NOTE

Encapsulation Efficiency and Release Kinetics of Solid and Liquid Pesticides Through Urea Formaldehyde Crosslinked Starch, Guar Gum, and Starch + Guar Gum Matrices

SANGAMESH G. KUMBAR,[1] ANANDRAO R. KULKARNI,[1] ASHOK M. DAVE,[2] TEJRAJ M. AMINABHAVI[1]

[1] Department of Chemistry, Polymer Research Group, Karnatak University, Dharwad, 580 003 India

[2] GSFC Science Foundation, Gujarat State Fertilizers Corporation, Vadodara, 391 750 India

Received 27 September 2000; accepted 20 December 2000

ABSTRACT: This article presents our preliminary experimental data on the release kinetics and encapsulation efficiency of urea formaldehyde (UF) crosslinked matrices of starch (St), guar gum (GG), and starch + guar gum (St + GG) for the controlled release of solid (chlorpyrifos) and liquid (neem seed oil) pesticides. The data reveal variable release rates in relation to the polymer type and especially the pesticide type. It is possible to slow the release rates of pesticides using cheaply available materials such as starch and guar gum. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2863–2866, 2001

INTRODUCTION

Starch (St) and guar gum (GG) are the naturally occurring biodegradable polymers, which, after derivatization/crosslinking,[1,2] can be effectively used as the encapsulating membrane materials in the controlled release (CR) of agrochemicals. In recent years, the development of modified naturally occurring polymers as CR devices in agroindustries has emerged as a new technology with a better commercial viability than the use of the conventional synthetic polymers since these are known to create some environmental concern.[3–5] Therefore, research has been ongoing to find a suitable alternative and film-forming membrane material that can be safely used in agroindustries.[2] This is very essential in the present day to alleviate or minimize the toxic effects of some of the widely used pesticides. In this pursuit, we undertook extensive research on the development of environmentally safe CR agroproducts.[6] Most recently, Hong and Park[7] reported the possibility of using polyurea microcapsules to encapsulate both liquid and solid bioactive compounds, but these systems are not cost-effective in agroindustries.

A process for the encapsulation of pesticides using urea formaldehyde (UF) crosslinked starch[8] and guar gum[6] matrices was reported in the earlier literature. In continuation of this research, we report here preliminary experimental data on the effect of the physical nature of naturally occurring core material such as starch and guar gum on its encapsulation efficiencies as well as the release kinetics of a solid pesticide (chlorpyrifos) and a liquid pesticide [neem (Azadirachta Indica A. Juss.) seed oil (NSO)]. Chlorpyrifos is an organophosphorous compound used against pests like white grub and holotrichi consanguine blanch. However, when chlorpyrifos is applied to plants or mixed

Correspondence to: T. M. Aminabhavi (aminabhavi@yahoo.com).

Part of this work was presented at the Post-Symposium Workshop on Controlled Release Technology in Agriculture and Veterinary Practice, Ooty, India, October 2, 2000.

Contract grant sponsor: GSFC Science Foundation.

Journal of Applied Polymer Science, Vol. 82, 2863–2866 (2001)

Table I Results of Particle Size, Entrapment Efficiency, and *k* and *n* Values

Matrix	Active Agent	Density[b] (g/cm^3)	Particle Size (mm)	Percent Entrapment Efficiency	k (min^{-n}) 10^{-3}	n
St	Chlorpyrifos	1.1694	2.3 ± 0.23	97.4 ± 0.98	0.08	0.36
GG	Chlorpyrifos	1.7313	2.21 ± 0.31	98.3 ± 1.31	0.03	0.42
St + GG[a]	Chlorpyrifos	1.4891	1.99 ± 0.36	99.3 ± 1.55	0.03	0.42
St	NSO	1.1786	2.54 ± 0.96	96.8 ± 1.67	0.52	1.42
GG	NSO	1.6859	2.32 ± 0.26	97.6 ± 1.88	0.17	1.59
St + GG[a]	NSO	1.4326	2.01 ± 0.61	98.4 ± 2.31	0.96	1.24

[a] 50 : 50 of St + GG matrix.
[b] Density of swollen matrix.

with soil, it will produce toxic effects to the environment, especially to the ozone layer.[9] On the other hand, NSO finds applications as a liquid spray to control pests affecting cotton, vegetables, etc. This communication reports on the experimental results of the encapsulation efficiency, bead size, and release kinetics of the polymer type both individually and in combination as well as the pesticide type.

EXPERIMENTAL

Detailed experimental procedures for the prepartion of UF-crosslinked St, GG, and (St + GG) granules containing different pesticides were explained earlier.[6] In brief, the granules were prepared in two steps: (i) the UF prepolymer was first prepared by mixing urea and formaldehyde (previously made alkaline with a 10 % NaOH solution) in a 1:2 molar ratio in a 500-cm^3 beaker and refluxing it for 30 min in a water bath maintained at 70°C and (ii) the gelatinized St or GG or St + GG (50:50) blend containing the pesticide was prepared by boiling it in water. Then, the pesticide was finely dispersed into the mucilage formed above. The mucilage-containing pesticides were crosslinked with the previously prepared UF prepolymer as explained in step (i). The mass thus formed was sieved through a 10#-size mesh ASTM sieve and the granules formed were dried in a vacuum oven at 30°C under a pressure of 600 mmHg for overnight. The dried granules were then sieved through a 22#-size mesh superimposed on 44#-size mesh (ASTM) sieve to obtain uniform-size granules varying in size between 1.0 and 2.0 mm, as measured by a micrometer screw gauge.

The encapsulation efficiencies for both the chlorpyrifos and NSO were calculated by estimating the pesticides before (theoretical) and after encapsulation (actual loading).[6,10] The dissolution experiments were performed by a static method in 250-cm^3 conical flasks containing 30 % (w/v) methanol in water (100 cm^3) as the dissolution media. These flasks were closed with the closer caps and kept in an incubator (WTB Binder, Germany) at 35°C. At definite intervals of time, a 10-cm^3 aliquot was pipetted out and analyzed for the amount of NSO using a UV spectrophotometer (Secomam, Anthelie, France). In the case of chlorpyrifos, the analysis was done by gas chromatography (Hewlett–Packard, HP-6890, USA).[3] The chlorpyrifos-loaded granules were further analyzed by an X-ray diffractometer (USIC, Shivaji University, Kolhapur, India) to confirm the polymorphism of the solid pesticide particles after encapsulation.

RESULTS AND DISCUSSION

The encapsulation efficiency of the polymer is a function of both the nature of the matrix material and the pesticide type. If the membrane polymer is highly rigid, then the matrix will be a good encapsulating material for both solid and liquid forms of pesticides.[7] The three different types of encapsulation matrices used in this research are of natural origin, which are further modified by crosslinking with the UF prepolymer to achieve an efficient encapsulation of both chlorpyrifos and NSO. The X-ray data suggest a uniform dispersion of solid chlorpyrifos particles in the bead matrix. The results of the percent entrapment efficiency, particle size, and density of the matrices for all the systems are given in Table I. The particle size varied from 1.99 to 2.54 mm, with a narrow size distribution. The percent entrapment efficiency ranged between 97 and 99 for chlorpyrifos and varied from 97 to 98 for NSO. The density of the matrices varied between 1.16 to 1.73 g/cm^3.

The release of pesticides from the granules depends on their water-uptake characteristics. For instance, a highly swollen matrix releases the pesticide more when compared to the less swollen matrix. The results of the water-uptake data by St, GG, and St + GG granules are presented in Figure 1. The UF-crosslinked St matrix exhibited a higher water uptake. On the other hand, the GG matrix exhibited the least uptake. This is due to the more rigid structure of GG after crosslinking

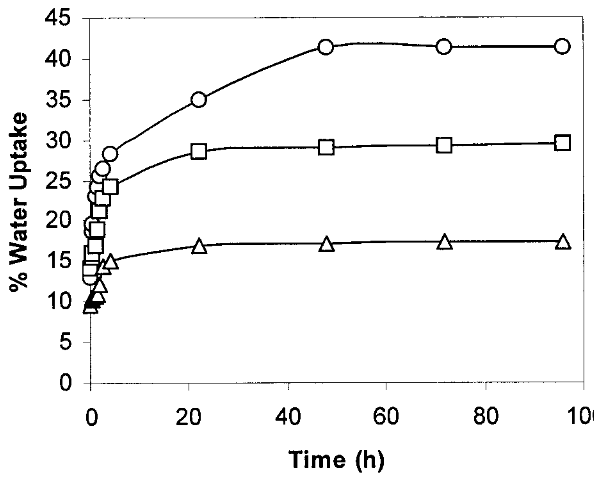

Figure 1 Percent water uptake of (○) St, (△) GG, and (□) St + GG matrices.

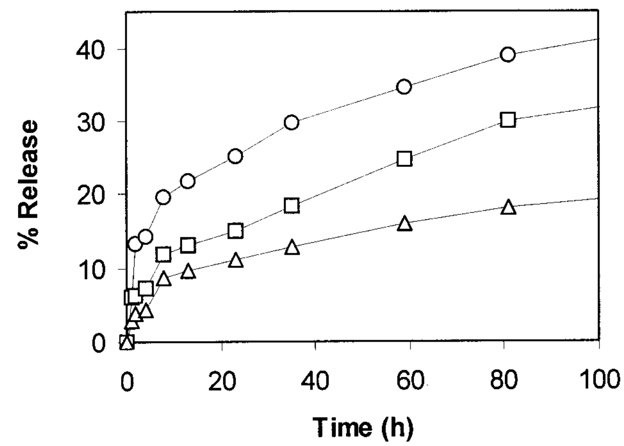

Figure 2 Chlorpyrifos release from (○) St, (△) GG, and (□) St + GG matrices.

when compared to the St matrix. The UF-crosslinked St + GG matrix exhibited an intermediary water uptake between those of St and GG. In the systems studied here, the St matrix shows the highest % release while the least release is shown by the GG matrix. The maximum percent release observed in the case of the St matrix is due to its loose network structure, because its highly hydrophilic nature might have been converted into a partially hydrophobic nature after crosslinking with UF. On the other hand, the more hydrophilic GG after crosslinking becomes more rigid.

The percent release data versus time for the St, GG, and St + GG matrices loaded with chlorpyrifos and NSO are presented at 35°C in Figures 2 and 3, respectively. The release of chlorpyrifos was somewhat faster in comparison to NSO. See, for example, Figure 2, wherein the release rates from starch granules are higher than are those from the GG matrices. Also, for the chlorpyrifos-loaded GG granules, the release follows zero-order kinetics. On the other hand, see, for example, Figure 3, wherein higher release rates are observed for the NSO-loaded starch granules, but for the GG as well as St + GG granules, a zero-order release kinetics is prevalent. Notice that in all the granules the initial release rates are very quick with the solid pesticide-loaded matrices, but there is a time-lag period in the case of liquid pesticide-loaded matrices (see Figs. 2 and 3). This is possibly because the UF-crosslinked GG is swollen to a lesser extent (Fig. 1) when compared to St as well as to St + GG granules

The static fraction release data, M_t/M_∞, were fitted to an empirical equation[11–13] of the type

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

Here, the parameter k represents the nature of the interaction between the pesticide and the polymer, while the exponent value of n decides the nature of the transport mechanism. The values of n and k were estimated by the method of least squares, all at a correlation coefficient value of >0.999. These data are given in Table I. For solid chlorpyrifos, the release follows the Fickian type because the n values are slightly smaller than 0.5, but not less than 0.35; this is possibly because the granules are irregular in shape. Such values were also reported in the earlier literature.[8,13] For the NSO-loaded granules, the n values are between 1.24 and 1.59. This is indeed the range expected of Case II transport.[12] Also, the k values are higher for the NSO-loaded matrices when compared to the chlorpyrifos-loaded granules, which further substantiates higher interactions of the liquid NSO with the matrix materials than with the solid chlorpyrifos.

In conclusion, the pesticide-loaded granules developed in this research may be useful in agroindustries as these seem to be effective in the control release of toxic pesticides into the soil, further alleviating the environ-

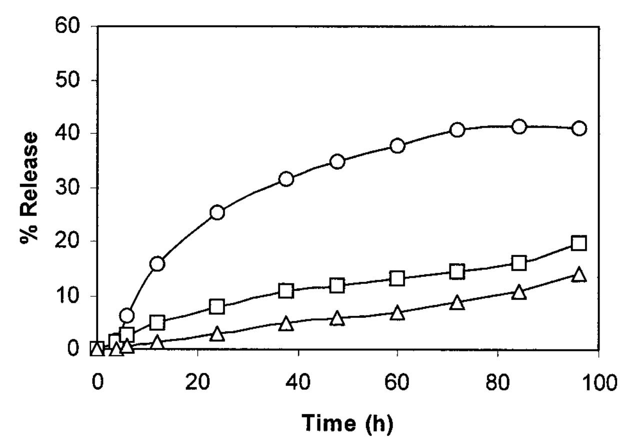

Figure 3 NSO release from (○) St, (△) GG, and (□) St + GG matrices.

mental hazards. However, the release rates are dependent upon the nature of the polymer as well as upon the pesticide type.

The authors are grateful to the GSFC Science Foundation for supporting this research under the Phase-II program sponsored through the Dr. S. Rame Gowda Research Institute of Science and Technology, Dharwad.

REFERENCES

1. Kulkarni, N. V.; Rajgopalan, N.; Kale, R. P.; Khilar, K. C. J Appl Polym Sci 1992, 45, 915.
2. Dave, A. M.; Mehta, M. H.; Aminabhavi, T. M.; Kulkarni, A. R.; Soppimath, K. S. Polym Plast Technol Eng 1999, 38, 673.
3. Kulkarni, A. R.; Soppimath, K. S.; Mehta, M. H.; Dave, A. M. Aminabhavi, T. M. J Haz Mater A 2000, 80, 9.
4. Kulkarni, A. R.; Soppimath, K. S.; Aminabhavi, T. M. J Chem Eng Data 1999, 44, 836.
5. Kulkarni, A. R.; Soppimath, K. S.; Aminabhavi, T. M. J Chem Eng Data 2000, 45, 75.
6. Kulkarni, A. R.; Soppimath, K.S.; Aminabhavi, T. M.; Dave, A. M.; Mehta, M. H. J Appl Polym Sci 1999, 73, 2437.
7. Hong, K.; Park, S. J Appl Polym Sci 2000, 78, 894.
8. Shukla, P. G.; Rajagopalan, N.; Bhaskar, C.; Sivaram, S. J Control Rel 1991, 15, 153.
9. Philip, H. Handbook of Environmental Fate and Exposure Data for Organic Chemicals; Lewis: Chelsea, MI, 1991; pp 132–144.
10. Kulkarni, A. R.; Soppimath, K. S.; Aminabhavi, T. M. J. Microencapsulation 2000, 17, 449.
11. Aminabhavi, T. M.; Harlapur, S. F.; Balundgi R. H; Ortego, J. D. J Appl Polym Sci 1996, 59, 1857.
12. Crank, J. The Mathematics of Diffusion, 2nd ed.; Clarendon: Oxford, 1975.
13. Ritzer, P. L.; Peppas, N. A. J Control Rel 1987, 5, 37.