Abstract

In this study a novel encapsulating matrix for pesticides based on readily available biodegradable natural polymer starch has been studied. Carbofuran, a broad spectrum carbamate pesticide was chosen as a candidate for encapsulation. Granular encapsulated carbofuran formulation was prepared using gelatinized starch crosslinked with urea formaldehyde resin (St-UF). The effect of parameters like degree of crosslinking, percent loading, particle size and solubility of carbofuran in eluting solvent on release kinetics and swelling are described. The water uptake and carbofuran release of this system fits in with the generalized equation $M_t/M_\infty = kt^n$ applicable to controlled release systems involving swelling. The St-UF matrix shows an inverse relationship between rate of release and extent of crosslinking. The release rate at a particular crosslinking value is not affected by the extent of loading at low levels (3-10%) but increases at higher loading level (20%) due to increase in porosity. Porous nature of the matrix at higher loading was confirmed by studying release rates in mixtures of water and methanol at various methanol levels and by scanning electron micrograph. Single particle release studies were conducted by a novel procedure for the first time for a matrix dispersed system of irregular shape. The results establish that the mechanism of release is non-Fickian (anomalous).

The influence of physical state and solubility of encapsulant on the rate and mechanism of release and swelling of the crosslinked St-UF matrix has been studied by encapsulating model

organic compounds. The St-UF matrix shows inverse relationship of release rate with degree of crosslinking for all the encapsulants studied. The solid encapsulants have n value in the range of 0.22 to 0.41 indicating Fickian or anomalous mechanism. Further, the release rate increases with solubility of encapsulant. The liquid encapsulants have n values in the range of 0.5 to 1.5 indicating Case II or Super Case II transport mechanism. The release rates for liquid encapsulants are lower by one to three orders of magnitude than these for solid encapsulants and are not influenced by encapsulant solubility. This indicates a polymer chain relaxation controlled mechanism of release for liquid encapsulants.

Solid state ^{13}C CP/MAS NMR studies of St-UF matrixes have been conducted to elucidate its structure and dynamics. ^{13}C NMR spectra and spin-spin relaxation time (T_2) were obtained for various St-UF samples having different degrees of crosslinking. Line width and T_2 measurements of starch carbons show that maximum degree of crosslinking is obtained at urea to starch (w/w) ratio of 0.6. Increasing the urea to starch ratio beyond 0.6 leads to competing self condensation of methylol urea. These results also establish that chemical crosslinking occurs through the primary hydroxyl groups of C-6 position of starch. By studying ^{13}C NMR spectra of St-UF matrix containing carbofuran, it has been established that carbofuran is physically trapped in the matrix and no chemical bond formation occurs. ^{13}C CP/MAS NMR data (line width and T_2 measurements) show good correlation with release and swelling kinetics results.

Extensive field studies of these controlled release carbofuran formulations have been conducted for variety of crops. This results of this study are in good agreement with in vitro laboratory studies (Appendix)