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Preparation and Characterization of Chemical Structure Composition of Polyurethane's Microcapsules Pesticides

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Microencapsulation of pesticides and other agrochemical compounds has been performed for some years. In general, the object of producing such compositions has been to provide controlled release of the active ingredients and particularly to provide a release for longer term efficacy so that it is released over a period of time and is available throughout the effective period. This is particularly significant for pesticides or other ingredients, which are degraded or decomposed over a relatively short period of time or under certain environmental conditions. In general, microencapsulated forms of pesticides are mostly produced by interfacial polymerization and the microcapsule walls are formed from polymeric material. In this paper, we have produced the microcapsulated form of chloropyrifos (one of the high usage solid phosphorus insecticides) and fenitrothion (one of the high usage liquid insecticides) in the lab and bench scale by use of interfacial polymerization by polyurethane. We changed some of the conditions (temperature, stirring rate and time) and found the better of them and also obtained the size of particles, the release of pesticides in a period of time, the graph of particle size distribution and the SEM images of particles.

Key Words: Microencapsulation, Chloropryfos, Insecticide, Fenitrothion, Pesticide, Interfacial polymerization.

INTRODUCTION

Controlled release polymeric systems are becoming increasingly important in a variety of agrochemicals like fertilizers, insecticides, fungicides and herbicides etc.[1] The macromolecular nature of these delivery systems allows for control of rate of delivery, mobility and period of effectiveness for biologically active components. The controlled release systems are better in enhancing the efficiency for application of agrochemicals[2]. Controlled release systems may be of two types: one in which the polymers are covalently bonded with the agrochemicals either as structural units along the black-bone or as pendant groups. Biological activity in these cases appears to be dependent upon cleavage of chemically labile bonds to release the free agrochemical or the active agent[3]. In the other agrochemical or any physiologically active agents are physically dissolved, adsorbed, entrapped or dispersed in a polymeric matrix. However, if the polymer

matrix is biodegradable, the active agent may be slowly released during biodegradation[4]. Microcapsulation of pesticides and other agrochemical compounds has been performed for some years[5]. This is particularly significant for low melting solid and high vaporization liquid pesticides or other ingredients, which are degraded or decomposed over a relatively short period of time or under certain environmental conditions. For the most part, microcapsulation of pesticides is utilized when a slow or controlled release of the pesticide is desired[6, 7]. This is accomplished by encapsulating particles or droplets of a material containing a pesticide within a polymeric shell through which the pesticide migrates at a controlled rate. This rate is determined by both the nature of the pesticide and by the type, structure and properties of the capsule shell[8]. The nature of the shell, in turn, can be predetermined or constructed by selection of the type and quantity of polymer and the conditions under which the shell wall is formed (Fig. 1). Microencapsulated formulations or compositions have a number of additional advantages relating to safety and toxicity. Since the pesticide is contained within a polymeric wall, there is in general less dusting and much lower toxicity associated with the production handling and application of pesticides so formulated, as well as lower animal toxicity.

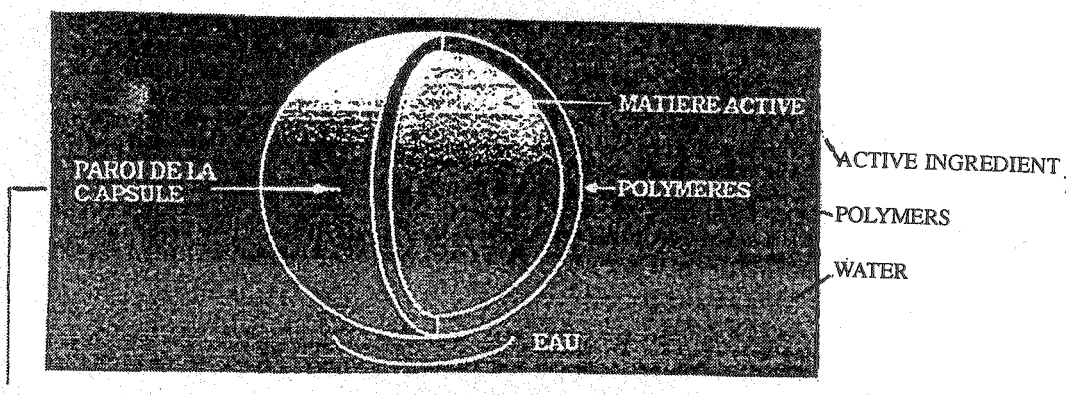
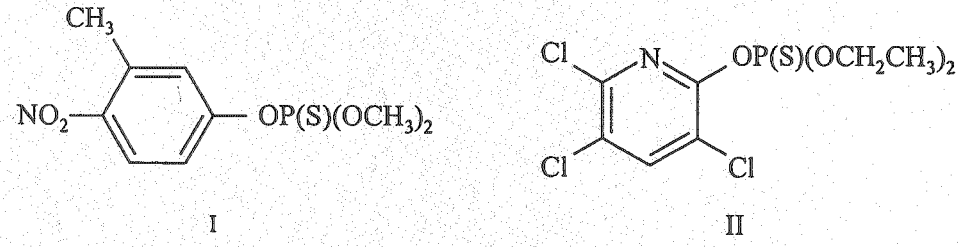


Fig. 1. Microcapsule

It is also possible to produce microencapsulated formulations of pesticides in which controlled release is not the objective. Such compositions contain the pesticide in microcapsules, which are generally on the smaller side, and tend to have relatively thin walls. Microencapsulated pesticides of this type would be intended for certain foliar applications, in situations in which a relatively quick release of the entire contents of the microcapsules is desired. However, even though controlled release may not be an objective, it is nevertheless desirable to take advantage of the lessened toxicity and dust formation of microencapsulated pesticides as compared to non-microencapsulated forms. Microencapsulated pesticides, whether of the controlled release or the quick release variety, are usually sold in the form of aqueous suspensions of the microencapsules. Such suspensions naturally result from the process for the production of microcapsules which in general involves the formation of the dispersion or emulsion of a relatively non-water soluble liquid ("oil") in an aqueous medium. The oil phase contains a pesticide to be encapsulated as well as one or more monomers, which

will form the polymeric microcapsule wall. Forming the oil/water dispersion, followed by heating and other means to produce polymerization, results in polymeric microcapsules containing the non-water soluble liquid material suspended in the aqueous phase. In general, it would be further advantageous to provide such microencapsulated compositions in dry form, rather than as aqueous suspensions. Dry formulations may be prepared with relatively high loading of the pesticide, are easier to remove from containers, produce less contamination in the environment, may be stored for long periods of time and their storage and transportation does not require the simultaneous storage and transport of large volumes of water. In addition, since pesticidal microcapsules are typically applied by dilution of the microencapsulated formulation with water in spray tank to form a sprayable emulsion, it would be convenient to provide a solid formulation of microencapsulated pesticides which is water dispersible, *i.e.*, can easily be mixed with water to produce such a sprayable material.

Chloropyrifos (Fig. 2) is one of the high usage solid phosphorous insecticides, the insecticidal activity of which has been reported by E.E. Kenaga *et al.*. This insecticide is cholinesterase inhibitor and the mode of action is non-systemic with contact, stomach, and respiratory action. It is used for controlling coleoptera, diptera, homoptera, lepidoptera, etc. Fenitrothion (Fig. 2) is one of the high usage liquid insecticides whose insecticidal activity has been reported by Y. Nishizawa *et al.*[10, 11]. This insecticide is also a cholinesterase inhibitor and the mode of action is non-systemic with contact and stomach action. It is used for controlling of chewing, sucking and boring insects in cereals, soft fruits, topical fruits, vines, rice, sugarcane, vegetables, turf and forests.



I II

Fig. 2. Structural formula of fenitrothion (I) and chlorpyrifos (II)

In this work, the microencapsulated form of chloropyrifos and fenitrothion have been produced in lab and bench scale with good yield and quality by use of polyurethane formation in interfacial polymerization reaction. Then, we changed some of the conditions (temperature, stirring rate and time) and found the better of them and also obtained the size of particles, the release of pesticides in a period of time, the graph of particle size distribution and the SEM images of particles.

EXPERIMENTAL

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) and fenitrothion (O,O-dimethyl O-4-nitro-*m*-tolyl phosphorothioate), as pesticide samples, were purchased from Cheminova Company. MDI (4, 4-methylene-bis-phenylisocyanate) as polyisocyanate sample, ethylene diamine as water-soluble monomer, gum arabic as surfactant, CMC (carboxymethyl cellulose) as thickener

were purchased from Merck Company. Scanning electron microscopy (SEM) apparatus (DSM 960A, Zeiss, Germany) was also used for showing the changes of particles in microencapsulating procedure. UV-spectroscopic analyses of mentioned pesticides were performed with a Shimadzu UV-260 spectrophotometer.

Synthesis of microcapsules

Fenitrothion: A mixture of 100 g (0.36 mol) fenitrothion and 1.2 g (0.005 mol) MDI were stirred in a flask for 10 min. Then this solution was added slowly to a solution of 178.64 g gum arabic (6.25%) with stirring for 15 min. After dissolving, a solution of 6 g ethylene diamine (5%) as second monomer was added and the polymerization reaction was started (Fig. 3). The polymerization reaction time was 60 min and at the end of it, a solution of 220 g CMC (3%) was added to this suspension of microcapsules in water as thickener and the mixture was stirred for 15 min. The microcapsules of fenitrothion with the best quality and yield were obtained.

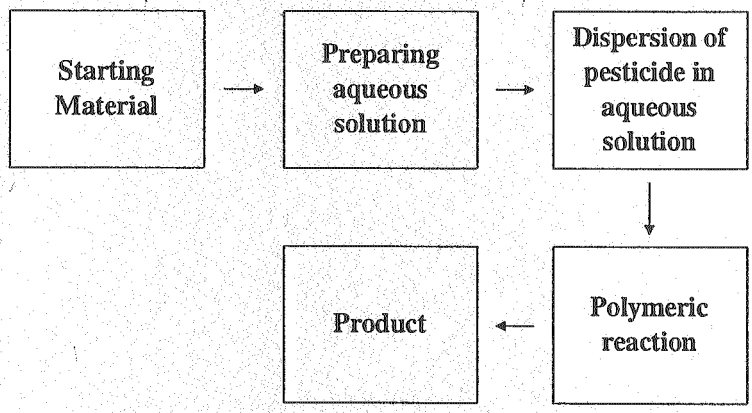


Fig. 3. Schematic diagram of microcapsule synthesis

Chlorpyrifos: 126.2 g (0.36 mol) chlorpyrifos was dissolved in 30 mL xylene and the other conditions were kept the same as in the previous method. The microcapsules of chlorpyrifos with the best quality and yield were obtained.

RESULTS AND DISCUSSION

Microcapsules containing pesticides may be prepared by any of the known microcapsulation techniques. However, in this paper, interfacial polymerization process preferably was used to prepare them. In this process, a relatively water-insoluble (generally termed an "organic" or "oil") liquid phase was prepared which contained one or more liquid or solid pesticides dissolved or suspended in a solvent, optionally one or more surfactants and one or more monomers which will become polymerized to form a polymeric shell for the capsule. The organic phase was then added to an aqueous phase with agitation, forming a dispersion or emulsion of organic (discontinuous) phase droplets in the

aqueous (continuous) phase. The aqueous phase may contain one or more surfactants, protective colloids and other ingredients as known in this paper. The dispersion was then subjected to conditions (usually agitation and heating) so as to cause the monomer or monomers contained in the organic phase droplets to polymerize at the interface between the organic and aqueous phase, forming shells of polymer around the droplets. The product was obtained as a suspension of microcapsules in the aqueous phase.

In the previous papers has been discussed the process of production of some microencapsulated pesticides that were different from our pesticides and other agrochemicals in some of the types of polymerization reactions and in the use of two or more solvents, surfactants and other ingredients[12, 13] but in this work, we used any (for fenitrothion) or one (for chlorpyrifos) low price solvent and only one cheap surfactant and thickener for both of them, for decreasing the price of the products. Therefore, our method is very economical and can be used in industries. We also changed the rate and time of stirring as effective factors and found that, when we changed the rate of stirring to higher speed, the size of particles was decreased (Fig. 4) and when we changed to higher time of stirring, this factor did not affect the particle size and number. We also obtained the release of these pesticides as two graphs (Figs. 5 and 6), the particles size distribution

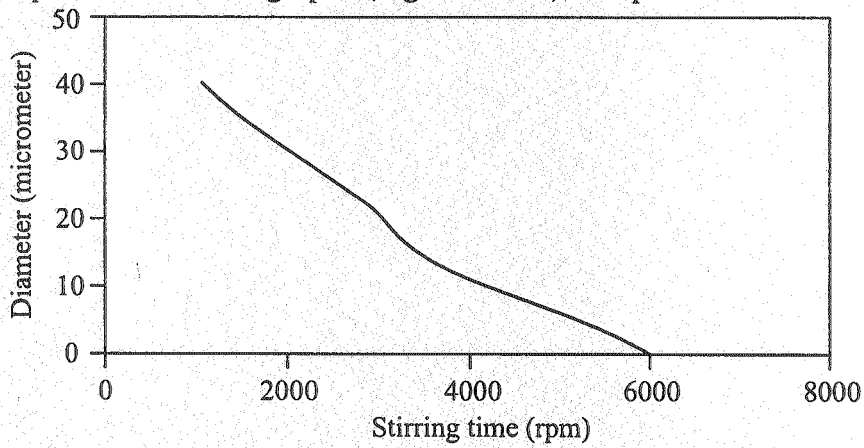


Fig. 4. Effect of stirring time on microcapsule diameter

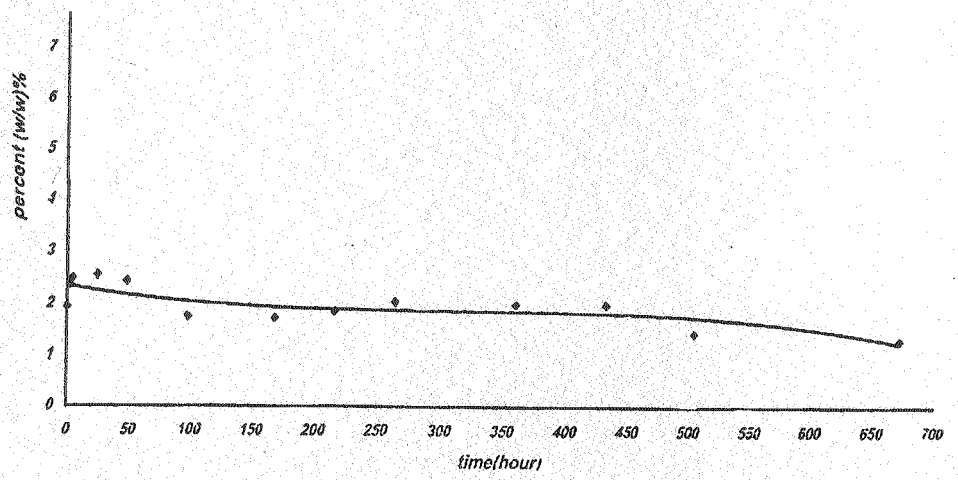


Fig. 5. Release of fenitrothion pesticide

(Fig. 7) and the temperature effect on the release of these pesticides (Fig. 8) in the other graphs.

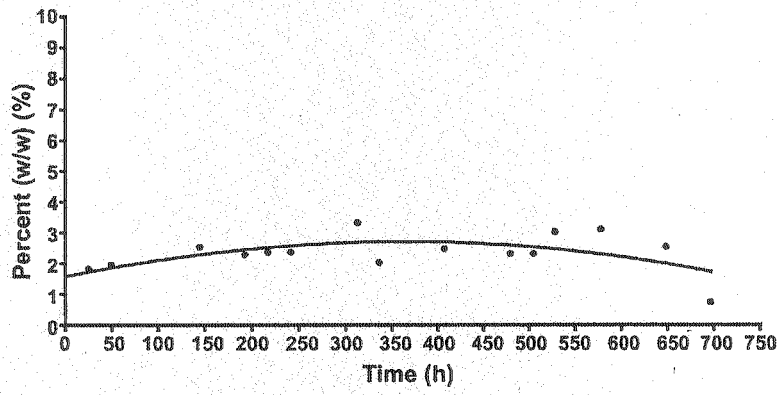


Fig. 6. Release of chloropyrifos pesticide

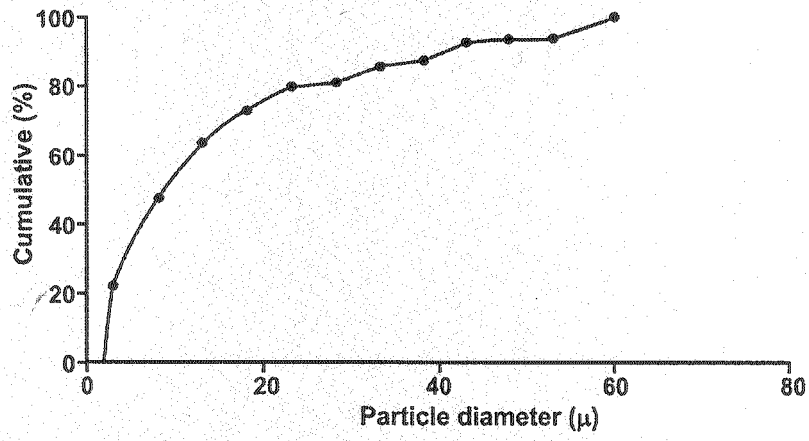


Fig. 7. Particle size distribution

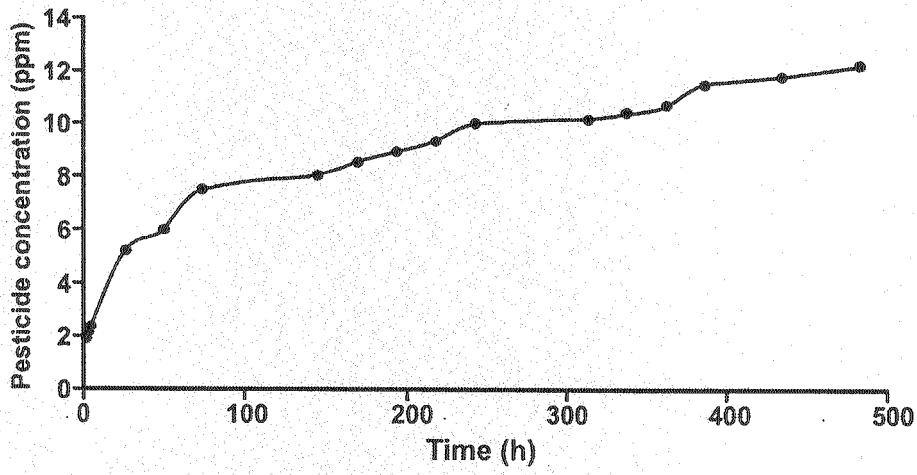


Fig. 8. Effect of temperature on release of pesticide

We also measured the average size of particles (14.5–20 μm) (Fig. 9) and percentages of free pesticides (not microcapsulated) in suspension (0.5%). Scanning electron microscopy (SEM) showed the spherical particles with flat surfaces (Figs. 10 and 11).

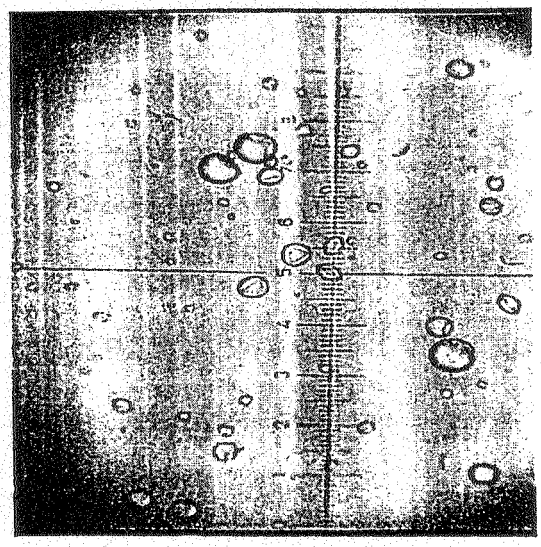


Fig. 9. Size of microcapsules

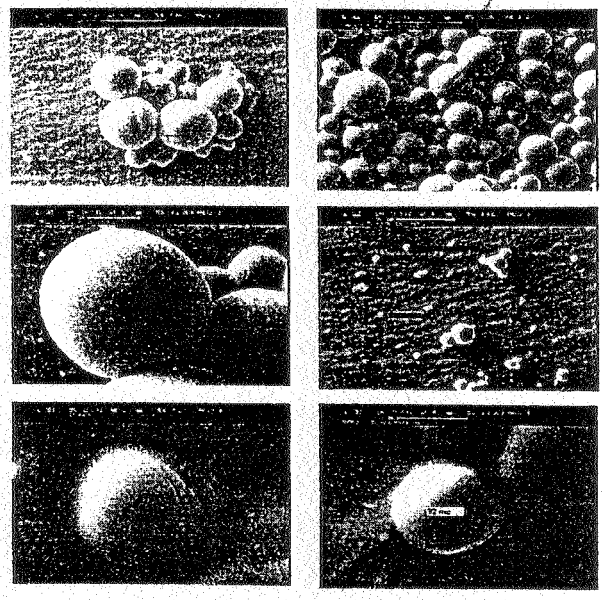


Fig. 10.. The microcapsules SEM photo of pesticides

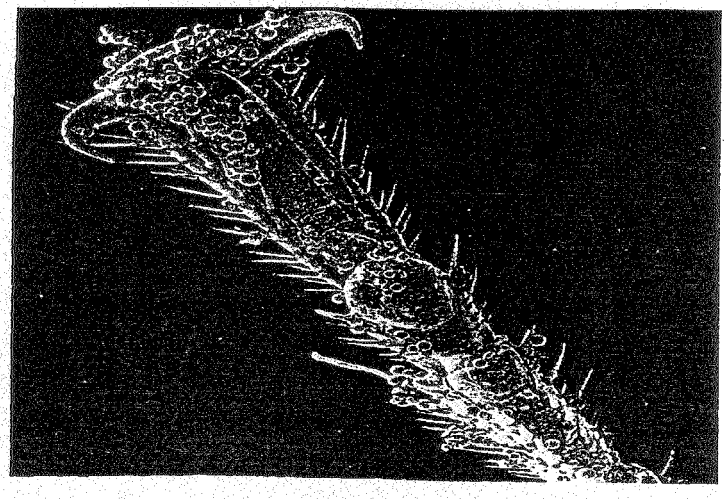


Fig. 11. The sticked mirocapsules SEM photo of pesticides on insect body

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