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Mthokozisi Sibanda, Andreas Leuteritz, Harald Brünig, and Walter Focke

Development Of Polyolefin Bicomponent Filaments As Controlled Release Devices Of Volatile Repellents For Use In Malaria Vector Control

Mthokozisi Sibanda[1,a)], Andreas Leuteritz[2,b)], Harald Brünig[2,c)] and Walter Focke[1,d)]

[1]*Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, Private Bag x20, Pretoria, 0028*
[2]*Leibniz Institute for Polymer Research Dresden (IPF), Hohe Straße 6, 01069 Dresden*
[a)]Corresponding author: u29709874@tuks.co.za
[b)]andreas.leuteritz@ipfdd.de
[c)]bruenig@ipfdd.de
[d)]walter.focke@up.ac.za

Abstract. The work presented here describes the development of controlled release and affordable mosquito repellent bicomponent polymer filaments. These filaments may be used in the production of alternative malaria vector control interventions aimed at reducing outdoor malaria transmission in resource-limited communities. The approach was to develop a bicomponent polymer filament with a core containing the volatile repellent active and an outer membrane layer that reduces the rate at which a volatile active is released to the atmosphere. The bicomponent filament was produced by a simple melt extrusion and drawing process. The core polymer used was poly(ethylene-co-vinyl acetate) (EVA) and the sheath polymer was high density polyethylene (HDPE). 40 wt.% N,N-Diethyl-*m*-toluamide (DEET) was incorporated into the EVA via a simple absorption process at a temperature of approximately 81 °C. Scanning electron microscopy (SEM) studies indicated that a bicomponent core-sheath structure was successfully formed by the melt extrusion and drawing process. Raman studies showed that a concentration gradient developed across the bicomponent filament after the manufacturing process. The Raman results suggest that the release of the repellent from the bicomponent filament is a diffusion controlled process, a characteristic of controlled release. With these findings, the study should proceed to the upscale of repellent impregnated bicomponent yarn production and fabric knitting. Such a fabric can be further studied for effectivenes in reducing outdoor malaria transmission in laboratory and field trials.

Key words: bicomponent, controlled release, malaria, mosquitoes, repellent

INTRODUCTION

Malaria is a debilitating parasitic disease that is transmitted by mosquitoes. Malaria mostly affects sub-Saharan Africa. Of the 394200 deaths recorded in Africa in 2015, 292000 were in children under the age of 5 [1]. Currently, there are no adequate interventions that can be used to mitigate outdoor mosquito bites. Further successes in malaria reductions in Africa will rely on the development of alternative vector control [2]. It is clear that targeting outdoor biting mosquitoes will have a significant impact in reducing malaria transmission. Topical repellents may be 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 [3]. The main problem with topical repellents is that they have a residual efficacy of a few hours, which is very short [4]. To maintain effective residual repellent efficacy, these topical repellents must re-applied repeatedly. This makes them expensive for use in poor communities where malaria is most prevalent. The three most dominant malaria vectors in Africa i.e. *An. arabiensis, An. Gambiae s.s.* and *An. Funestus* have been shown to have a strong preference of feeding close to the ground level particularly targeting lower limbs, ankles and feet. This is regardless of whether they are indoors or outdoors [5]. Furthermore, it was shown that if the subjects were lying down they were

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randomly bitten on lower edges of parts of the body in contact with the ground. Another important detail is that if the lower limbs were protected i.e. mid calf and below, these vector mosquitoes did not attempt to fly higher in search of alternative biting sites but instead preferred to seek another victim. These findings present a simplified problem of reducing malaria transmission by protecting selected body sites. In this study, we report on the development of controlled release and affordable mosquito repelling bicomponent polymer filaments. These filaments can be knitted or woven to produce textiles used in the production of affordable personal protection clothing items such as insect repellent socks or ankle covers. The approach was to develop a bicomponent polymer filament with a core polymer impregnated with a volatile repellent active and a sheath layer that reduces the rate at which the volatile active is released to the atmosphere (figure 1). This proposed technology may offer significantly cheaper and more effective repellent fabrics than currently available repellent fabric technologies.

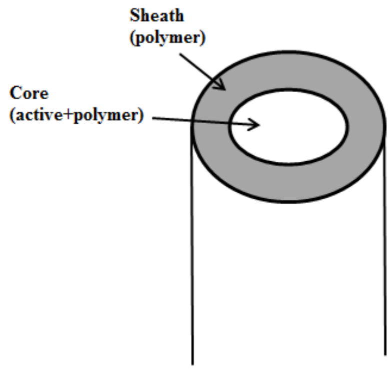


FIGURE 1. Schematic of envisaged bicomponent filament

EXPERIMENTAL

High density polyethylene (HDPE) (Borealis VL9500) with a melt flow index (MFI) of 34 at 190 °C/2.16 kg was used as the sheath polymer. Poly(ethylene-co-vinyl acetate) (EVA) (19 – 21%) (Evatane 2020) with an MFI of 21 at 190 °C/2.16 kg and a VA content of 19-21% was used as a core polymer. DEET with 97% purity, a density of 0.998 g/cm^3 and a normal boiling point is 288 °C was obtained from Sigma Aldrich. Bicomponent filament spinning trials were done using an in-house developed extrusion and melt drawing equipment. The equipment consisted of two heated cylinders with a plunger, one extruding the core and the other extruding the sheath. Scanning electron microscopy (SEM) images of produced filaments were recorded using a Zeiss Ultra Plus field emission spectroscope. The samples were embedded in an epoxy resin and frozen to -175 °C using nitrogen and cut with a diamond knife. The samples were then coated with gold before viewing. The concentration of DEET as a function of depth was studied using a RAMAN Imaging System WITec alpha300R. The spectra were taken using a 785 nm laser with an intensity of 75 mW. The objective used was 20x (Zeiss). The integration time was 0.5 s and accumulation was 200 acc. Total DEET content in the filaments was characterised using thermogravimetric analysis (TGA). The sample was placed in a Perkin Elmer TGA 4000 and the temperature was ramped up at a rate of 10 °C/min. The purge gas was nitrogen flowing at 50 mL/min. The mass loss was tracked as a function of temperature. The mechanical testing of the spun filaments were conducted using a Zwick/Roel Z05 universal test machine.

RESULTS

Extrusion and filament spinning

DEET was first incorporated into EVA pellets via absorption at 81 °C over a 24 hour period. The bicomponent melt spinning was a fairly simple process. The final melt temperature used was 160 °C and the maximum filament draw down speed was 800 m/min. The core-sheath melt throughput was fixed at 0.5 g/min respectively.

Thermogravimetric analysis

Figure 2 shows TGA traces of the produced bicomponent filament. The first mass loss event is attributed to DEET evaporation from the filament. The results indicate that a maximum of *ca.* 20 wt.% (based on total filament weight) was impregnated into the bicomponent filament.

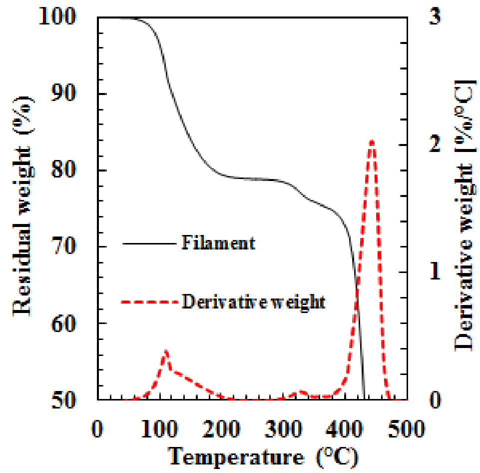
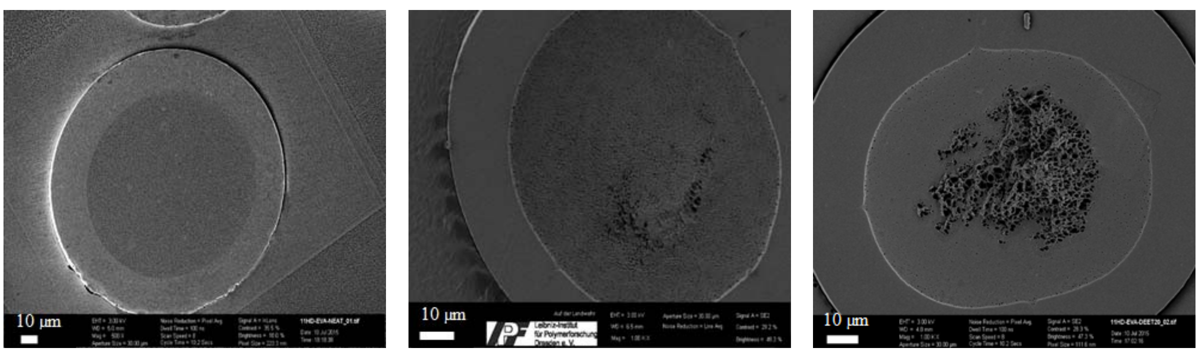


FIGURE 2. TGA traces of the lower and higher DEET content bicomponent filaments

Scanning Electron Microscopy

SEM cross-sectional micrographs of neat and DEET impregnated bicomponent filaments are shown in figure 3. All the filaments were produced at an equal core-sheath throughput of 0.5 g/min at 160 °C and a filament winding speed of 50 m/min. The micrographs show a perfectly formed core-sheath structure.

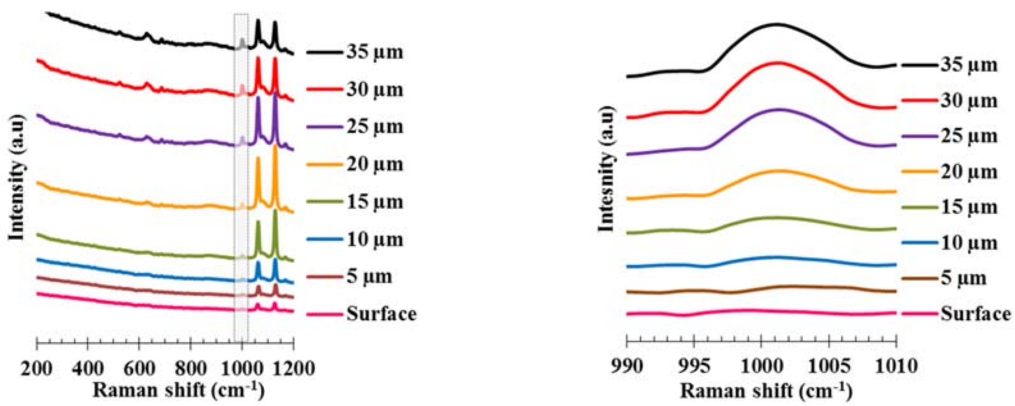


(a) (b) (c)

FIGURE 3. SEM micrographs of HDPE/EVA bicomponent filaments. (A) neat filament, (B) filament impregnated with *ca.* 10 wt.% DEET and (C) filament impregnated with *ca.* 20 wt.% DEET

DISCUSSION

The process of bicomponent filament spinning involves the drawing and cooling of melt. This aligns the polymer chains in the axial direction increasing the tenacity of the filament. At the same time, both polymer phases crystallize diminishing the amount of amorphous matrix available for dissolving the repellent active. The solubility of the active in the crystallized polymers drastically reduces creating a state of supersaturation. This causes blooming of the active relatively quickly in an effort to return to equilibrium [6]. DEET is a spatial repellent. It has to be available as a vapour in the immediate atmosphere surrounding the filament in sufficient quantities to effectively repel mosquitoes. The repellent in the vapour phase must constantly be replenished by the liquid repellent that has diffused to the surface of the filament. This implies unsteady diffusion of the liquid repellent from the core of the filament (EVA) to the surface via the HDPE sheath. If this was the case we would see a concentration gradient built up across the filament cross-section up to the centre point [7]. To test whether a concentration gradient had developed, we carried out a concentration profile study with increasing filament depth. In this study a Raman laser beam was focused within the filament at different depths to determine the respective DEET concentrations. Figure 4 shows Raman spectrograms at different depths for the filament containing *ca.* 20 wt.% DEET. The absorption at *ca.* 1000 cm^{-1} is attributed to DEET.



(a) (b)

FIGURE 4. Raman spectrograms of bicomponent filament containing 20 wt.% DEET based on total mass of fibe. (A) shows the spectra generated for the bicomponent filament. (B) shows zoomed in spectrograms attributed to DEET at *ca.* 1000 cm^{-1}

This absorption band gradually increases in size and in area as the filament is penetrated by the laser from the surface to the centre. This observation clearly shows a build up of a concentration gradient indicating the controlled release of DEET from the bicomponent filament. The development of the bicomponent filament has been done using HDPE and EVA. These polymers are relatively cheap and this will make the final product affordable. DEET was used as the volatile active. The reason we used DEET is because it is the most widely used and most effective repellent on the market [4]. In future studies, we should consider incorporating alternatives to DEET into the bicomponent filaments. IR3535 and picaridin are effective synthetic alternatives. P-menthane-3,8-diol may be considered as a potential natural repellent alternative.

CONCLUSIONS AND RECOMMENDATIONS

Increasing the residual effectiveness of repellents can make a significant impact in reducing outdoor malaria transmission. This work has proven the concept of trapping a liquid repellent and slowly releasing it into the environment using bicomponent filaments in laboratory scale studies. These filaments can be manufactured cost effectively by a simple melt extrusion and drawing process. This technology may offer a longer lasting residual repellent effectiveness compared to microencapsulation whilst offering a cost advantage. A wide range of repellent actives should also be considered for impregnation into the bicomponent filaments as alternatives to DEET. Further work needs to be carried out in upscaling the production of bicomponent yarn impregnated with repellent. This yarn can be knitted into a fabric that can be subjected to laboratory and field repellence testing. These studies will shed light on the effectiveness of this technology in reducing malaria transmission.

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