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Bicomponent fibres for controlled release of volatile mosquito repellents

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ABSTRACT

Core-sheath structured fibres were developed for application as part of an alternative malaria vector control intervention aimed at reducing outdoor malaria transmission. The fibres were prepared by melt spinning of high density polyethylene (HDPE) as sheath and with a concentrate containing volatile *N*,*N*-Diethyl-*m*-toluamide (DEET) in poly(ethylene-co-vinyl acetate) (EVA) as core. The concentrate was prepared by a simple absorption processes to a content up to 40 wt% DEET. Scanning electron microscope imaging confirmed the formation of a bicomponent core-sheath fibre structure. Confocal Raman spectroscopy revealed the development of a concentration gradient of DEET in the sheath layer, suggesting a diffusion controlled release process. Excellent processability was demonstrated on an extrusion system melt spinning with take up speeds reaching 3000 m min^{-1}. Sample textiles knitted from such filaments showed high residual repellence activity even after 20 cold washes or after eight months ageing under laboratory conditions. These findings indicate that this technology offers an alternative way to prevent outdoor mosquito bites in an effective and affordable manner.

1. Introduction

Mosquito-borne pathogens remain the single most important cause of infectious disease on our planet. Of these, malaria tops the list, with 216 million cases recorded globally in 2016, resulting in 445,000 deaths [1]. Lymphatic filariasis, also known as elephantiasis which potentially manifests as painful and profoundly disfiguring cases, afflicted an estimated 120 million people according to a 2007 report [2]. Increasing concern is also widely being expressed due to the spread of a number of mosquito-borne arboviruses across large regions of the globe, including dengue, chikungunya, Zika, but also several others affecting millions of people [3, 4]. Control of these diseases is in most cases based on interventions aimed at reducing mosquito populations. In the case of malaria, the most important control strategy globally has been Indoor Residual Spraying (IRS) of insecticides and use of Long-Lasting Insecticide Nets (LLIN's) [1]. However, widespread and increasing resistance to the most commonly used insecticides within the main vector mosquito species adapting to these indoor-targeted interventions has now resulted in clear indications of increasing malaria [1]. There are also indications that the aggressive deployment of IRS and LLINs has altered the feeding behaviour of mosquitoes from indoors to outdoors [5, 6]. If this is the case, further reductions in the malaria incidence in Africa will require implementation of alternative vector control techniques [7, 8]. Therefore, targeting outdoor biting mosquitoes could have a significant impact in reducing malaria transmission. Topical repellents are used to prevent or at least reduce mosquito bites in typical outdoor settings. *N*,*N*-Diethyl-*m*-toluamide (DEET) is the most widely used topical repellent active [9–11]. The main problem with topical repellents is that their residual efficacy lasts for a few hours only [12]. This means that the repellent must be re-applied repeatedly and this makes it expensive for use in poor rural communities where malaria is most prevalent. Effective alternative formulations, including microencapsulated repellents that offer longer lasting residual efficacy are available but these tend to be prohibitively expensive for use in Africa [13].

The three most common malaria vectors in Africa, i.e. *An. arabiensis*, *An. gambiae* s.s. and *An. funestus* have a strong preference for feeding close to ground-level [14, 15]. In particular, for rural village inhabitants engaged in typical cooking and social activities, these mosquitoes overwhelmingly target the lower limbs, ankles and feet regardless of whether they are indoors or outdoors [14, 16]. It has also been shown that under such conditions of standing or being seated, preventing

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access to these preferred areas of the body does not result in these malaria vector mosquitoes moving to other parts of the body, but that they will instead fly off to find other hosts with exposed lower limbs [14]. These findings suggest that the simple approach of protecting the selected body sites, i.e. ankles and feet, should help to reduce outdoor malaria transmission [17, 18].

Malaria is endemic in mostly poor and underprivileged areas of Africa [19–22]. Children in these areas often walk barefooted. This makes them vulnerable to malaria infection via lower limb mosquito bites. An intervention that can protect the lower limb region, the ankles and the feet, may therefore significantly reduce malaria transmission rates, particularly amongst children in Africa.

Long-lasting repellent fabrics have been developed. The most widely used insect repellents used for treating such fabrics are DEET and permethrin [23–25]. These repellents have been incorporated into the fabric materials using innovative techniques e.g. direct coating of permethrin onto fabric yarn [26] or microencapsulated repellents in fabric finishes [23, 27–29].

In this study, we report on the development of mosquito-repelling polymer fibres. The fibres were knitted into repellent fabrics intended for the protection of ankles and feet. The concept is based on bicomponent polymer filaments with the polymer in the core containing a volatile repellent added as a concentrate while a less permeable polymer is employed in the sheath layer. The development was conducted in two steps. In a first part principle parameters of core sheath fibre preparation was investigated using a piston spinning device. In a second part melt spinning was performed using universal spinning equipment with two extruders. The fibres were then knitted into repellent fabrics intended for the protection of ankles and feet. The durability of the repellence activity of such fabrics against cold washing as well as time was tested. The proposed technology may offer a route to cost-effective repellent textiles that may compete with other currently available repellent textile technologies. Such fabrics may facilitate affordable personal protection clothing items such as insect repellent socks or ankle covers.

2. Materials and methods

2.1. Materials

High density polyethylene (HDPE) was chosen as the sheath polymer. It was expected that it would feature a low permeability to the insect repellent because of its high crystallinity and the low solubility of DEET in this material. Borealis HDPE VL9500, a fibre grade HDPE suitable for bicomponent fibre extrusion, was chosen for the laboratory filament extrusion experiments. The melt flow index (MFI) of this material was 34 g/10 min at 190 °C/2.16 kg. Owing to material availability issues, the pilot scale production trials utilised instead DOW grade 25055E (MFI 25 g/10 min at 190 °C/2.16 kg; density 0.953 g cm^{-3}) as the sheath polymer. According to the manufacturer, the latter materials have a very narrow molecular weight distribution. Based on the density, the crystallinity of this material is estimated at 70 wt% while that of the Borealis grade VL9500 was 65 wt% [30].

Preliminary tests showed that poly(ethylene-*co*-vinyl acetate) grades of high vinyl acetate content swell and absorb significant amounts of DEET when exposed to the liquid at elevated temperatures. Therefore Arkema EVA grade Evatane 2020 (MFI 17–23 g/10 min at 190 °C/2.16 kg, density 940 kg m^{-3} and a VA content of 19–21%) (EVA) was chosen for the core of the bicomponent filaments. DEET (stated purity of 97% purity, a density of 0.998 g cm^{-3}, vapour pressure of < 1 Pa at 25 °C and a normal boiling point of 288 °C) was supplied by Sigma Aldrich and used as is. DEET has relatively very low volatility at room temperature. In a previous unpublished study, thermal stability investigations indicated that DEET is physically and chemically stable at melt fibre spinning conditions.

2.2. DEET absorption by EVA

The EVA pellets were loaded with DEET by facilitating swelling at elevated temperatures [31]. An excess quantity of DEET liquid added was sufficient to fully submerge the pellets in glass bottles. The containers were sealed and heated in a convection oven with the temperature set 81 °C for 24 h. The excess DEET was drained from the sampled bottles and methanol was used to rinse away any excess DEET still remaining on the surface of the polymer pellets. The pellets were then allowed to dry for a few minutes on paper towels before weighing. This process yielded swollen EVA pellets containing 40 wt% DEET. This was established by thermogravimetric analysis (TGA) on a PerkinElmer TGA 4000 as follows: Samples in alumina pans were heated to high temperature at a rate of 10 °C min^{-1} using inert nitrogen as the purge gas flowing at 50 mL min^{-1}. EVA samples containing lower amounts of DEET were prepared by reducing the oven exposure time. Those were only used for the purpose of finding optimal fibre spinning conditions.

2.3. Filament extrusion and fibre spinning

Laboratory scale bi-component filament extrusion trials were conducted on the in-house designed-and-built piston melt spinning equipment at Leibniz Institute of Polymer Research Dresden e. V. (IPF Dresden e. V.). This system comprised two heated piston plunger pumps, one for the core component and the other for the sheath component. Drawdown was not possible with this setup but it was possible to vary the winding speed. Initial experiments aimed to establish the spinnability of the neat EVA in combination with the HDPE. Once suitable process conditions and material combinations were found, bicomponent filament extrusion using DEET impregnated EVA pellets commenced, starting with low DEET levels and slowly increasing the concentration.

The pilot scale melt spinning trials were performed on a bicomponent extruder melt spinning machine. It consisted of two extruders. A single screw extruder was used for the core (Emil Blaschke model 74,060–067) and a co-rotating twin screw extruder (Leistritz model MIC 18/GL-300) for the fibre sheath component. The melt spinning temperature was set at 160 °C. The melt generated by these two extruders was metered via separate gear pumps into the bicomponent die spinning head pack.

2.4. Fibre and yarn characterization

The filament or fibre samples were embedded in epoxy resin, cooled to liquid nitrogen temperatures after setting, and cut with a diamond knife. The specimens were gold coated before viewing on the SEM. The images were recorded with a Zeiss Ultra Plus field emission electron microscope at an acceleration voltage of 3 kV.

The concentration gradient of DEET in a laboratory-prepared filament was determined with a WITec alpha300R confocal Raman Imaging System as a function of filament depth. A 20× Zeiss objective was used. The Raman spectra were recorded using a 785 nm 75 mW laser. The integration time was 0.5 s and an average of 200 accumulations was recorded.

Tensile properties of the extruded filaments and pilot scale-produced yarn were determined on a 100 N Zwick/Roel Z0.5 universal testing machine at a draw speed of 200 mm min^{-1}.

2.5. Knitting

Knitting trials were performed at ITM, TU Dresden using a Shima Seiki flat knitting machine SWG091mini gauge E15. This machine type is ideally suited for the seamless manufacturing of net shape products. Slide needles and sinkers positioned very close to the needle enable a knitting process of complete net shape garments without the need of using a takedown system. To ensure a proper fabric structure six single