Effect of Inert Fillers on Diffusion and Controlled Release of Penetrant in Polymer Matrices

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ABSTRACT: This study investigates the characteristics of leaching into a solvent of an active used as termiticide, Bifenthrin® (a synthetic pyrethroid) entrapped in polymer, and the effect of layered silicates on this diffusion. Two contrasting solvents, water and acetone, were used to understand this phenomenon; the active is soluble in acetone but has very low solubility in water. The data are used to understand the migration characteristics of Bifenthrin when encapsulated in polyurethane to form a termite barrier. The absorption characteristics of Bifenthrin in polyethylene were also studied for comparison. Bifenthrin-polyurethane blends containing 0, 0.5, and 5% of layered silicates were prepared and monitored for the release of Bifenthrin. Using the time-concentration dependence of the active in polymer, diffusion coefficients of Bifenthrin from the polymer were inferred assuming Fickian diffusion. The presence of silicates had no significant effect on the diffusion behavior. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3593–3600, 2008

Key words: additives; barrier; clay; diffusion; polyurethanes

INTRODUCTION

Termites serve an important ecological function by converting dead trees into organic matter but also cause considerable damage to wooden structures. The damage of wood by termites has enormous commercial significance worldwide in terms of time, human resources and financial cost. Current control methods usually involve the use of chemicals or physical barriers. Traditional pesticides pose a biohazard, and physical methods to prevent damage are difficult to implement on a large scale. The use of organochlorides[1] and pyrethroids[2] as pesticides has been quite popular. Until 1995, organochloride pesticides were used as termiticides,[3,4] but have since been banned from sale in many countries, and more environmentally friendly termiticides have come to use. The new termiticides have shorter environmental half-lives and require reapplication every 3–5 years. Self-resistant wood[5] has also been used experimentally. Apart from these methods, physical barriers such as stainless steel, mortar, glue traps, and baits containing hexaflumuron, sulfluramid, or diflubenzuron are currently used.[6] The use of such barriers requires flawless implementation; even a chink on the surface can defeat the purpose of this barrier, because it can give termites the purchase they need to damage the structure.

Given the negativities associated with conventional methods of preventing termite damage, there is a need to develop an alternative barrier for a range of wooden structures that will be relatively inexpensive, easy to apply and will last a longer period of time without the need for reapplication. An innovative approach to barrier design is developed and tested here. This is a polyurethane- (PU-) based elastomeric barrier, which has a much longer half-life and which incorporates the specific features of slow release chemicals, which are more acceptable to

the environment and public health. The diffusion characteristics (particularly diffusion coefficients) of active in the new system are measured in the present study, which provide a basis for product optimization.

The idea of using active impregnated polymer to prevent termite damage is fairly new. Recent studies with novel laminate polymer has shown encouraging results: it has been reported that such barrier technology can be far more effective than the liquid treatments now in use.[7]

One such system is the use of polyethylene-based barriers, which have been examined using lambda cyhalothrin (a 1 : 1 mixture of (S)-α-cyano-3-phenoxy-benzyl (Z)-(1R,3R)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (R)-α-cyano-3-phenoxybenzyl (Z)-(1S,3S)-3-(2-chloro-3,3,3-trifluor-oprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate, also denoted as a 1 : 1 mixture of (Z)-(1R,3R), S-ester and (Z)-(1S,3S), R-ester as the termiticide.[8] It was found that the treated polyethylene was more effective than the untreated specimen, probably indicating that controlled diffusion of an active from polymer was possible. It was also reported that with passage of time, the amount of active diffusing out of the polymer increased and the amount of active detected outside the polymer was a function of the rate of diffusion from the medium and the degradation of the active outside the medium; this suggests non-Fickian diffusion.

The polymeric medium used in our case is PU. The termiticide chosen here, Bifenthrin[®] [2-methyl-3-phenyl-phenyl) methyl 3-(2-chloro-3, 3,3-trifluoro-prop-1-enyl)-2,2-dimethyl-cyclopropane-1-carboxylate], is a synthetic pyrethroid. This may interact with PU because of the similar solubility parameters of the hard segment of the polymer and Bifenthrin; these were obtained[9] using group additivity.[10] The diffusion characteristics of Bifenthrin being the central part of the study, questions related to load and usages of a carrier are also taken into consideration.

It is known that Bifenthrin interacts well with soil and soil-like particles such as clay and sand.[11,12] For this reason, the study uses Bentonite (a layered silicate) as a carrier for Bifenthrin. The interaction of PU and layered silicates has been investigated in the past.[13–18] The present article studies diffusion characteristics with and without the presence of layered silicates.

Aggregation of layered silicates in PU is a matter of concern,[19] but since the present study focuses on the interaction of Bifenthrin and layered silicates in the polymeric medium, any aggregation would not pose a serious problem, in terms of influencing the properties of the polymer; moreover, layered silicates are not used here to reinforce PU. However, the lack of dispersion of layered silicates in PU might influence the interaction between Bifenthrin

and layered silicates and eventually the diffusion characteristics of either.

Another significant aspect that may impact the interaction between layered silicates and Bifenthrin is the nature of carrier used. The organic carbon content of clay may have a strong influence on the carrier capacity of layered silicates with Bifenthrin. It was reported[20] that the persistence of pyrethroids (Bifenthrin being one of them) with soil/clay is enhanced with the enrichment of organic carbon. This observation was further supported by the fact that the absorption coefficient of the pyrethroids to soil was increased.

In this study, there were two different ways in which the interaction between Bifenthrin and clay has been tested: first, direct exposure of layered silicates to molten Bifenthrin (its melting point is 68–70°C) and second, exposing clay-laden polymer to molten Bifenthrin. The interaction between Bifenthrin and layered silicates was examined with X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Controlled diffusion of Bifenthrin from PU was studied using two different media: water and acetone. Although Bifenthrin is barely soluble in water, it is completely soluble in acetone. The two media represent two ends of the spectrum in terms of reactivity with Bifenthrin. The values of diffusion coefficients were determined from the time evolution of the concentration of active.

MATERIALS AND METHODS

Polyurethane

The PU used was an Erapol E83A supplied by Era Polymers (Sydney, Australia). Erapol E83A is a two-part PU made from an isocyanate-terminated prepolymer (Part A) based on poly(tetramethylene ether glycol) (PTMEG, $HO[CH_2CH_2CH_2CH_2O]nH$) and toluene diisocyanate (TDI, $C_9H_6N_2O_2$) and Etha-cure E300 chain extender (di(methylthio) toluene diamine, Part B).

Part A was heated in an oven for 24 h at 100°C. Part A was mixed with Part B to give a 100% stoichiometry and after degassing, the mixture was poured into metal molds coated with silicone oil-based mold-release compound (supplied by U.T.I Chemicals, Australia). Sheets were produced using a mold 17 cm × 17 cm × 0.25 cm. After casting at room temperature, the PU sheets were heated in a vacuum oven at 85°C for at least 16 h.

Polyurethane and Bifenthrin blends

Bifenthrin was supplied by FMC Australia as a waxy solid. Bifenthrin is a synthetic pyrethroid with
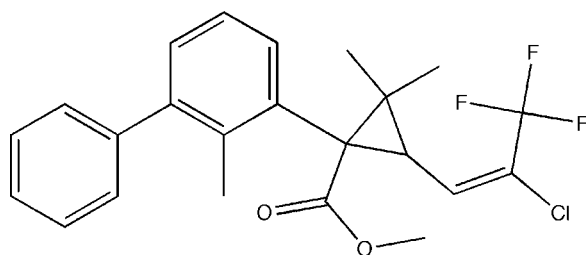
Figure 1 Structure of Bifenthrin.

the chemical structure shown in Figure 1. Bifenthrin was added to the PU in three ways. Firstly, molten Bifenthrin was added to the degassed Part A before mixing with the curative. Blends were made with varying concentrations of Bifenthrin, depending upon the purpose of the experiments. Curing the PU/Bifenthrin blends followed the same procedure as for the unblended PU described above.

Bifenthrin was also added into PU using layered silicates as a carrier. Unmodified Bentonite was used for this purpose. Molten Bifenthrin was absorbed on to commercial Bentonite kiln dried at 50°C and added to the prepolymer.

In a third series of experiments, Bifenthrin was infused into the molded PU sheets. Disks (1 cm in diameter) of pure PU and the PU/Bentonite composite (containing 5% by weight of Bentonite) were cut out of the molded sheets using a mechanical punch. The samples were weighed and immersed in molten Bifenthrin for different intervals of time at 70°C. Each sample was removed and reweighed at times up to 2500 min.

Polyethylene and Bifenthrin blends

Blends of medium density polyethylene and Bifenthrin were melt-mixed in a Brabender blender at 170°C. The polyethylene used was Alkatuff 711UV from Qenos (Melbourne, Australia) with a melt flow index (190°C, 2.16 kg) of 3 g/10 min and a nominal density of 0.938 g cm^{-3}. Polyethylene/Bentonite blends containing 5% by weight of Bentonite were also prepared by melt mixing in a Brabender.

Polyethylene blends from the Brabender were chipped and then compression molded into flat sheets of 1 mm thickness at 170°C and then cooled to 50°C at 4°C/min. One-centimeter diameter disks cut from the polyethylene sheets were immersed in molten Bifenthrin for absorption tests (as described earlier for PU).

Scanning electron microscopy

Fluorine is a part of the Bifenthrin molecule but is not present in either of the polymers. Consequently,

the fluorine signal was used to track the distribution of Bifenthrin in the polymer using elemental analysis via energy dispersive X-ray spectroscopy (EDS). Images of the samples were obtained using a JEOL JSM 6460 LA low vacuum analytical scanning electron microscope. This was equipped with an integrated JEOL Hyper mini-cup, 133 eV resolution, ultra thin window, SiLi crystal, energy dispersive X-ray spectrometer. Elemental analysis was carried out in low vacuum mode to obviate a metal coating, with JEOL Analysis Station (V3.51) software. Acquisition conditions on the SEM were 20 kV, 10 mm working distance and 30 s live time acquisition at ∼ 10–15% dead time.

Samples were studied for vertical and horizontal distribution of Bifenthrin using replicated spot and line analyses. Clumped or clustered components (Bentonite) were also investigated for major shifts in Bifenthrin concentration in comparison with surrounding polymeric material.

Two types of samples were analyzed. First, samples of PU with 4% Bifenthrin by weight were made as described above. Such a high concentration of Bifenthrin was required for analysis by gas chromatography mass spectroscopy (GCMS), since the equipment does not detect low concentrations of Bifenthrin in PU. The second set of samples had Bifenthrin absorbed into PU. Samples of pure PU and PU with Bentonite immersed for 24 h in molten Bifenthrin were chosen for analysis. Each sample was cut ensuring flatness of the surface for accurate analysis. Samples were mounted on carbon tabs on 12-mm diameter aluminum SEM mounts.

Samples of polyethylene with/without Bentonite and Bifenthrin were also analyzed by EDS following the same procedure as for the PU samples.

Chemical analysis and effusion tests of the samples

A series of PU samples containing nominally 4 wt % Bifenthrin was made to quantify loss of the active during processing of the blends. The first sample was a control sample that contained the active and the polymer that was neither cured nor degassed. The second sample was cured but not degassed. The third sample was degassed but not cured. The fourth sample was both cured and degassed. Chemical analysis of the blends was conducted on small cutouts from the sheets and analyzed for Bifenthrin using a Shimadzu 5050A GCMS.

Effusion tests were carried out to quantify diffusion of Bifenthrin from the impregnated polymers. Two model environments were tested. The PU-Bifenthrin samples were exposed to either tap water or acetone for different time intervals.
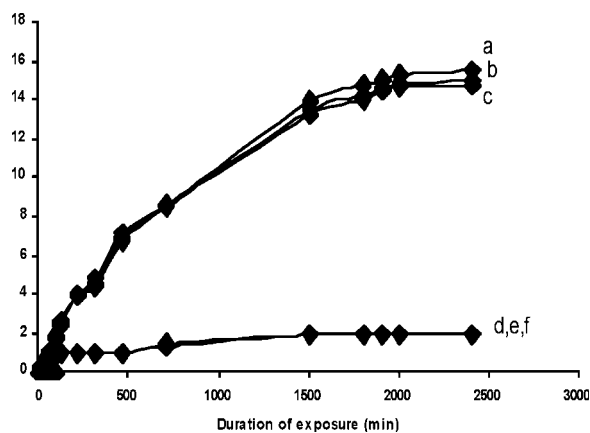
Figure 2 Absorption curves showing weight gain of polyurethane and polyethylene in Bifenthrin at 75°C. Curves a–c denote absorption of Bifenthrin in polyurethane with 0, 0.5, and 5% Bentonite respectively, while d–f denote absorption of Bifenthrin in polyethylene with 0, 0.5, and 5% Bentonite, respectively.

Water was chosen due to its practical importance if the barrier materials were used in the field, while acetone was chosen as it is a good solvent for Bifenthrin. The samples were stirred on a magnetic stirrer for 2, 24, 36, 48, 72, and 96 h at room temperature. The polymeric samples and the solvent in which they were stirred were analyzed for Bifenthrin by GCMS.

RESULTS AND DISCUSSION

Absorption of Bifenthrin in polyurethane and polyethylene

Figure 2 shows the increase in weight for samples immersed in molten Bifenthrin as a function of time. PU showed high absorption of Bifenthrin with the weight gain increasing with time and reaching an asymptotic value of $\sim$ 15% after $\sim$ 2000 h. PU samples loaded with 0.5 and 5 wt % commercial Bentonite showed very similar trends to the unfilled PU. The final absorption was marginally lower than the unfilled material.

Polyethylene samples showed a low absorption of Bifenthrin ($\sim$ 2 wt %) with or without the presence of Bentonite in the sample.

Scanning electron microscopy: EDS

Figure 3 gives the elemental spectra obtained from EDS that show the presence of Bifenthrin in the PU or polyethylene polymer sheets without and with layered silicates. Since fluorine is not present in either of the polymers and only in the active, it was used as the indicator for the presence of Bifenthrin.

Figure 3(a) shows the EDS spectrum of pure PU. Bifenthrin was clearly detected in PU, when infused into the polymer [Fig. 3(c)].

With the addition of layered silicates to the PU, there was no change in the concentration of Bifenthrin infused into the polymer [Fig. 3(b)]. The results indicate the inability of layered silicates to absorb Bifenthrin more than the polymer.

In samples where Bifenthrin was mixed with PU, the concentration of Bifenthrin was observed to be lower on the layered silicates [Fig. 3(d)]. This result was consistent at low (0.5 wt %) and higher concentrations (5 wt %, shown in Fig. 3) of layered silicates across the sample. Instead the spot analyses on the polymeric regions surrounding the clusters of layered silicates showed higher concentration of Bifenthrin [Fig. 3(e)]. The observation suggests that despite exposure to high temperature during the curing stages of the polymer (100°C, which is higher than the boiling point of Bifenthrin, 86°C), the active component binds more strongly with the polymer rather than the layered silicates.

Polyethylene samples used for absorption studies did show evidence of Bifenthrin on surface, when infused with the active [Fig. 3(h)]. The concentration of fluorine was insignificant, indicating extremely low absorption of Bifenthrin. The result was consistent with samples containing layered silicates [Fig. 3(g)], further evidence that commercial layered silicates show poor carrier capacity for Bifenthrin (see also Fig. 4).

The melt mixed samples of polyethylene, with [Fig. 3(i)] and without [Fig. 3(j)] layered silicates showed negligible amounts of Bifenthrin, which is likely to be due to lack of bonding between polyethylene and Bifenthrin at high temperature conditions of the process, at which Bifenthrin degrades.

With the addition of layered silicates to the PU, there was no obvious change in the concentration of Bifenthrin infused into the polymer [Fig. 3(b)]. This is determined by taking into account the size of the spectral peak for fluorine. When the clay is present, the peak for F overlaps with an iron peak. If fluorine were present in higher quantities in the clay component, then this peak would be a sum of F and Fe and significantly higher than the F peak in the PU alone. The results indicate that the layered silicates do not absorb more Bifenthrin than the polymer.

The lack of absorption or attachment of Bifenthrin with layered silicates might be due to low organic carbon content of the clay used. Commercial Bentonite is one such case. The organic carbon content largely determines the binding ability of pyrethroids with soil-like particles.[20–22] When analyzed, the organic carbon content of Bentonite used in the study was found to be as low as 0.14%.
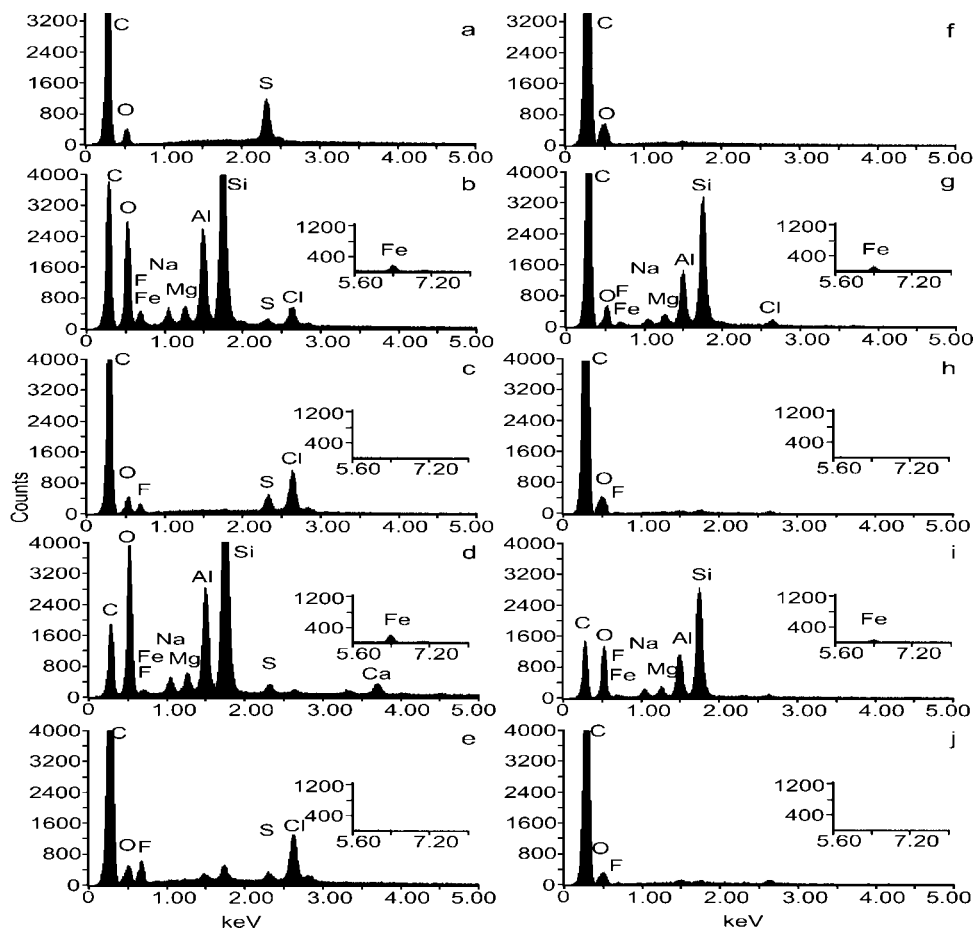
Figure 3 Surface elemental spectra from EDS analyses. (a) Pure polyurethane (PU). (b) Spot analysis on clay of a Bifenthrin soaked (absorbed) sample of PU with Bifenthrin. (c) Spot analysis on polymer of a Bifenthrin soaked (absorbed) sample of PU with Bifenthrin. (d) Spot analysis on clay of a Bifenthrin mixed (reacted) sample of PU with Bifenthrin. (e) Spot analysis on polymer of a Bifenthrin mixed (reacted) sample of PU with Bifenthrin. (f) Pure polyethylene (PE). (g) Spot analysis on clay of a Bifenthrin soaked (absorbed) sample of PE with Bifenthrin. (h) Spot analysis on polymer of a Bifenthrin soaked (absorbed) sample of PE with Bifenthrin. (i) Spot analysis on clay of a Bifenthrin mixed sample of PE with Bifenthrin. (j) Spot analysis on polymer of a Bifenthrin mixed sample of PE with Bifenthrin.

The absence of increase in basal spacing of Bentonite by Bifenthrin is supported by the XRD imaging shown in Figure 4. To perform XRD, 2 g (an arbitrary
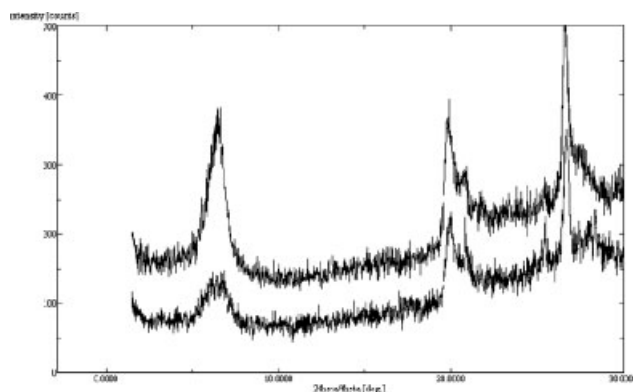

Figure 4 XRD of Bentonite with (top) and without (bottom) Bifenthrin.

amount) of Bifenthrin was dissolved in acetone and mixed with 2 g Bentonite. The blend was spread over a porcelain tile and analyzed by XRD. When mixed with a solvent such as ethylene glycol, layered silicates typically show an increase in basal spacing[23]; the XRD data of Figure 4 show that this effect is not present when Bifenthrin is made to react with the clay.

Figure 5 shows the XRD image of Bentonite, when mixed with the polymer. Pure Bentonite shows distinct peaks obtained around $2\theta = 6°$ (as observed in the Fig. 4). The peak is strongly attenuated in the XRD plot of the blend. The absence or high reduction of the peak possibly suggests exfoliation of the layered silicates or an immiscible system.[24] The system appears to be immiscible because the SEM images showed a large number of unevenly distributed clay particles (Fig. 6).

The exfoliation of layered silicates by the polymer may have interfered with the bonding of layered
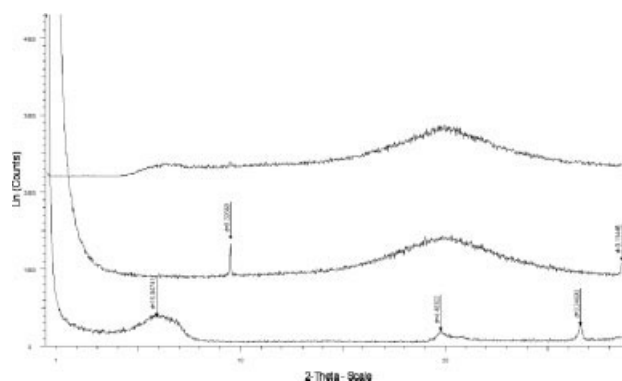
Figure 5 XRD scattering as a function of angle (θ) of Bentonite (bottom) pure polyurethane (middle) and the blend (top).

Figure 7 Time dependence of residual mass for Bifenthrin diffusing from polyurethane (containing 0, 0.5, and 5% Bentonite) washed with water and acetone. Curves a–c: elution of Bifenthrin from polyurethane in water with 0, 0.5, and 5% Bentonite, respectively; d–f: elution of Bifenthrin from polyurethane in acetone with 0, 0.5, and 5% Bentonite, respectively.

silicates with Bifenthrin; this being an immiscible system the structure of the layered silicates seems undisturbed by the polymer and should not affect the interaction of Bifenthrin with the layered silicates. However, the concentration of Bifenthrin was consistently higher on the polymer than the layered silicates, confirming the poor carrier capacity of commercial Bentonite for Bifenthrin.

Chemical analysis and effusion tests of the samples

Since the concentration of Bifenthrin absorbed (possibly adsorbed) (Fig. 2) and incorporated in polyethylene systems [Fig. 3(j)] was found to be negligible, effusion tests on the samples were not undertaken for this matrix.

Chemical analysis by GCMS of Bifenthrin-laden PU showed that when a nominal 4 wt % Bifenthrin was added to the PU, the measured concentration of Bifenthrin was found to be in the range of 3.3–3.7% by weight. The sample that was neither cured nor degassed showed 3.7% Bifenthrin by weight, while
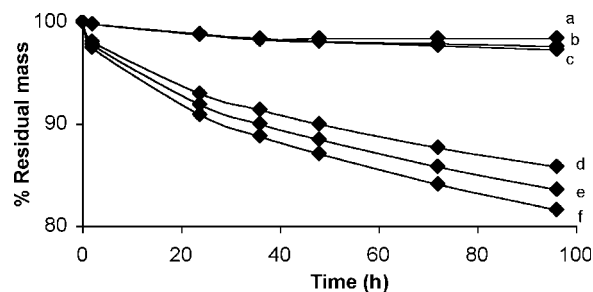
the degassed samples showed 3.3% Bifenthrin by weight, indicating that some of the active may have been lost during the degassing stages. These losses notwithstanding, the concentration appears to be reasonably close to the amount of Bifenthrin added to the polymer.

Since the study concerns controlled diffusion of the active from the polymer, it is useful to understand the migration characteristics of Bifenthrin from PU. This phenomenon can be understood by conducting effusion tests by monitoring the quantity of Bifenthrin lost from the PU. Figure 7 shows the elusion trend of Bifenthrin from PU in the two media, water and acetone. The effusion rates were different for each. The effusion experiments showed that Bifenthrin could be leached from PU into acetone, probably because the acetone swells the PU and also because the Bifenthrin is soluble in acetone. Water did not seem to influence the movement of Bifenthrin to the same effect irrespective of the presence of Bentonite. Although the residual mass of Bifenthrin in PU may be higher in reality (considering the experimental losses during chemical analyses by
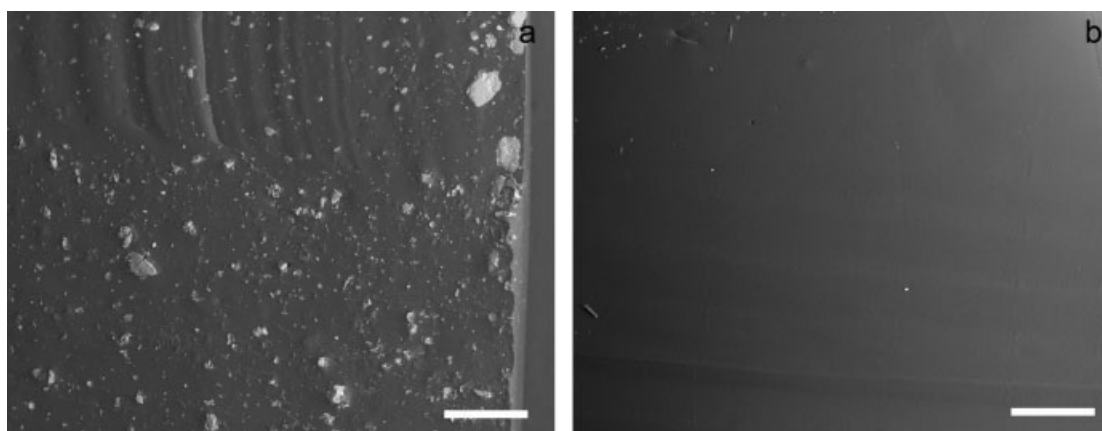

Figure 6 SEM image of an immiscible Bentonite-polyurethane blend (left) and pure polyurethane (right).

TABLE I
Diffusion Data for Bifenthrin Diffusing from Polyurethane (Containing 0, 0.5, and 5% Bentonite) Washed with Water and Acetone

	Diffusion data					
	Water medium			Acetone medium		
Duration of exposure (h)	A	B	C	D	E	F
0	100	100	100	100	100	100
2	100	100	100	99	99	98
24	99	98	98	99	98	98
36	98	98	98	92	91	89
48	98	98	97	90	87	84
72	98	97	97	87	84	82
96	98	97	97	84	82	82
Diffusion coefficient ($cm^2 s^{-1}$)	6.88×10^{-8}	7.5×10^{-8}	7.5×10^{-8}	1.7×10^{-6}	2.3×10^{-6}	2.8×10^{-6}

Columns A–F give residual mass (%) of Bifenthrin after each duration of stirring. Here A–C denote washing in water with 0, 0.5, and 5% Bentonite, respectively, D–F denote washing in acetone with 0, 0.5, and 5% Bentonite, respectively.

GCMS), the data are useful in establishing the effusion trend of Bifenthrin from the polymer.

The time dependence of the concentration of active, as shown in Table I and Figure 7, can be fitted to standard diffusion models to obtain a diffusion coefficient. Water does not swell the PU, whereas acetone does (although the PU does not dissolve in the acetone). The question arises as to what will be the correct diffusion model to apply. The swelling by acetone is likely to follow Type II diffusion,[25] which is likely to be relatively rapid compared with the diffusion of the penetrant (active) out of the (swollen) polymer matrix. It is supposed here that the diffusion of the active for both water and acetone follows simple Fickian diffusion. Using the standard result for diffusion from a flat plate,[26,27] to which a disk can be approximated, the fraction F of active remaining at time t is given by

$$F(t) = 1 - \frac{f(t)}{f(t = \infty)}$$

where

$$f(t) = \sum_{n=1,\infty} \frac{1}{(2n-1)^2} \left[1 - \exp\left(-\frac{(2n-1)^2 \pi^2 tD}{L^2} \right) \right]$$

Here L is the sample thickness and D is the diffusion coefficient of the active. The value of D in this expression was fitted to time-dependent data for $F(t)$. The numerical evaluation of $f(t)$ to acceptable accuracy requires the inclusion of $\sim 10^2$ terms in the summation, and also working with high-precision floating-point arithmetic to avoid round-off error; in the present case this was implemented by coding in Fortran with double precision arithmetic and using Simplex nonlinear least-squares fitting.

It is observed that the diffusion coefficients of Bifenthrin from the polymer in acetone ($\sim 10^{-6}$ $cm^2 s^{-1}$) are significantly higher than those in water. The diffusion coefficients also related to the varying concentrations of Bentonite in PU. Results are shown in Table I.

There is a systematic increase in diffusion coefficient with increasing amount of clay. This may be ascribed to the clay being not completely covered by the matrix and thus leading to cavities. The diffusion coefficients for the acetone medium, which swells the PU, are of the order of magnitude expected for a moderate size (molecular) penetrant in a matrix above the glass transition temperature of the matrix.

The samples of PU with no clay and only Bifenthrin showed comparatively slower effusion as against clay-laden samples. Again, this is probably indicative of the low binding ability of commercial layered silicates with Bifenthrin. Also, the diffusion coefficients of Bifenthrin alone were found to be higher, probably because the layered silicates were not exfoliated.

The results indicate that only a solvent, which is likely to interact strongly with matrix and dissolve the active (acetone in this case, when compared with water) is effective at removal of active from the matrix. Since the PU used here is an ether-based polymer, it is highly impermeable to water, and Bifenthrin is not soluble in water.

SUMMARY

The efficacy of the synthetic barrier material discussed strongly depends on the availability of the insecticide under natural conditions. The results of this study indicate the persistence of Bifenthrin within the polymer unless subjected to strong chemical effusion, which is unlikely in the field.

Although Bifenthrin has strong affinity for clay and clay-like particles and was expected to bind the active more effectively than the polymer (considering the system aims to retain as much active as possible), commercially available layered silicates were not found to effectively carry Bifenthrin within the polymer. The clay contains low levels of organic carbon (as seen in most commercial clays) and this may be an important factor in determining the binding ability of Bifenthrin with layered soil and related particles. Consequently, it may have influenced the faster diffusion rates of Bifenthrin from the polymer. The persistence of Bifenthrin with PU is largely due to the interaction of Bifenthrin with the PU, due to their partial aromatic nature which is not the case with an aliphatic system such as polyethylene.

The data fitting suggests that Fickian diffusion forms an adequate description for leaching of the active from the polymer matrix. This opens the way in the future to choose a matrix to conform to desired leaching characteristics. There are various *ab initio* and semiempirical models for diffusion coefficients of penetrants in polymer matrices, e.g., Refs. 28–31. All of these contain parameters whose values need to be fitted to data, but given parameter values from a series of carefully chosen experiments, diffusion coefficients and hence leaching rates can be calculated for other (related) systems.

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