

The Molecular Arrangement of Bifenthrin[®] in Ether Based Polyurethane: Designing a Synthetic Termite Barrier

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ABSTRACT: An ether based polyurethane (EPU) was blended with a synthetic pyrethroid, Bifenthrin[®], to produce a material for potential use as a termite barrier for timber structures. FTIR was used to investigate the interaction between the active component and the polymer, whereas distribution of the active was probed using X-ray photoelectron spectroscopy. The aromatic end of the Bifenthrin molecule was found to interact with the hard segments of the EPU,

whereas the active end of the Bifenthrin[®] molecule was found to be concentrated at the surface of the blend. The efficacy of the blends was demonstrated to induce high mortality rates when the blend was directly tested against termites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1635–1639, 2010

Key words: biological applications of polymers; polyurethanes

INTRODUCTION

Although termites are one of the agents that convert wood into organic matter in natural ecosystems, the extent of commercial damage they cause as a result of foraging on wood is substantial. Conventional strategies to prevent termite damage to wood involve the use of pesticides. These are chemical treatments that have a number of problems. The traditionally used organochloride pesticides pose major environmental challenges^{1–3} and have been banned in many markets since 1995. New “environmentally friendly” pesticides, such as, synthetic pyrethroids, have come into use but these often possess short half-lives and need reapplication every few years (3–5 years).⁴ Various physical methods have also been used to prevent termite damage. Typical products include fine stainless steel mesh⁵ and ground granite and fine gravel.⁶ Such physical barriers need to be continuous (unbroken) to avoid termite entry into the protected space. Apart from these physical barriers, baits have also been used to concentrate foraging termites and provide a way of introducing toxicants to the colony.

An alternative to existing protection strategies is to use polymers impregnated with a termiticide, which provides both a physical and a chemical barrier. The system chosen for this study is an ether based polyurethane elastomer (EPU) impregnated with Bifenthrin[®], a synthetic pyrethroid. This is a novel approach to the problem as previous approaches using impregnated polymers have tended to use rigid polymers. The use of polyurethane elastomers allows the ready coating of irregular shapes. In addition, the chemical structure of polyurethanes may permit interactions between the host polymer and the active, which would retain the active within the barrier for long periods of time. In a previous paper,⁷ it has been shown that high levels of Bifenthrin[®] can be incorporated in the EPU and that the diffusion rates of the active into water from the impregnated polymer are very slow. These results indicate the possibility of extending the life of environmentally friendly pesticides using this concept and limiting the release of actives into the environment. Here we investigate the interaction of the active with the polymer and the bioavailability of the active in impregnated polymer systems.

Bifenthrin[®] is comprised of aromatic and nonaromatic groups, Figure 1, and thus there exists the possibility of interaction between the aromatic groups of the active and the isocyanate group of the EPU, in this case toluene di-isocyanate (TDI). Although FTIR has been used to analyze EPU⁸ and

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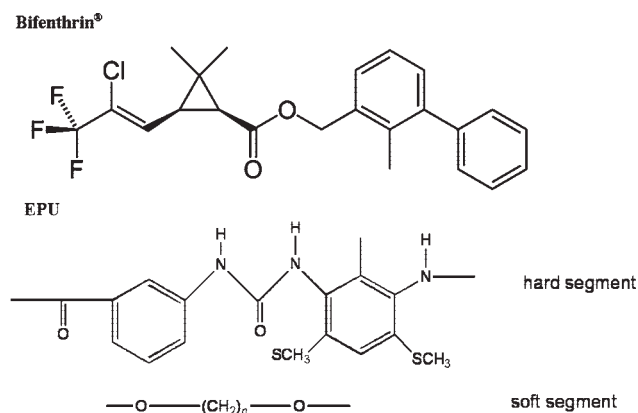


Figure 1 Structure of Bifenthrin[®] and the hard and the soft segments of the EPU.

pyrethroids⁹ separately, their interactions have not been explored. The Bifenthrin[®] molecule also contains fluorine and this element presents an excellent marker for X-ray photoelectron spectroscopy (XPS) analysis of the distribution of the active within the EPU and its presence on the surface. While surface analyses of EPU has been investigated in the past^{10–12} analyses of a pyrethroid encapsulated in this elastomer has not been done.

Presence of the active on the surface of the barrier material may be of critical importance to the efficacy of the barrier. A more direct measure of the efficacy of the barrier is to test it directly with termites. Plastic laden with insecticide has been tested previously against termites.¹³ Substantial diffusion of lambda cyhalothrin has been detected in polyethylene systems, resulting in termite repellence and mortality.¹⁴ It has been shown previously that the diffusion of the active from EPU is quite low and appears to be controlled,⁷ but it is not known if this is sufficient to kill or repel the targeting termite pest. This aspect is addressed in this work.

MATERIALS AND METHODS

Preparation of EPU samples

The EPU used was Erapol E83A supplied by Era Polymers (Sydney, Australia). This is a two part EPU made from an isocyanate terminated prepolymer (Part A) based on poly(tetra methyl ether)glycol and TDI and Ethacure E300 chain extender (Part B).

Part A was heated in an oven for 24 h at 85°C. Molten Part A was degassed at room temperature for 3 min and mixed with Part B to give a 100% stoichiometry and after degassing, the mixture was poured into metal molds, 17 cm × 17 cm × 0.25 cm, that had been coated with silicone oil based mold release (supplied by U.T.I Chemicals, Australia). The cast sheets were post cured at 100°C for at least 16 h. The sheets cured to a nominal hardness of

Shore A 83. These sheets were used to perform FTIR spectroscopy.

EPU and Bifenthrin[®] blends

Bifenthrin[®] was supplied by FMC Australia as a waxy solid that melts at 68–70°C. This insecticide is a synthetic pyrethroid with a chemical structure as shown in Figure 1. Bifenthrin was melted at the melting temperature and added to the degassed Part A of the EPU before mixing with the curative. Blends were made with varying concentrations of Bifenthrin[®] from 0.03% to 4% by weight. Curing the EPU/Bifenthrin[®] blends followed the same procedure as for the unblended EPU described earlier. Previous work⁸ has shown that in a sample containing nominally 4 wt % Bifenthrin[®], ~ 10% of the Bifenthrin[®] is lost during the degassing and curing procedure.

Preparation of samples for X-ray photoelectron spectroscopy and surface analysis

XPS was used to detect the presence of Bifenthrin[®] at the surface of the EPU samples by monitoring the concentration of fluorine from the Bifenthrin[®]. Thick samples of EPU were prepared by curing the EPU in a polypropylene mold (30 mm diameter and 50 mm in height). Silicone mold release was not used in order to eliminate the contamination of the surface with silicone. The samples were cut layer by layer using a new clean razor blade for each cut to avoid contamination. Each exposed surface was analyzed for the presence of fluorine.

XPS was conducted using a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was Monochromatic Al X-rays (1486.6 eV) at 150 W (15 kV, 10 mA). Survey (wide) scans were taken at analyzer pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV. Survey scans were carried out over 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} torr and during sample analysis 1.0×10^{-8} torr.

Fourier transform infrared spectroscopy (FTIR)

Samples were assessed using Fourier transform infrared spectroscopy (FTIR) on a PerkinElmer FTIR Spectrum 2000 Spectrometer using a DuraSamplIRII to obtain attenuated total reflectance (ATR) spectra. To check the energy throughput, a total of eight background scans were collected, whereas no samples were on the surface of the diamond. Spectra

were obtained from the pure EPU by placing a small sample of diameter 1 cm on the diamond disk surface and collecting the spectra using a 1 mm spot. A spectrum of the pure Bifenthrin[®] was also collected by placing 2 mL of molten Bifenthrin[®] (measured using a micropipette) on the disk. To understand the interaction between the two, EPU samples with low concentrations of Bifenthrin[®] (0.1%) by weight were prepared for analysis under FTIR. Although it was possible to identify Bifenthrin in the blend, it was not possible to identify any interaction between the two components due to low concentrations of Bifenthrin[®] in the polymer. Therefore, EPU samples with higher concentrations of Bifenthrin[®] (4 wt % in EPU) were prepared and analyzed.

Mortality tests on termites

To investigate contact toxicity of Bifenthrin[®] impregnated into EPU at different concentrations to worker termites of *Coptotermes acinaciformis*, adult worker termites were continuously exposed to various concentrations of Bifenthrin[®] impregnated EPU by introducing them into a container where they were forced to walk on the test material.

The primary economic Australian species of termite, *Coptotermes acinaciformis*, was collected from near Townsville and maintained in the laboratory on Radiata pine wood before experiments.

Test containers consisted of 70 mL plastic specimen containers with screw top lids. A strip of filter paper 20 mm × 1 mm was dampened with distilled water and attached to the inside of each container by catching one end in the thread of the lid.

Test EPU material of thinner width was prepared following a modification to the methodology described earlier: the mixed polyurethane (PU) was poured onto a glass plate (150 mm × 150 mm × 2.5 mm) coated with mold release and a second glass plate was placed on top of the uncured PU. The two plates were squeezed together using weights of 3 kg. The thickness of the sheets produced was controlled by positioning 0.3-mm thick wires of length 5 cm between the plates.

The test material was cut into disks to fit flush with the edges of the test container at the base. Control EPU disks were identical except for the absence of insecticide. Termites were assayed in groups of 20 worker class termites, with five replicates for each of the six treatment concentrations (Bifenthrin[®] content: 0, 0.03, 0.7, 0.13, 0.26, and 0.5%, respectively). Termites were transferred into the test containers with the aid of soft haired paintbrush to avoid damaging the insects. Experiments were carried out at room temperature.

Observations were made every half an hour until 2 h, thereafter, every hour until 10 h and then 3 h

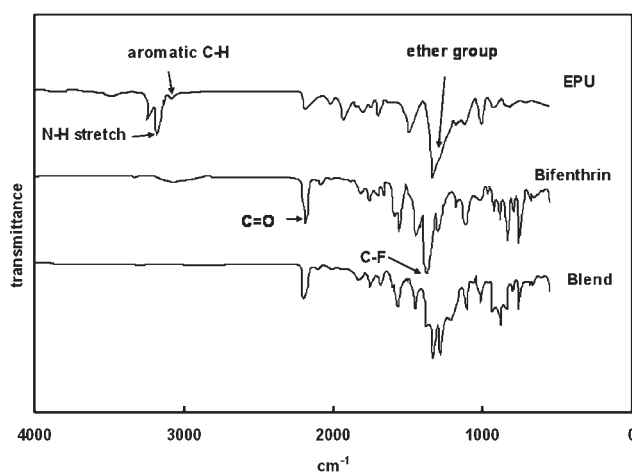


Figure 2 FTIR spectra of pure EPU, pure Bifenthrin[®], and the EPU with Bifenthrin[®] blend.

until 25 h, when the experiment was terminated. Termites were categorized as either alive or dead. Dead termites were determined by lack of movement of the antennae and legs. The test was considered to be valid when control mortality remained at an acceptable level (<10%). Determination of lethal continuous exposure time (LET90) was calculated using probit analysis¹⁵ with SPSS software.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FTIR)

The molecular structure of the Bifenthrin[®] and the soft and the hard segments of the polyurethane are shown in Figure 1. Figure 2 shows the FTIR spectra of the pure EPU, pure Bifenthrin[®], and EPU/Bifenthrin[®] blend. The most obvious change in the spectra seen in the blending of EPU with Bifenthrin[®] was the disappearance of, or major reduction in, the peaks corresponding to N—H (3296 cm^{-1}) and CH (3070 cm^{-1}). Both absorbances correspond to the hard segment of EPU. The ether group from the soft segment of the polyurethane with an absorbance at 1103 cm^{-1} appeared undisturbed with the presence of the Bifenthrin[®].

The spectra for pure Bifenthrin[®] shows a strong absorbance at 1131 cm^{-1} associated with the C—F, which was undisturbed on blending with the PU. Although there appeared to be noticeable changes in the region of the aromatic CH bending region of the Bifenthrin[®] spectra from 650 to 1050 cm^{-1} , these were difficult to resolve in the blend due to multiple overlapping peaks. However, the undisturbed ether linkage in the EPU and the strong disappearance of the N—H stretch, strongly suggested interaction between the hard segment of the EPU and the aromatic section of the Bifenthrin[®] molecule. This was also supported by the unchanged C—F absorbance.

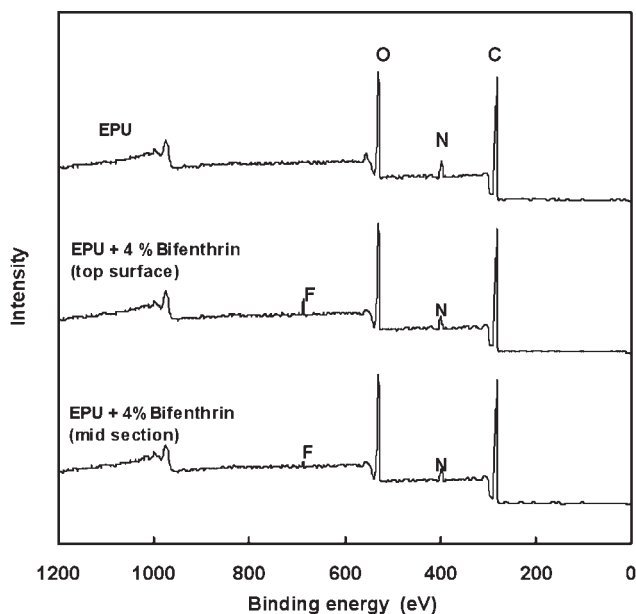


Figure 3 XPS spectra for the EPU material, the EPU with 4% Bifenthrin[®] measured on the top surface and the EPU with 4% Bifenthrin[®] measured on sectioned sample.

Bifenthrin[®] is a very stable molecule. If it occurred, degradation would be expected to cleave the carboxylate ester linkage.¹⁶ The ester group has an absorbance at 1720 cm^{-1} and its intensity appeared to be largely retained on blending with EPU although its position shifted slightly. This suggested there was not significant degradation of the Bifenthrin[®] molecule on blending and curing with the EPU.

X-ray photoelectron spectroscopy

The XPS spectrum of the surface layer of EPU shows clear peaks present at 286, 398, and 530 eV binding energies, which can be assigned to the carbon, nitrogen, and oxygen in the polymer, respectively, Figure 3. In addition, the surface layer of the EPU sample containing 4 wt % Bifenthrin[®] and a sectioned surface of this sample display a fluorine peak at 687 eV. With sectioning through the samples, the atomic ratio of fluorine to chlorine was found constant through the depths of the sample, which confirmed the presence of Bifenthrin throughout the sample. However, the results indicated that the amount of fluorine on the surface was significantly more than the nominal amount of fluorine in the blend for the given composition. XPS gives the total surface elemental composition (atomic percentage) of all the components present in a given system. The only source of fluorine was from Bifenthrin[®] and its concentration was found to be a maximum of 25 at % on the top surface of the sample. The amount of fluorine on the sectioned surfaces decreased with depth

from the surface to a range of 7–8 at % at the center of the block. This difference in concentration can be seen qualitatively in Figure 3 in the reduction in the ratio of the peak intensities of F to N. Data were consistent for each replicate of the EPU/Bifenthrin[®] system.

The very high concentration of fluorine on the surface suggests that Bifenthrin has the tendency to move to the surface of the polymer. Either there were complete Bifenthrin[®] molecules on the surface or the CF_3 group preferentially presented to the surface. The fact that there was still a strong nitrogen peak in the spectra indicates that either the surface was not completely covered with Bifenthrin[®] or there was only a very thin layer of the termiticide on the surface. In either case, because Bifenthrin[®] contains only 5.9 at % fluorine, the CF_3 group must be presenting preferentially at the surface.

The FTIR results suggested association between the Bifenthrin[®] molecule and the hard segments of the EPU, whereas the XPS clearly showed that there was a strong tendency for the fluorine of the Bifenthrin[®] to be present on the surface of the EPU blends. To further explore these trends, the solubility parameters of EPU and Bifenthrin[®] were calculated using the method of van Krevelen.¹⁷ EPU molecules have both hard and soft segments. The soft segments were calculated to have a solubility parameter of $21.53 (\text{J}/\text{cm}^3)^{1/2}$ and the hard segment of $25.3 (\text{J}/\text{cm}^3)^{1/2}$. These compare well with previously reported values of EPUs.^{18–21} The calculated value of the solubility parameter of Bifenthrin was $21.44 (\text{J}/\text{cm}^3)^{1/2}$. This is a reasonable value because it is similar to the solubility parameters of solvents, such as, acetone [$20 (\text{J}/\text{cm}^3)^{1/2}$] and DMAc [$22.1 (\text{J}/\text{cm}^3)^{1/2}$] in which Bifenthrin[®] is completely soluble. However, the overall value of the solubility parameter of Bifenthrin[®] was closer to that of the soft segments of the EPU than the hard segments. The aromatic section of the Bifenthrin[®] molecule has a solubility parameter of $\sim 24.5 (\text{J}/\text{cm}^3)^{1/2}$, which is very similar to the hard segments of the EPU molecule. Thus, it is likely that the aromatic section of the Bifenthrin[®] molecule interacts with the hard segments of the EPU, whereas the active fluorinated end is rejected to the surface of the blend.

Effect of Bifenthrin[®] on termites

Mortality of termites in control trials for samples that did not contain Bifenthrin[®] was <10% during the period of the experiment. Higher mortality was evident in all trials containing Bifenthrin[®], Figure 4. The mortality of the termites increased with increasing concentration of Bifenthrin[®] in EPU. At higher concentrations, termites were observed to have disturbed behavior almost immediately upon

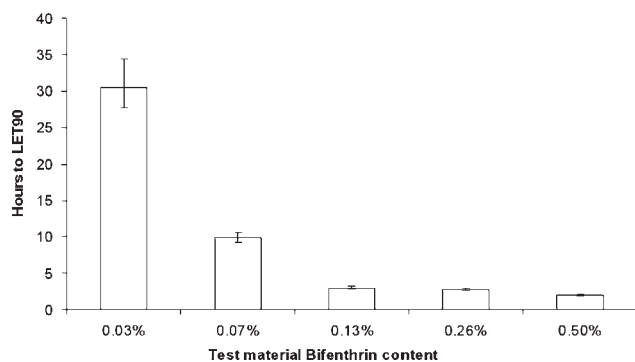


Figure 4 LET 90 (Lethal continuous Exposure Time) for *Coptotermes acinaciformis* exposed to Bifenthrin[®] incorporated into EPU at various concentrations. Bars indicate 95% confidence intervals.

introduction to the test apparatus. EPU with high concentrations of Bifenthrin[®] (0.13–0.5 wt %) caused up to seven times the mortality of EPU with a low concentration of Bifenthrin[®] (0.03 wt %). Termiticides have been found to diffuse from polymeric materials in soil and dry conditions.³ In a previous study, Bifenthrin[®] was shown to diffuse slowly from the EPU in aqueous media.⁷ However, the XPS data above indicated that the active fluorine containing group of Bifenthrin[®] was preferentially on the surface of the EPU. Moreover, higher concentrations than the average bulk concentration of the active was also observed on sectioned surfaces suggesting that the hydrophobic F groups rapidly migrate to the surface. The repellence and disturbed behavior of termites upon mere contact with the surface of EPU containing Bifenthrin[®] is probably, therefore, due to slow diffusion of the active to the surface.

It appears that Bifenthrin[®] interacts chemically with EPU, but not at the cost of insecticidal activity. Wolansky and Harrill²² consider that the activity of pyrethroids is governed by the stereochemistry of all functional groups around the active group (the cyclopropane ring) meaning that for Bifenthrin[®] to be effective, the molecule needs to be available in entirety. The FTIR results indicated that the active region was not cleaved from the Bifenthrin[®] molecule during incorporation into the EPU. This suggests that free molecules of Bifenthrin[®] must be present on the surface of the impregnated EPU despite the apparent compatibility of the aromatic functional groups of EPU and Bifenthrin[®]. This must occur even at quite low incorporation levels for the Bifenthrin[®] because even at 0.03 wt %, measurable mortality was seen. The partial compatibility of Bifenthrin[®] and EPU may control the diffusion of Bifenthrin[®] and consequently increase the effective life of a barrier.

CONCLUSIONS

A synthetic pyrethroid, Bifenthrin[®] impregnated EPU elastomer has been prepared as a possible termite barrier. FTIR spectroscopy showed interactions between the aromatic groups of the Bifenthrin[®] molecule and the hard segments of the polyurethane. It demonstrated the ester linkage between the aromatic groups and the active cyclopropane ring in the Bifenthrin[®] was not degraded during incorporation into the EPU. Despite these interactions, XPS clearly showed that the active fluorine containing group of Bifenthrin[®] was preferentially at the surface of the blends. Low levels of incorporation of Bifenthrin[®] into the EPU were shown to cause mortality in termites.

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