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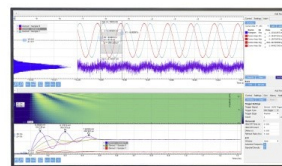
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# Blooming of Chlorfenapyr from Polyethylene Films

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**Abstract.** FTIR, in ATR and in transmission modes, enabled the tracking of the migration of the insecticide Chlorfenapyr to the surface of a polymer film. It also allowed estimation of the apparent solubility in the polymer. However, SEM investigations revealed that a portion of the insecticide is trapped, in a crystalline state, inside the polymer matrix.

## INTRODUCTION

Interventions based on indoor residual spray (IRS) and long-life insecticidal bed nets (LINNs) play important roles in reducing the malaria disease burden. In future, insecticidal wall linings (IWLs) may prove to provide a similarly effective malaria vector control strategy. Both LINNs and IWLs rely on the presence of insecticides on the fiber or filament surfaces. The World Health Organization (WHO) recommends bed nets containing insecticides such as alphacypermethrin and chlorfenapyr because of their low mammalian toxicity, low volatility, and high contact-toxicity against mosquitoes<sup>1</sup>. When the target mosquitoes touch the surface of the net, they pick up toxic amounts of the poison causing them to perish.

Polyethylene wall linings are produced by directly incorporating the insecticides into the polymer melt during the Netlon mesh extrusion process. Since the insecticides are contact poisons, only that portion present and exposed at the surface of the filaments is effective at killing the target insects. Therefore, it is necessary for the insecticide to bloom, i.e., to migrate to the surface and precipitate there. Solubility usually increases with increasing temperature. Polyethylene is processed at temperatures ranging from 180°C to 250°C. It is likely that, at these high processing temperatures, the insecticides are fully dissolved in the polymer melt. However, after the polymer melt has been shaped into fibers, films or filaments, it cools down and partially crystallizes. Guest molecules are excluded from the crystalline domains, being soluble in the amorphous regions of the polymer only. This means that as the polymer cools and crystallizes the portion of the matrix available for dissolution of the additive decreases proportionally. Together with the lowered temperature, this sets up a supersaturated state for the non-volatile insecticide present. This explains

the tendency for additives to migrate to the surface where they accumulate<sup>2</sup>. This is important as blooming can only occur when the migrating species is present at supersaturated levels in the polymer<sup>3</sup>. It will continue until the concentration at the polymer surface falls to saturation.

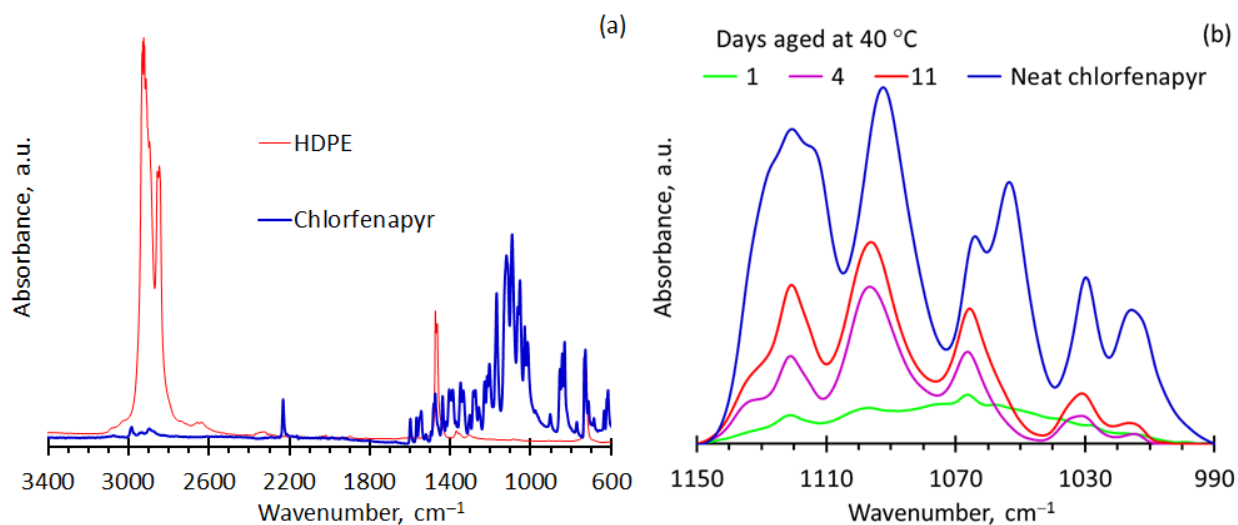
Calvert and Billingham<sup>3</sup> assumed that the active ingredient, in its supersaturated state, is initially homogeneously and uniformly distributed in the polymer matrix. This simplifies the mathematical modelling of the process. The kinetics of the process depends upon on the sample geometry, the solubility of the additive and its diffusion coefficient within the bulk of the polymer<sup>3</sup>. The mechanism of the blooming process entails the diffusion from the supersaturated state inside the polymer to the surface covered by crystals of the neat active. This means that the surface concentration is fixed and that the internal concentration will, over time, decay to the solubility limit in the polymer. A polymer film is approximated by an infinite flat plate of thickness  $L$ . After a sufficiently long time (see below), the average concentration, for the insecticide remaining in the film is given by:

$$\frac{(\langle C \rangle - C_\infty)}{(C_o - C_\infty)} \approx 0.8105 \exp\left[-2.4674 \frac{Dt}{L^2}\right] \quad (1)$$

where  $\langle C \rangle$  and  $C_\infty$  correspond to the mean concentration and solubility of the insecticide in the polymer, respectively;  $D$  is the diffusion coefficient and  $t$  is the time. This expression provides good approximations for blooming times exceeding  $t < 0.1 L^2/D$ .

Spatafore and Pearson<sup>4</sup> found that the propensity to bloom of a phenolic antioxidant, initially present at very high concentrations in polypropylene, could indeed be described simply in terms of such a Fickian diffusion model. Similarly, Möller and Gevert<sup>5</sup> found that the diffusion of antioxidants in low-density polyethylene (LDPE) is indeed Fickian with concentration-independent diffusion coefficients and an Arrhenius-type temperature dependence.

The quantification of the low levels of insecticides inside, or on the surface, of polymer films or filaments is not a simple matter. It requires the use of very sensitive analytical techniques to measure the low levels of additives used in practice<sup>4</sup>. Fourier transform infrared spectroscopy (FTIR) is a simple analytical technique that was successfully applied to measure the diffusion coefficients of antioxidants in low-density polyethylene<sup>5</sup> and to study the blooming of additives from polypropylene films<sup>4</sup>. Furthermore, attenuated total reflection (ATR) infrared (IR) spectroscopy has been employed to estimate the surface concentration of additives that have bloomed from LDPE<sup>6</sup> and from epoxy coatings<sup>7</sup>. This study employed FTIR in transmission mode together with FTIR-ATR to probe the blooming of Chlorfenapyr from high-density polyethylene (HDPE) films.



**Figure 1.** FTIR-ATR spectra. (a) Comparing the spectra for the neat Chlorfenapyr powder to that for virgin HDPE. (b) Change in the FTIR-ATR spectra with ageing time at 40 °C for the Chlorfenapyr-containing film compared to the neat spectrum obtained for the neat insecticide powder.

## EXPERIMENTAL

### Materials

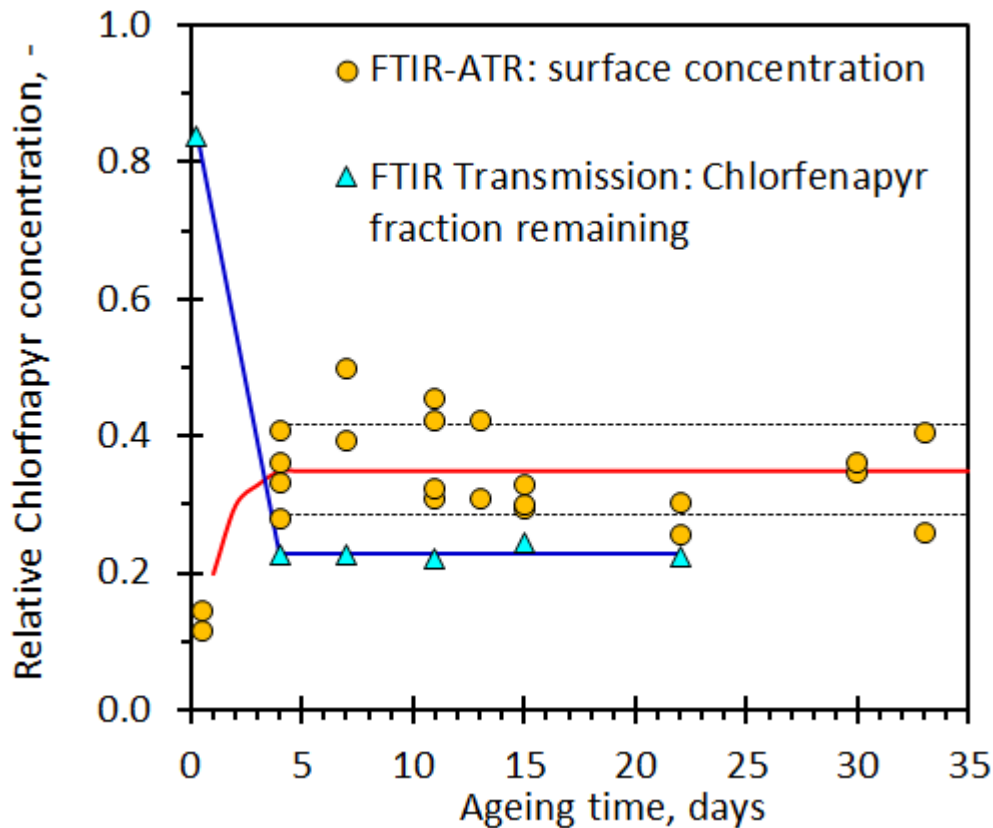
Films were blown using high-density polyethylene (HDPE) grade Safrene H 4765 ex Safrisol. The melt flow index and density were 0.33 g/10 min @ 190°C/2.16 kg and 0.958 g/cm<sup>3</sup> respectively. The Chlorfenapyr-containing masterbatch was supplied by Xyris Technology. It contained nominally 10 wt-% active insecticide in a proprietary polyethylene carrier. The masterbatch addition was done such that the final films contained 2.5 wt-% Chlorfenapyr.

### Methods

#### *Sample preparation and conditioning*

Films were blown on a Collin BL 180/400 laboratory film-blowing unit. It featured a single screw extruder with a diameter of 30 mm and  $L/D = 25$ . The extruder was operated at 50 rpm and the temperature profiles was, from hopper to die, 180/180/185/185/185/185/210/190 °C. Films nominally 40 µm thick were blown but films with double the thickness were also prepared and used for SEM analysis.

The films were suspending vertically in a forced convection oven and aged at 40 °C. Small pieces were cut from the films samples at regular intervals and submitted for analysis.



**FIGURE 2.** Normalized Chlorfenapyr content of HDPE film as a function of ageing time at 40 °C. The transmission data indicates composition estimated from spectra recorded after rinsing the films with acetone. The FTIR-ATR data indicates the accumulation of the Chlorfenapyr on the surfaces of the film. The dotted lines indicate the error band corresponding to the standard deviation.

## Characterization

### *FTIR spectroscopy*

FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 instrument in both transmission and ATR mode. The spectra represent averages of 16 scans scanned at a resolution of  $4\text{ cm}^{-1}$ . The samples evaluated included the neat insecticide powder (using ATR only), the neat polyethylene film and the insecticide-containing film before and after oven ageing at  $40^\circ\text{C}$ . The same insecticide film samples were re-analyzed in transmission and ATR mode after removal of all surface deposits by rubbing with tissues paper wetted with acetone. Following this treatment, the ATR spectra featured HDPE absorption bands only. This confirmed that all of the insecticide, that was present on the surface, was effectively removed by this procedure.

FTIR-ATR spectra for virgin HDPE and neat Chlorfenapyr powder are shown in Fig. 1(a). The band located between  $1420$  and  $1490\text{ cm}^{-1}$  is unique to HDPE while the bands located between  $990$  and  $1150\text{ cm}^{-1}$  are characteristic of Chlorfenapyr. The Chlorfenapyr content of the films was estimated from the ratio of the two areas defined by two wavenumber regions. The acetone wipe removed all the insecticide present on the film surface. Therefore, the transmission spectrum recorded after this cleaning action enabled the estimation of the insecticide remaining in the film at that point in time. The FTIR-ATR spectra for the insecticide-containing films were normalized with respect to the spectrum obtained for the neat Chlorfenapyr powder.

### *Scanning Electron Microscopy*

Films were clamped in a small (50 mm wide) vice, immersed and held under liquid nitrogen, and cut/fractured using a sharp single edge razor blade to expose a view across machine direction. The cut samples were allowed to air dry after dipping briefly in absolute ethanol before sputter coating with Cr and viewing in a Zeiss Supra 55 FEGSEM at 5 kV.

## RESULTS AND DISCUSSION

### Morphological analysis

Figure 1(b) shows FTIR spectra for the neat Chlorfenapyr and the time-evolution of the spectrum for the Chlorfenapyr-containing film. Fig. 2 shows the normalized Chlorfenapyr content of the HDPE film as it changed over time on ageing at  $40^\circ\text{C}$ . The plotted composition data obtained from the transmission spectra, after rinsing with acetone, indicate the amount of insecticide remaining at any specific point in time. Right after the film was made, the Chlorfenapyr inside the film amounted to 84 % of the initial concentration of 2.5 wt-%. However, the data for day 4 to day 22 are the same and they indicate  $22.8 \pm 0.9\%$  of Chlorfenapyr remaining indefinitely in the polymer matrix. This can be interpreted as an apparent solubility of the insecticide in the HDPE. Fig. 3 is a SEM micrograph of an edge-on view of the machine direction of an insecticide-containing film. This is an extreme example as it shows where the film fractured at a weak spot caused by the presence of an insecticide agglomerate. Well-defined large insecticide crystals with a needle-like habit are clearly visible. Most likely, the insecticide as a separate crystalline phase, is unable to migrate to the surface. The implication is that the apparent solubility includes a contribution from material trapped in the form of solid crystals. The measured surface concentrations show considerable scatter after Day 4. The apparent surface concentration corresponded to  $35 \pm 7\%$  of the absorption measured for the neat insecticide powder. First, the sample area for the ATR test was probably much smaller and secondly the distribution of the insecticide was probably less homogeneous.

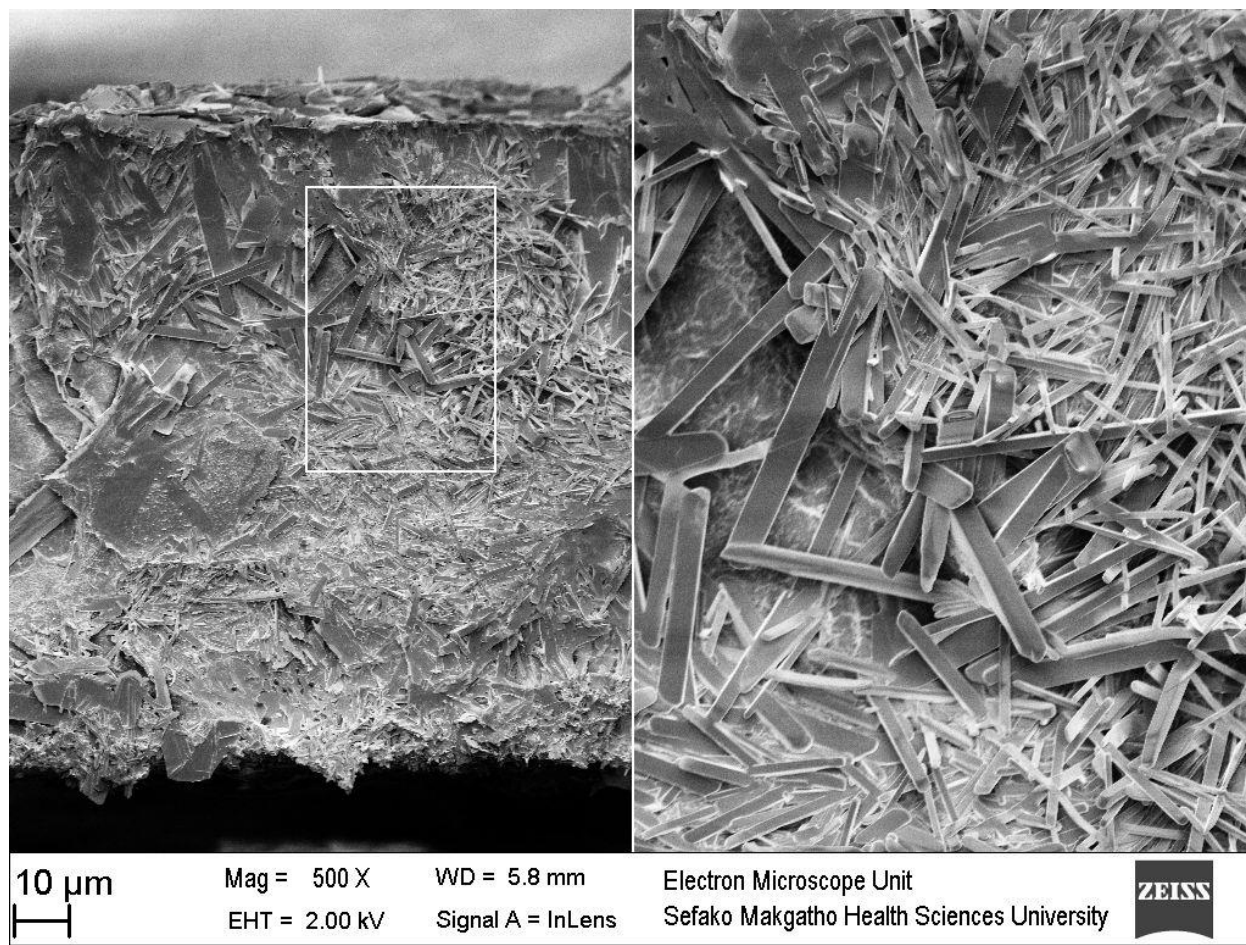
## CONCLUSIONS

Chlorfenapyr was successfully incorporated into high-density polyethylene films at a concentration of approximately 2.5 wt-%. The migration of this insecticide to the surface can be tracked using FTIR-ATR while the amount remaining inside the film can be estimated from FTIR in transmission mode after removal of surface deposits with an acetone rinse. The blooming process was complete in less than four days oven ageing at  $40^\circ\text{C}$ .



## ACKNOWLEDGMENTS

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**FIGURE 3.** SEM micrographs of a fractured HDPE film surface nominally containing 2.5 wt-% Chlorfenapyr.

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