CHAPTER IV
CARBOFURAN-POLYETHYLENE AND CHLORPYRIPHOS-KRAFT
LIGNIN CONTROLLED RELEASE FORMULATIONS
PART A : CARBOFURAN-POLYETHYLENE CONTROLLED RELEASE FORMULATIONS

4.0 INTRODUCTION

Rapid advancement in polymer science during the past several decades has made possible the creation of controlled delivery systems which previously could not have been conceived. Polymer-pesticide combinations designed to render protection for the crops lower the labour cost due to its less frequent application\(^1\). The polymeric pesticides also minimize the pollution hazards due to the fact that the amount of pesticide needed for a biological response is small. Since this material is released under controlled conditions, it is either being adsorbed or trapped by the host or being degraded in the soil. Pesticides can be physically trapped or chemically bound to the polymers to achieve controlled delivery systems. Various techniques employed for the preparation of controlled release systems are discussed in Chapter I.

The only problem associated with synthetic polymers which are non-biodegradable is that they persist in the soil for longer periods retaining undesirable pesticide residues causing soil contamination. But this can be overlooked due to other advantages such as minimum requirement of the active agent, safe to non-targets, less environmental pollution by hazardous chemicals etc.
Dursban was impregnated into polyvinyl chloride (PVC) pellets in concentrations ranging from 10 to 40%. Formulations were prepared by varying the basic polymer resin, plasticizer and the amount of each. One series of tests used $^{14}$C-labelled dursban. Release rate results indicated that dursban slowly released from PVC formulations under static laboratory conditions. Variation of the PVC resin or plasticizer had little effect on the release rate.

A controlled release insect attractant of porous polymer film containing fine droplets of liquid agrochemical was reported. A controlled release system was prepared by trapping pheromones in polyethylene, polypropylene or poly(ethylene propylene) and evaluated for release rates.

Suscon, a controlled release soil insecticide containing chlorpyriphos in a thermoplastic granule matrix was reported. This formulation provides an alternative to persistent organo-chlorine insecticides and can probably be used with some nematicides and fungicides. A composition containing chlorinated polyethylene, thermoplastic elastomers, and pesticides and/or insect repellent controlled release material was prepared and its efficacy was tested. Some sustained release formulations were manufactured by incorporating pyrethroids into thermoplastic polymers (polyethylene, PVC).

Three polyvinyl chloride (PVC) formulations of malathion were
prepared and tested as controlled release formulations against mosquito larvae. Non-expanded formulations give effective control, with 100% larval mortalities, for 23-51 days, followed by expanded (16-33 days) and foamed (14-27 days) formulations. The results indicated that increasing the percentage of active ingredient in the formulations increased their effective control against mosquito larvae for longer periods.

4.1 Present Work

Carbofuran is well recognised as a useful pesticide to control rice pests but its application poses problems due to its high mammalian toxicity. Also the desired duration of activity is not often achieved. Thus to develop a more efficient, economic and safe controlled release formulation, it is desirable to microencapsulate carbofuran in the polyethylene matrix for specific applications where the non-biodegradable nature of the polymer is required. This work was carried out under research contract No.3549/GS of a Joint FAO/IAEA/GSF programme of "Research to Develop and Evaluate Controlled Release Formulations of Pesticides to Reduce Residues and Increase Efficiency, Utilizing Radioisotopes".

4.2 Results and Discussion

Synthetic polymers are widely used to trap the active agent in their matrix to achieve an extended pesticidal activity. In the
present work, polyethylene a relatively cheap synthetic polymer was employed to coat carbofuran, and inert materials like kaolin and talc were used as filling agents. Since polyethylene is crystalline, it is treated with solvent to favour coating of the pesticide. The formulation was converted to pellets for ease of application near the root zone. $^{14}C$-carbofuran was induced in the controlled release pellets to evaluate the release rates (See Chapter V).

4.2.1 General method of preparation

Polyethylene was refluxed in benzene to get a clear solution. To this solution carbofuran dissolved in benzene was added and stirred vigorously. Later, the solvent was partially evaporated. A slurry containing polyethylene-carbofuran was obtained. To this slurry the mixture of inert filling materials was introduced and mixed by stirring to obtain a uniform mixture. The solvent was completely removed from the mixture. The mixture was ground to fine powder and pellatized. Five formulations ($F_1 - F_5$) were prepared with varying compositions (Table 1).

4.2.2 Analysis

The percentage of carbofuran encapsulated in polyethylene matrix was determined after soxhlet extraction from a known amount of the formulation. The percentage of carbofuran encapsulated in polyethylene matrix is 5.
TABLE 1: COMPOSITION/RELEASE OF CARBOFURAN
AFTER A WEEK

<table>
<thead>
<tr>
<th>C.R. Formulation</th>
<th>Polyethylene %</th>
<th>Kaolin %</th>
<th>Talc %</th>
<th>% of carbofuran released in 1 week</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>10</td>
<td>85.00</td>
<td>1</td>
<td>67.6</td>
</tr>
<tr>
<td>F2</td>
<td>10</td>
<td>1</td>
<td>85.00</td>
<td>13.8</td>
</tr>
<tr>
<td>F3</td>
<td>10</td>
<td>17.00</td>
<td>68.00</td>
<td>38.74</td>
</tr>
<tr>
<td>F4</td>
<td>10</td>
<td>16.00</td>
<td>64.00</td>
<td>32.92</td>
</tr>
<tr>
<td>F5</td>
<td>10</td>
<td>25.50</td>
<td>59.5</td>
<td>45.68</td>
</tr>
</tbody>
</table>
4.2.3 Infrared (IR)

Carbofuran encapsulated in the polymeric matrix was identified by IR after its extraction from the respective formulation. Carbofuran remains intact in the polyethylene matrix.

In order to select the best controlled release system containing the polyethylene, talc, kaolin and carbofuran which will deliver the desired quantity of carbofuran for an extended period, five formulations containing different quantities of the first three ingredients were prepared in the form of pellets containing $^{14}$C-labelled carbofuran. The estimation of the amount of carbofuran released during the first week in water was helpful in deciding the most useful controlled release system for continued evaluation. The composition of the controlled release $^{14}$C-labelled carbofuran formulations (5%) and the percentage of carbofuran released in water during the first week are given in Table 1.

The desired duration of activity is not often achieved by conventional formulations. Hence, repeated applications are recommended. Thus to circumvent the problems associated with the conventional formulations polyethylene based controlled release carbofuran formulations were prepared and evaluated for chemical assay and bioassay (See Chapter V).
4.3 Experimental

4.3.1 Measurements and Materials

IR spectra were recorded on Perkin-Elmer 283B. Soxhlet extraction was employed to recover the pesticide from the controlled release formulation. $^{14}$C-carbofuran was obtained as a gift from Seibersdorf Laboratories, International Atomic Energy Agency, Vienna. Carbofuran was obtained as a gift from Rallis India Limited, India.

4.3.2 Preparation of carbofuran-polyethylene controlled release formulations

A) $F_3$ formulation

In a three-necked, R.B. flask fitted with a mechanical stirrer and condenser, polyethylene (0.6 g) was refluxed with benzene (25 ml) under constant stirring for 1 h to obtain a homogeneous solution. Stirring was continued throughout the experiment. To the above solution, carbofuran (0.3 g) dissolved in benzene (5 ml) was added. After 15 min. the reaction mixture was concentrated to 15 ml and a uniform mixture of inert materials, kaolin (1.02 g) and talc (4.08 g) was added. The reaction mixture is in the form of slurry. The slurry was refluxed for 5 min. and then benzene was evaporated. The controlled release product thus obtained was ground to powder uniformly and converted into pellets (6.3 mm, dia and 2.95 mm thick).
B)  \(F_4\) formulation

This formulation was prepared in a manner analogous to the preparation of \(F_3\) formulation. Here carbofuran (0.3 g), polyethylene (0.9 g), kaolin (0.960 g) and talc (3.84 g) were taken in benzene (30 ml).

C)  \(F_5\) formulation

\(F_5\) formulation was prepared as above by taking carbofuran (0.3 g), polyethylene (0.6 g), kaolin (1.53 g) and talc (3.57 g) in benzene (30 ml).

D)  \(F_1\) and \(F_2\) formulations

\(F_1\) and \(F_2\) formulations were prepared in a manner analogous to \(F_3\) formulation and the quantities for 6 g scale are given below:

\[\begin{align*}
F_1 & \quad \text{polyethylene (0.6 g); kaolin (5.1 g); talc (nil); carbofuran (0.3 g).} \\
F_2 & \quad \text{polyethylene (0.6 g); kaolin (nil); talc (5.1 g); carbofuran (0.3 g).}
\end{align*}\]
PART B : CHLORPYIRPHOS-KRAFT LIGNIN CONTROLLED RELEASE FORMULATION

4.4 INTRODUCTION

The forest product industries generate an enormous amount of solid waste in the form of bark and lignin and although many uses have been devised, much of this waste is discarded or burned. These methods of disposal may cause air and water pollution. Furthermore, since the world production of wood pulp is rapidly increasing, the magnitude of this solid waste problem will increase with time. All forest derived solid waste consist predominantly of cellulosic or phenolic macromolecules. All these contain a multitude of reactive hydroxyl groups and are ultimately bio-degradable. Hence, these materials can be regarded as polymeric assets rather than environmental liabilities.

Naturally occurring materials such as polysaccharides, starch, cellulose etc. polypeptide (casein, leather wastes) polyphenolics (lignins) and their natural mixtures (eg. wood dust) are abundantly available and suitable as formulating agents for controlled release by chemical or physical methods.

Lignin occurs in most dry land plants and is thus the most abundant naturally occurring polymer. Kraft lignin is produced as a byproduct of the Kraft pulping process. It is a polyphenolic polyether
soluble in alkaline aqueous solutions but insoluble in neutral and acidic media. The structure of kraft lignin is complex as a result of the random synthesis of the parent lignin in the plant and changes during the pulping process. In solution the macromolecule exhibits properties which would suggest a roughly spherical or disc like structure with an average molecular weight of 1600 Daltons for pine kraft lignin. In comparison with carriers currently available to the pesticide industry, kraft lignin offers certain advantages: (1) the highly aromatic nature of lignin makes it an excellent protective matrix for chemicals sensitive to degradative process, initiated by the UV radiation of the sunlight. Pesticides of this type include aniline derivatives, natural and synthetic pyrethroids (2) the anti-oxidant properties of lignin add further stability to chemically unstable pesticides and (3) Biodegradability has also been identified as a property of pine kraft lignin. In view of the current and undoubtedly future trends in chemical pest control, this property makes it highly desirable as a carrier.

A controlled release system is prepared either physically trapping or chemically binding the pesticide to lignin matrix. Thus, by binding the pesticides chemically to sawdust, bark or lignin, their lives will be prolonged since attack by degrading bacteria is reduced because of inaccessibility of the pesticide within a protective insoluble matrix. Moreover, the pesticides cannot be readily leached into the subsoil and hence to rivers and streams. As the pesticide-wood waste
combination in the soil gradually decompose, the active pesticide is continuously released over a long period of time. The effective result is a more controlled application of the pesticide than is now usually achieved. This increased efficiency should therefore reduce the overall volume of pesticides applied to environment.

4.4.1 Chemical methods

Pesticides have been directly bonded via covalent bonds as pendant substituents to a natural polymer. The most obvious means of achieving chemical combination between a pesticide and lignin matrix would be by esterification. Herbicides containing carboxyl groups can be converted into acid chlorides which can react with saw-dust, bark and lignin containing hydroxy groups\textsuperscript{9}. Ester, anhydride and amide linkage are favourable for binding pesticides to these polymers.

The extent of esterification\textsuperscript{11} achieved depends upon the proportion of the reactants, but the combined herbicide-polymer weight ratio at maximum substitution are determined by the concentration of accessible hydroxyl groups in the polymeric substrate and by the molecular weight of the pesticide. Successful formulations of lignin with pesticides such as 2,4-D, carbetamide, carbofuran\textsuperscript{12} as well simazine, pentachloronitrobenzene, hexachlorophene and methyl parathion\textsuperscript{13,14} have been reported. Various methods for chemically binding the pesticides to the polymers are discussed in Chapter I.
4.4.2 Physical methods

Pesticides have been physically entrapped either by dissolving or coprecipitation or microencapsulating it in the lignin matrix. In this method, no specific functional group within the pesticide molecule is necessary. The method therefore has general applicability for the controlled release of a wide variety of biologically active materials. However, for agriculture and forestry applications the production cost for chemical approach, like synthesis of ester derivatives is seldom more and thus the use of physical methods for controlled release based on polymers has been investigated. Kraft lignin\textsuperscript{15,16} is suitable for this purpose and with compatible materials, a matrix can be formed which will provide protection from environmental degradation\textsuperscript{17}. A lignin based formulation of carbofuran has been reported\textsuperscript{18}.

A controlled release formulation can be achieved\textsuperscript{19} by removal of common solvent from a lignin-pesticide mixture, or by coprecipitation route. In the coprecipitation process a determined amount of sodium or ammonium salt of alkali lignin in aqueous solution is intermixed with the pesticide. The alkali lignin solution and the pesticide are thoroughly mixed to form a stable emulsion. Mixing is usually carried out at room temperature. The emulsion is then acidified using a mineral acid such as sulfuric acid to a pH about 5 to 6 to precipitate the pesticide-lignin emulsion within the lignin
to form the macro-dispersion. The precipitated material can be dried by various methods.

4.5 Present Work

The present work was initiated as sponsored by IAEA/FAO, Vienna, under the contract number 3549/GS to bring about an effective controlled release formulation to control rice pests. Chlorpyriphos, a pesticide used for rice pest control was entrapped in the kraft lignin matrix, obtained as a waste from paper industry, and formulated suitable for root dip application (See Chapter V).

Chlorpyriphos in water decomposes fastly to its inactive metabolites. The entrapment of chlorpyriphos in the lignin matrix protects it from decomposition and making available the pesticide for a longer period. $^{14}$C-chlorpyriphos was incorporated in the chlorpyriphos-lignin controlled release product to evaluate the release rate (See Chapter V).

4.6 Results and Discussion

Entrapment of pesticides in the lignin matrix was reported by Wilkins$^{20}$. In the present work lignin, in the form of black liquor, a waste from the paper industry was employed to prepare a controlled release chlorpyriphos product.

Black liquor containing lignin is highly alkaline and by introducing
pesticide to this solution may undergo decomposition. Hence, black liquor was treated with an acid to reduce its alkalinity, where the pesticide does not decompose and the lignin still present in the solution.

4.6.1 Preparation of chlorpyriphos-lignin

The pesticide dissolved in dichloromethane was introduced to the pretreated lignin solution with acid. This solution was further neutralized with acid to precipitate lignin while trapping the pesticide in its matrix. The precipitated product was filtered and air dried to obtain a controlled release formulation.

4.6.2 Preparation of $^{14}$C-chlorpyriphos induced chlorpyriphos-lignin

Preparation of $^{14}$C-labelled induced chlorpyriphos-lignin formulation prepared in a similar manner as described above, except doping $^{14}$C-chlorpyriphos with the cold-chlorpyriphos before introducing the pesticide to alkali lignin solution.

4.6.3 Estimation of chlorpyriphos entrapped in lignin matrix

A known amount of $^{14}$C-chlorpyriphos induced lignin controlled release product was dissolved in sodium hydroxide solution (pH 8) and then chlorpyriphos was extracted with dichloromethane quantitatively. Dichloromethane from the extract was completely removed under reduced pressure. The residue was dissolved in toluene making up to a known volume. A portion of toluene was placed
in scintillation fluid for analysis by liquid scintillation counting. The percentage of chlorpyriphos in the lignin matrix was 26.

Pesticides encapsulated in the polymeric matrices were identified by IR after their extraction from the controlled release formulation. The pesticide remains intact in the polymer matrix.

— To encapsulate the pesticide in the lignin matrix, the following points are taken into consideration: pH of the black liquor is an important factor. It is desirable to maintain the pH of black liquor (8.05) where it has a minimum basicity to retain lignin in the solution to which the pesticide could be introduced to get encapsulated in the polymeric matrix of lignin. At pH 6.75 lignin is completely precipitated after trapping the pesticide in its matrix. The time required to precipitate lignin while encapsulating the pesticide in its matrix is important for the reproducibility of the product. Chlorpyriphos is relatively unstable in water\textsuperscript{21}. However, by microencapsulation of chlorpyriphos in the lignin matrix the life of the pesticide is enhanced because the release was observed for an extended period (See Chapter 5).

4.7 Experimental

4.7.1 Materials and measurements

IR spectra recorded on Perkin-Elmer 283B. Digisun-909 pH meter was used. \textsuperscript{14}C-chlorpyriphos was obtained from Seibersdorf
laboratories, IAEA, Vienna. Lignin in the form of Black liquor was obtained from Sirpur Paper Mills, Sirpur Kaghaznagar, A.P., India.

4.7.2 Preparation

A) Determination of the lignin content in Black liquor

To encapsulate chlorpyriphos in the lignin matrix, a series of experiments were conducted to estimate the amount of lignin that gets precipitated from Black liquor upon neutralization and this estimated amount of lignin was taken as basis to decide the amount of chlorpyriphos to be encapsulated. The black liquor is a basic fraction which contains lignin in a dissolved state. The pH of black liquor was 10.2. Black liquor was neutralised with HCl (32%) to precipitate lignin. The precipitated lignin was filtered, washed with distilled water and then air dried. To neutralize 100 ml of black liquor, 7 ml of HCl was required, i.e. to alter the pH of black liquor from 10.2 to 6.75. The amount of lignin obtained was 6.578 g. Triplicate experiments were performed to get an average weight of lignin precipitated from 100 ml of black liquor. The average weight of lignin obtained was 6.5 g.

B) Encapsulation of chlorpyriphos in lignin polymer matrix

The black liquor (100 ml) was taken into a 500 ml beaker and was stirred constantly with a mechanical stirrer. Initially 3 ml of HCl was added to the black liquor. Its pH alters from 10.2
to 8.05 and lignin is still present in dissolved state. At this pH level chlorpyriphos 3 g dissolved in dichloromethane was added to the black liquor while stirring. The remaining HCl (4 ml) was added dropwise, in about 10 min time interval to the solution of black liquor containing chlorpyriphos to precipitate the lignin which traps chlorpyriphos in its matrix, the product was filtered and washed with distilled water and then air dried. The weight of the product is 8.783 g. This procedure was repeated twice to establish the reproducibility of the product quantitatively.

C) Preparation of $^{14}$C-chlorpyriphos induced lignin controlled release formulation

The procedure for the preparation of $^{14}$C-chlorpyriphos induced lignin controlled release formulation is same as above. But the amount of cold chlorpyriphos taken was 2.996 g and labelled chlorpyriphos was 0.004 g. The weight of the product is 8.813 g.

D) Determination of percentage of chlorpyriphos entrapped in the lignin matrix

$^{14}$C-chlorpyriphos induced lignin controlled release formulation (200 mg) was dissolved in 100 ml sodium hydroxide solution (pH 8) and then chlorpyriphos was extracted with dichloromethane (250 ml). Extraction was done for 5 times with 50 ml dichloromethane for each extraction. Dichloromethane was completely removed from
the extract and the residue was dissolved in toluene (5 ml) and transferred it into a 10 ml standard flask quantitatively by rinsing the conical flask containing the extract with toluene, making up the solution to 10 ml in the standard flask. 2 ml of toluene extract from the 10 ml standard flask was placed in 8 ml scintillation fluid for analysis by liquid scintillation counting. The counting efficiency was 95.4% (unquenched standard).
References


