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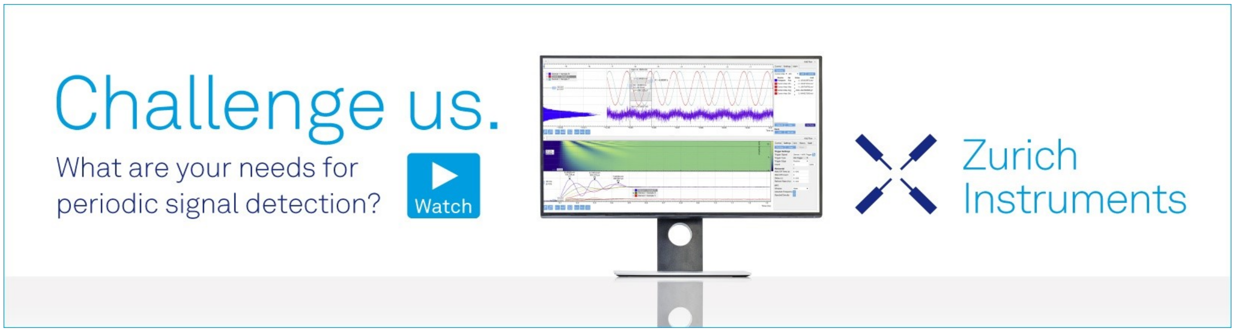

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Mosquito Repellent Microporous Polyolefin Strands

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Abstract. Pyrogenic silica and organoclay nanocomposite strands containing liquid mosquito repellents were prepared by twin-screw extrusion compounding. The mosquito repellents DEET and Icaridin were immobilized in the pores of a microporous polyolefin matrix. The nature and levels of the repellent and nanofiller employed affected the material phase morphology. The repellent release was followed as a function of ageing time in convection ovens set at 50 °C. The release rates were a described by a mathematical model that considered the microporous internal structure. In most cases, the integral skin covering the strands determined the repellent release rate. The implication of these findings is that Icaridin is an attractive candidate for long-lasting wearable mosquito repellent devices.

INTRODUCTION

Mosquito-borne diseases are the principal cause of infectious-disease morbidity and mortality in humans. Malaria, in particular, is a principal cause of illness and death in countries where the disease is endemic. According to the World Health Organization, in 2017 alone around 219 million malaria cases were reported with an estimated 435.000 malaria deaths [1]. Most of the reported cases occurred in sub-Saharan Africa. WHO recommends indoor residual spray of insecticides (IRS) and indoor use of long-lasting insecticide-treated bed nets (LLINs) as the practical methods for the prevention of malaria. However, relying solely on IRS and LLINs faces serious challenges. Furthermore, in some Africa countries vector resistance to insecticides (especially pyrethroids) is emerging. Therefore, development of complementary vector control methods is urgently required in order to prevent invective mosquito bites. Personal protection against mosquitoes by the use of repellents has become a useful method that can reduce and/or prevent transmission of many insect-borne diseases. Repellent products, such as creams, roll-ons and sprays, are available on the market for outdoor protection. However, most of these applications provide a very short period of protection. In the case of topical skin applications, they have very short protection periods and frequent applications are necessary. Thus, repeated application is required due to environmental effects such as excessive sweating, humidity and insect activity. Besides, frequent use of repellent products is not be affordable in poorer communities. Longer periods of protection from insect bites are thus required. The aim of the present investigation was to develop a new product (such as an anklet or bracelet) by incorporating mosquito repellents in a polymer matrix. The target was to repel mosquitoes for an extended period while at the same time keeping the product cost effective. Such a product will be especially valuable in outdoor situations. A possible method of achieving this is to use polyolefin strands filled with a repellent. Polyolefins were chosen because they are widely available and cost effective. This would make the total cost of the final product affordable, an important consideration in this project.

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The presence of impermeable clay sheets or platelets enforce a tortuous diffusion path in the polymer matrix. This increases the effective diffusion coefficient in the material. It in effect, it reduces the permeability of the polymer membrane limiting the release rate of the active ingredient, i.e. the volatile repellent [2,3].

EXPERIMENTAL

Materials

N,N-Diethyl-*3*-methylbenzamide (purity 97%) [CAS-No. 134-62-3] was supplied by SigmaAldrich. Icaridin (purity ≥ 97%) [CAS-No. 119515-38-7] was obtained from Endura S.pA. All compounds were used as received, i.e. without further purification. Linear low-density polyethylene (LLDPE) (Sasol HR411) was obtained from Sasol. The density was 0.939 g cm^{-3} and the MFI was 3.5 g/10 min (190 °C/2.16 kg). Dellite 43B organoclay was supplied by Laviosa Chimica Mineraria S.pA. Fumed silica (HDK® N20 pyrogenic silica) was supplied by Wacker silicones.

Methods

Extrusion compounding

Polymer nanocomposites (without repellent) were prepared by dispersing the clay into the polymer powder with a Sigma spice grinder.The extrusion compounding of the polymer-repellent strands was performed on the TX28P 28 mm co-rotating twin-screw laboratory extruder. The temperature profiles, from hopper to die, was set at 140/160/170/170 °C. The screw speed was 150 rpm. The exiting polymer strands were quench-cooled in an ice-water bath to ensure the formation of a co-continuous phase structure in the homogeneous polymer-repellent melt mixture exiting the extruder.

Repellent release rate study

The time-dependent release of the repellents from the strands was determined by ageing in a convection oven at 50 ºC for at least 125 days. The strands were suspended from the inside roof of the ovens in the form of loose coils. They were weighed twice a week. The time dependent release followed the implicit theoretical expression in equation 1. It links the elapsed time (*t*) to the amount of repellent remaining (*X*) in the microporous cylindrical body covered with a membrane coating [4]:

$$\kappa_1 t = \kappa_2 \left(1 - X\right) + X \ell n X \tag{1}$$

where t is the time, and κ_1 and κ_2 are parameters that depend on the strand structure and dimensions, the compositions as well as temperature dependent physical properties.

Characterization

Thermogravimetric analysis (TGA)

The repellent content in the polymer strands was characterized using thermogravimetric analysis (TGA) on a TA Instruments SDT-Q600 Simultaneous TGA/DSC. Samples, weighing approximately 16 mg, were heated from ambient temperature up to 300 °C at a rate of 10 K·min^{-1}. The purge gas was N_2 flowing at 100 mL·min^{-1}.

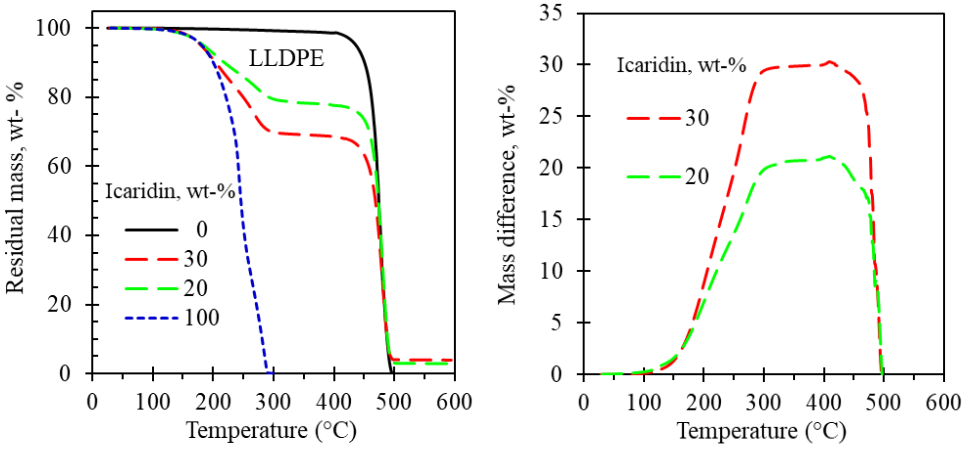
Scanning electron microscopy (SEM)

Repellent-free polymer strands were immersed in liquid nitrogen for approximately 1 h and then fractured. The fracture surface was coated six times with carbon using an Emitech K950X sputter coater prior to analysis. The morphology of the LLDPE strands was evaluated with a Zeiss Ultra 55 Field Emission Scanning Electron Microscope at acceleration voltages of 1 or 2 kV.

RESULTS AND DISCUSSION

Repellent content by TGA

Figure 1(a) shows typical TGA traces obtained for the repellent Icaridin, the neat LLDPE polymer, as well as representative Icaridin-filled polymer-clay nanocomposites. The evaporative mass loss of the neat Icaridin commenced just above 126 °C and was complete by 294 °C. The first mass loss in Icaridin is attributed to the volatilization of Icaridin. The evaporation of the repellent is suppressed when it is trapped in the LLDPE strand. The Icaridin content was evaluated as follows. The difference between the mass loss for the neat LLDPE and that for the nanocomposite was plotted against temperature as illustrated in Figure 1(b).

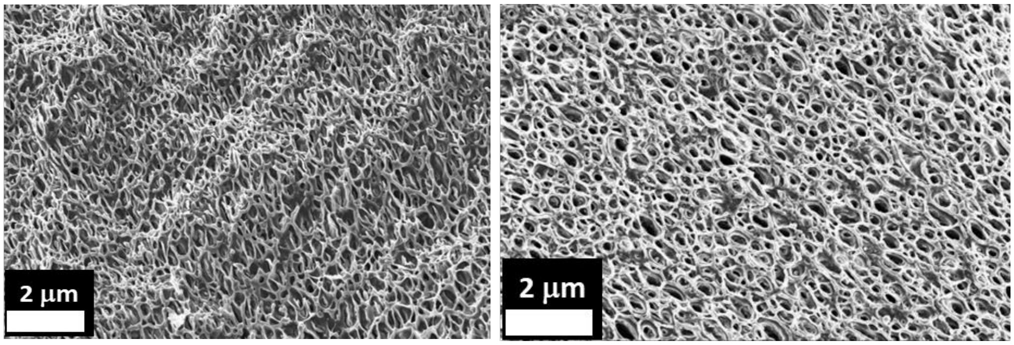


(a) (b)

FIGURE 1. (a) TGA mass loss traces for Icaridin, the neat LDDPE and two Icaridin-filled polymer nanocomposite strands containing 5 wt.% Dellite 43B clay obtained in a nitrogen atmosphere. (b) Plot of the difference in mass loss between the LLDPE and the nanocomposites.

Morphological analysis by SEM

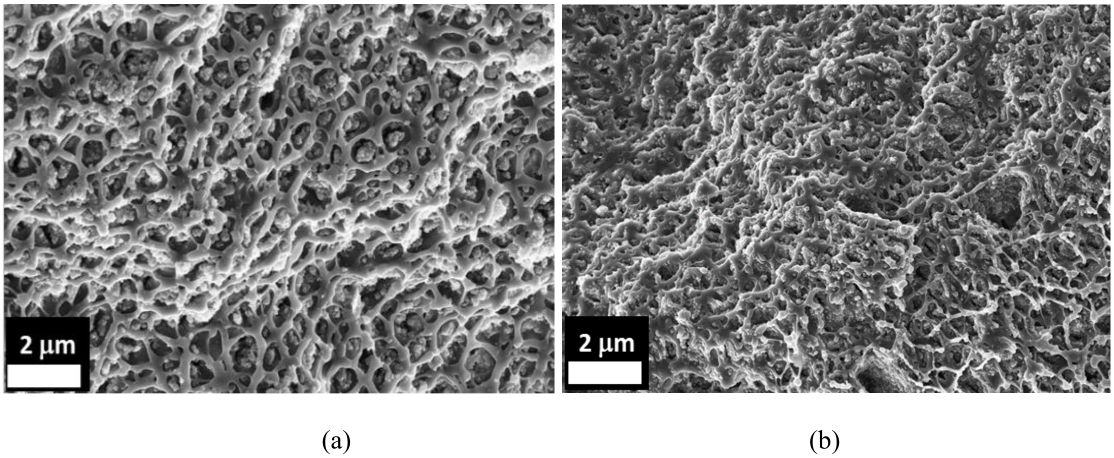
Figure 2 shows the effect of the repellent type DEET and Icaridin on the LLDPE phase morphology. The open-cell foam structure of the polymer scaffold comprising the internal parts of the strands is clearly visible. The open-cell acts as reservoir for large amounts of the repellent. It is clear that the type of repellent did affect the morphology of the strands, as it gave rise to different microporous structures.



(a) (b)

FIGURE 2. SEM micrographs showing the effect of insect repellent type on the structure of the internal microporous region of extruded LLDPE strands containg (a) 30 wt-% DEET; and (b) 30 wt-% Icaridin

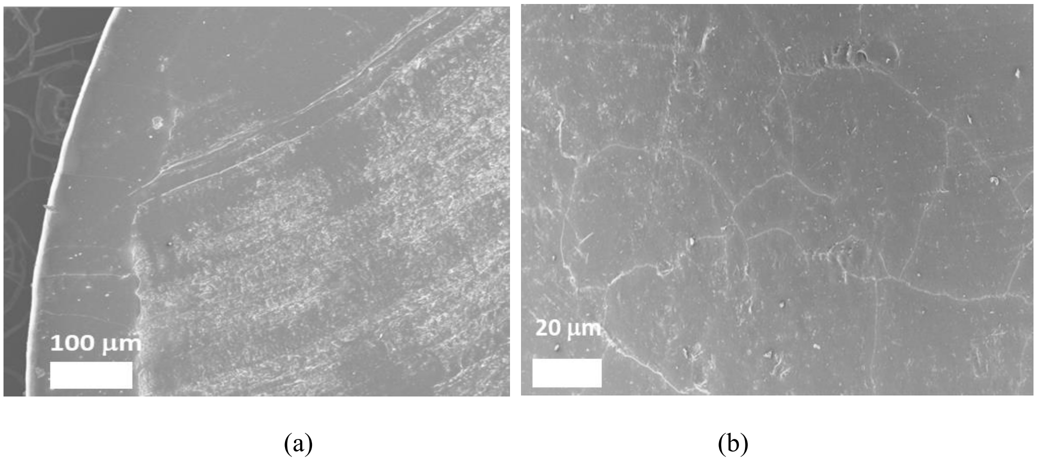
Figure 3 shows that the morphology of polymer strands changed with the incorporation of fumed silica into the microporous polymer strand effect of fumed silica. The micrographs reveal the presence of agglomerated fumed silica particles inside open cavities. This suggests that the fumed silica was primarily present in the repellent-rich phase after phase separation was complete. This behaviour was particularly evident in the LLDPE strand with Icaridin as repellent. See Figure 3(a) where the pore sizes are larger than in the LLDPE-DEET system.



(a) (b)

FIGURE 3. SEM micrographs showing the effect of silica and insect repellent type on the structure of the internal microporous region of extruded LLDPE strands. (a) 30 wt.% Icaridin; and (b) 30 wt.% DEET.

The outer surfaces of the LLDPE strands were also observed by scanning electron microscopy (SEM). Figure 4(a) shows a cross-section of a strand that clearly reveals the presence of a skin at the edge of the strand. The presence of a membrane-like skin covering the microporous polymer strands is also visible in Figure 4(b). This suggests that the skin may present a membrane-like barrier to outward migration of the actives. When diffusion of the active ingredient through the membrane is the mass transport-limiting step, a more gradual reduction in the release rate over time is realized. The permeability of membranes with respect to an active ingredient can be engineered by adjusting the membrane thickness and judicious selection of the polymer system to be used as a matrix [5].



(a) (b)

FIGURE 4. SEM micrographs obtained of strand initially containing 30 wt-% Icaridin and 5 wt-% Dellite 43B clay. (a) Cross-section evidently showing the outer skin covering of the strand; (b) The outer surface appearance of the skin.

Repellent evaporation from extruded strands

Figure 5 shows the release curves of DEET and Icaridin based LLDPE strands aged at 50 ºC for 125 days in a convention oven. Both strands initially contained 5 wt.% clay. The solid lines shown in this Figure represent fits to equation 1. DEET was released faster from the strands than Icaridin. The latter was released at an almost constant rate over a longer time. There are two reasons that explain the higher release rate of DEET: (i) the difference of membrane thickness (*S*) covering the LLDPE strands, and (ii) the difference of the vapor pressure of neat DEET compared to Icaridin.

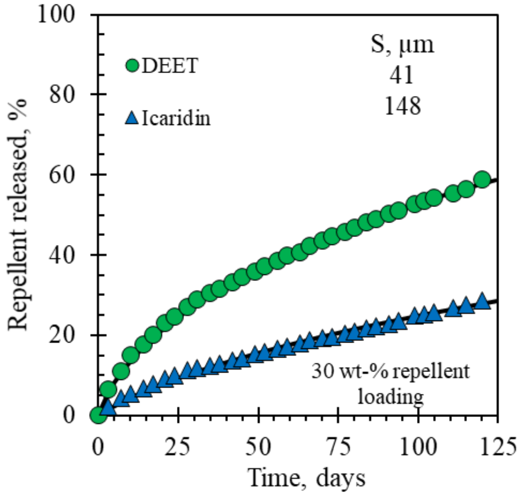


FIGURE 5. Release of 30 wt.% DEET, and 30 wt.% Icaridin from strands and the different of the membrane thickness (*S*) for strands. The strands contained 5 wt.% Dellite 43B clay.

CONCLUSIONS

Increasing the residual effectiveness of repellents can make a significant impact in reducing outdoor malaria transmission in endemic regions. This work has proven the concept of trapping a liquid repellent inside polymer strands and slowly releasing it into the environment. These strands can be manufactured cost effectively by a simple melt extrusion process. The low volatility of the mosquito repellent Icaridin make it an attractive candidate for long-lasting, wearable mosquito-repellent devices.

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