrin	0.38	100	100	Cone	Net
Betacyfluthrin	0.20	100	100	Cone	Sock
Betacyfluthrin	0.38	100	100	Cone	Sock and net
Deltamethrin	0.19	100	100	Cone	Sock
Deltamethrin	0.46	100	100	Cone	Sock
Deltamethrin	0.72	100	100	Cone	Sock
Lamdacyhalothrin	0.20	98	100	Cone	Sock
Negative	-	0	3	Cone	Sock

Notes: All concentrations are given on a mass basis. All yarn samples were prepared using a draw ratio of 2.37.

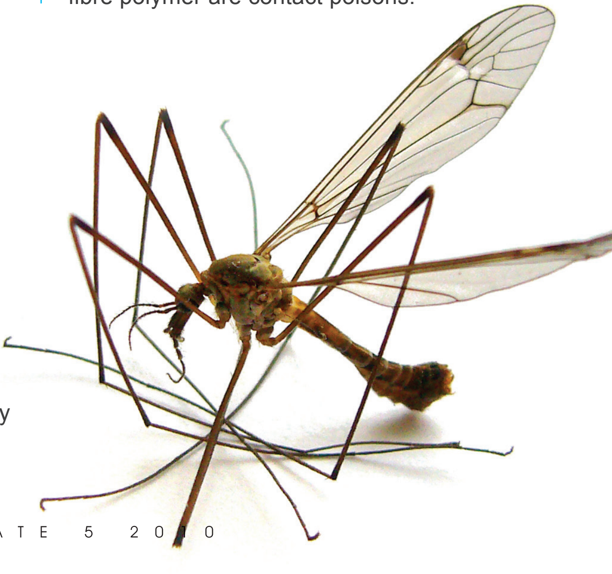
mechanical scuffing. The former rates are very slow for the current set of pyrethroids. They can probably be neglected for net lifetimes of less than five years. However, the latter mechanism also operates when the net is washed. Current WHO standards for long-lasting insecticide-treated nets require that long-lasting nets should retain their efficacy even after 20 ISO standardised washes. According to some sources, every wash removes about 30–50% of deltamethrin deposited on the surface. Other sources suggest that the figure may be as high as 95%. It is clear that the ability of multifilament yarn to retain efficacy beyond a few washes is of paramount importance. Following five washes, nets containing 0.38% betacyfluthrin or 0.29% alphacypermethrin have very high bioactivity when tested six weeks later, but the net containing only 0.19% bifenthrin does not meet the WHO criteria.

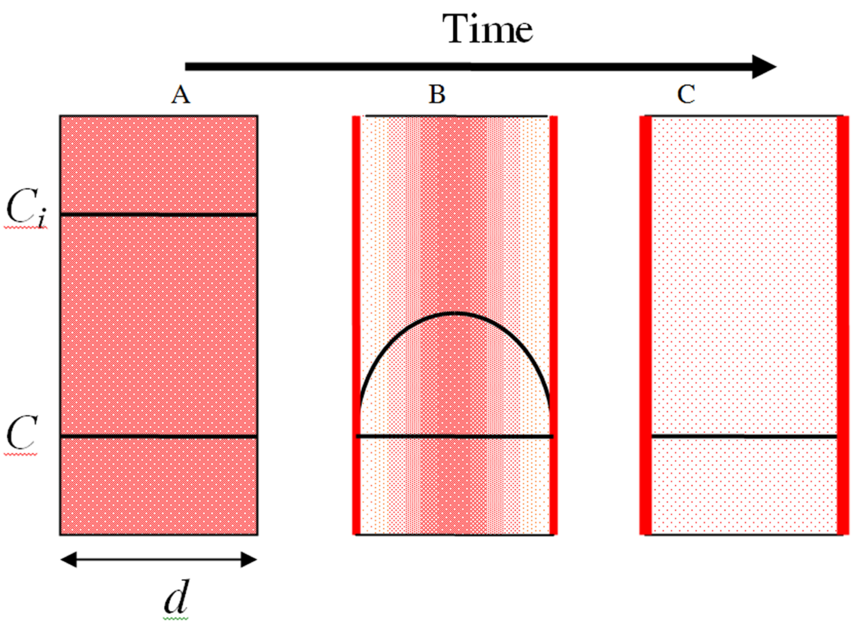
Insecticide solubility in polymers is determined by the temperature and the amount of amorphous phase available. Solubility generally increases with temperature. Polymer additives may dissolve in the amorphous parts of polymer matrices, but are insoluble in crystalline regions. This implies that the insecticide will have a higher solubility in the fully molten polymer than in the drawn fibre at ambient temperature. Full dissolution in the melt is advantageous, as it aids homogeneous dispersion of the solute in the matrix.

During fibre spinning, the melt is cooled, stretched and drawn. The process involves controlled polymer crystallisation. Concomitantly, the fraction amorphous phase available to dissolve the additive is diminished. In practice, the insecticide dosage level exceeds its solubility limit at ambient conditions and it therefore becomes trapped in a supersaturated state inside the polymer. In an effort to return to an equilibrium state, the additive may diffuse to the surface of the fibre. Here it accumulates and may eventually form crystalline deposits.

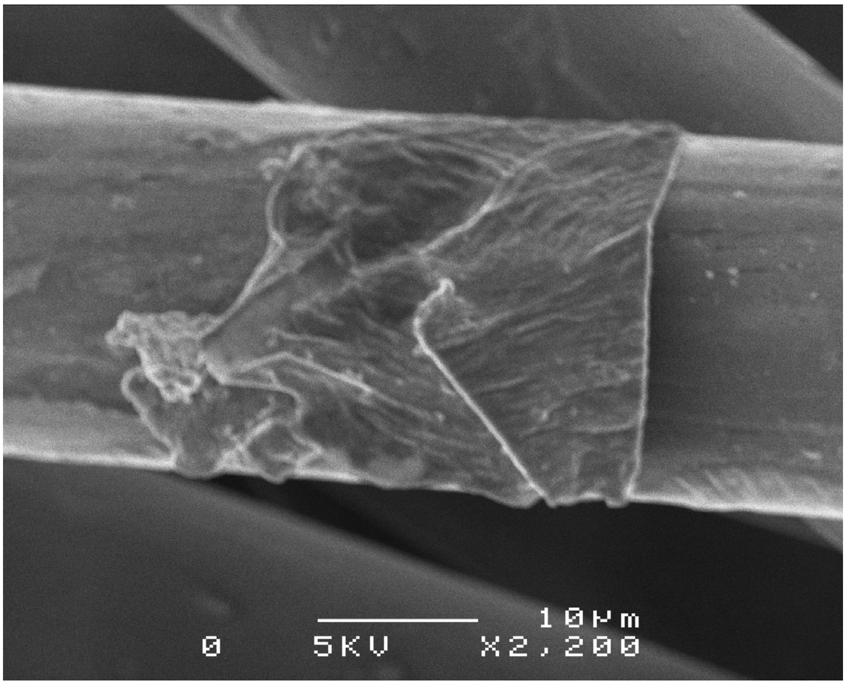
Data obtained during this investigation indicated that the pyrethroid additives stay amorphous when cooled rapidly from their melt. The idealised additive blooming process for an amorphous additive present above its glass transition temperature is illustrated schematically in Figure 1.

Blooming is an undesirable phenomenon when the additive is a stabiliser or colourant. It leads to the effective loss of active from the system and causes surface blights. The insecticides incorporated into the fibre polymer are contact poisons.





→ *1. Schematic representation of the surface blooming mechanism in a fibre with diameter d. The intensity of the red colour scales with the insecticide concentration.*

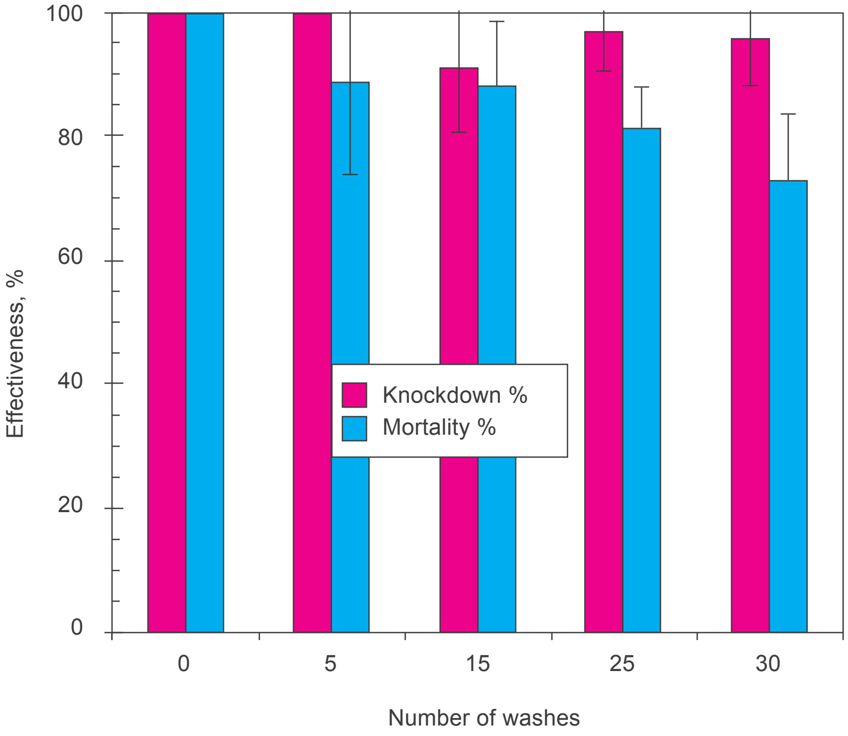


→ *2. SEM picture of a damaged part of a fibre containing 0.57 cyfluthrin that shows the covering "skin".*

To be effective, they have to be available above the minimum effective surface concentration on the outside of the fibre. Thus, in this application, blooming is a desirable process that facilitates additive transport to and accumulation at the fibre surface. The data presented in this research provides evidence that some nets at least retain their bioactivity for several wash cycles. It is, therefore, of interest to determine the actual distribution of the actives in the polymer fibre. Fortunately, some of the actives are fluorescent and this property was exploited through confocal microscopy. This technique facilitates three-dimensional (3-D) visualisation of the additive distribution in the fibre. Visual inspection of the 3-D image revealed the presence of small fluorescent spots throughout the fibre with areas of higher intensity fluorescence near or at the surface of the fibres. The image obtained for the net containing cyfluthrin showed very weak fluorescence, suggesting that virtually all the active was lost after even five washes. In contrast, a net made from deltamethrin still showed comparable fluorescence even after ten washes. This difference may be attributable to the difference in the physical nature of the two additives. Deltamethrin is highly crystalline with a high melting point (>100°C), while cyfluthrin is a viscous liquid at room temperature (it is amorphous and above its glass transition temperature). It is, therefore, easier to remove the cyfluthrin from the fibre through a washing process.

The second assumption made concerning the isotropic nature of the idealised fibre was found to be invalid. Scanning electron microscope (SEM) pictures of the fibres showed the clear presence of a thin skin-like structure that covers the outside of the fibres. It appears that this skin is not strongly bonded to the fibre core. It easily detaches to form blisters when the fibre is severely mechanically stressed.

Figure 2 shows a particularly striking picture of such a piece of skin folded back over the fibre shaft, revealing the structure underneath. Confocal microscopy revealed an intense fluorescence from the underside of this skin. This suggests that the skin may represent a membrane-like barrier to



→ 3. Efficacy testing results for nets containing 0.38% betacyfluthrin.

outward migration of the actives. Thus, active may be accumulating just below this skin rather than on the outside of the fibre. Clearly, if this were the case, better wash resistance would be the result. The skin morphology was also observed in neat polypropylene fibres. However, SEM pictures suggest that it is more pronounced in fibres containing low-density polyethylene.

Conclusions

Efficacy testing results for unwashed socks showed encouraging results. Most samples containing 0.19% active complied with the WHO requirements (>95% knockdown after 60 minutes and >80% mortality after 24 hours). Analysis reveals that blooming from the thin fibres in the multifilament yarn will be rapid with a time constant of less than one day. Washing is known to remove in excess of 30% active on the fibre surface per wash. This implies that it is unlikely that fibres containing amorphous additives such as cyfluthrin will achieve the minimum of 20 washes stipulated by the WHO. Better results were obtained with the crystalline betacyfluthrin form, as shown in Figure 3.

Multifilament polypropylene yarns that contain WHO-approved insecticides were successfully produced on a production spinning line. The fume generation during extrusion with pyrethroids necessitates superior ventilation, extraction and scrubbing systems.

***Prof Walter Focke** is a professor in the University of Pretoria's Department of Chemical Engineering, Director of the Institute of Applied Materials and incumbent of the Chair in Carbon Technology and Materials. He received a grant from the Bill and Melinda Gates Foundation for the development of an indoor spray to control malaria transmission.*

***Dr Walter van Pareen** is Business Support Team Manager at Sasol ChemCity. He completed his master's degree in Chemistry in 1991 and joined Sasol, where he gained valuable experience in entrepreneurship, including research and development, international marketing, business management, production management and financial management. He joined Sasol ChemCity in 2005, a Sasol subsidiary with the main focus of SMME development and job creation in the chemical and related industries.*

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