Controlled release from seed encapsulated with polylactic acid

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INTRODUCTION

Protection of seeds and germinating seedlings against pest damage is a key action in many crop situations which provide long term benefits to plant health and good yields. This is important for all crops and especially for those which have protection provided during the later stages of growth and development through genetic modifications. Depending on the active agent the protection of the seed can be provided by conventional dressing, or similar treatments, but may need extension of the duration of control to more effectively prevent damage or disease (Ester, 2003).

Imidacloprid,1-(6-chloro-3-pyridinymethyl)-N-nitroimidazolidin-2-ylideneamine, is a systemic insecticide used as a seed dressing, soil and foliar treatment in a range crops (Tomlin, 1999) such as brassicas. Delayed release of such a polar compound with reduction of soil concentrations would increase efficiency in use and reduced non-target impacts. High molecular weight polylactic acid (HMW) PLA (formed by catalysed addition of D,L-lactide dimers) has been evaluated for the controlled release of urea and herbicides (Sinclair, 1973; Taki, 2001) but this desirable biodegradable polymer is expensive. The hydrolytic degradation products of oligomeric and monomeric lactic acids provide growth regulation for soybean (Chang, 1996). More economically, the use of low molecular weight (LMW) PLA could be justified as this is produced by thermal polycondensation (via dehydration) of lactic acid (Hiltunen,1997) or with the aid of microorganisms. However, LMW PLA has been shown to undergo autocatalytic hydrolysis and thus a film of LMW PLA can be used as a degradable barrier (Wilkins, 2004, Zhao, 2005).

In the present study, LMW PLA was used for encapsulating seed of cauliflower as it may combine both advantages of seed treatment and controlled release, and to give a delayed release of the active ingredient imidacloprid. The release characteristics and the release mechanisms of imidacloprid were investigated using LMW PLA. The properties of the polymer, both in release of the active agent and its hydrolysis would be relevant to a range of barrier effects from microcapsules to flat films and this study comprises a preliminary evaluation of its unique functions.

MATERIALS AND METHODS

Materials. Polylactic acid (molecular weight 941 measured by end group base-titration) was provided by Croda Bowmans Chemicals Ltd. Cauliflower (*Brassica oleracea* var oleracea) seed pelletised with a standard quartz mineral (1.75-2.25mm dia), containing imidacloprid 1.35mg/seed was supplied by Incotec Ltd. Netherlands. Imidacloprid pesticide technical (98.8%) was purchased from Bayer Ltd. The seeds were encapsulated using a special drum coating method and PLA in acetone (15%w/v) at room temperature and dried with air. Batches were prepared to give 1.46mg PLA/seed (equivalent to capsule wall of 88µm), 1.94mg PLA/seed (120µm thickness) and 2.69mg PLA/seed (159µm thickness).

Release of imidacloprid from encapsulated seed. Treated seeds (10) were selected randomly from each of the three batches (along with non-coated seed), and each was immersed in 100ml distilled water in a flask. All treatments were stored in incubator at 25 ˚C under steady conditions. Water sampled from the flasks was taken and measured every interval of 5-10 days and made up to volume. Analysis was by a Shimadzu HPLC system with Nucleosil-C_8 (25 cm×4.0 mm, 5 µm particle size) reversed–phase column using a mobile phase of acetonitrile-water (80:20, v/v) at a flow rate of 1.5 ml/min. The detection was performed at 270nm, and sample injection volume was 20 µl. Data acquisition and processing were performed with a Gilson UniPoint LC system software (Baskaran, 1997).

Temperature and release of imidacloprid. 10 encapsulated seeds were randomly selected and immersed in 100 ml of static distilled water in a conical flask of 250ml volume with three replicates stored in incubators under steady state at 20 and 30 ˚C respectively. Immersion water was sampled at intervals of 2-10 days, and fresh distilled water was added to maintain 100 ml.

RESULTS AND DISCUSSION

Release of imidacloprid from encapsulated seed. The release profile of imidacloprid PLA cauliflower seed encapsulated in PLA are shown in Figure 1. The release profiles were similar for the three PLA thicknesses, namely a very slow release followed by a rapid release. The cumulative release of imidacloprid was low at the early stage of release, with 7.6%, 8.7% and 13.9% of imidacloprid released in 11 days for each of the thickness coatings of 1.46mg/seed, 1.94mg/seed to 2.69mg/seed, respectively. This release profile type contrasts with diffusion-based kinetics, with decreasing release rates, and has been referred to as lag-burst release.

The release rate decreased generally with the increase in thickness of encapsulating PLA polymer. Generally, a thinner coating resulted in a short delay in release of imidacloprid and a following burst release with comparatively slow release rate. However, a thicker coating resulted in a longer delay in release and the burst release with higher velocity (explosive release).

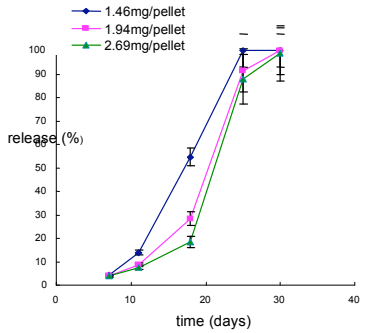

Figure 1. Release of imidacloprid from encapsulated seed

Coating thickness (mg/seed)	Release model (7d ≤ t ≤ 27d)	r^2	T_{50} (d)
1.46	$\mathrm{Ln}(M_t/M_\infty) = 0.1712\,t + 0.5752$	0.9511	19.5
1.94	$\mathrm{Ln}(M_t/M_\infty) = 0.1658\,t + 0.2745$	0.9937	21.4
2.69	$\mathrm{Ln}(M_t/M_\infty) = 0.1639\,t + 0.1602$	0.9933	22.9

Table 1. Release model of imidacloprid from encapsulated seed

Generally, the period of slow release the rate is linear, whereas the period of rapid release is exponential. The mechanism must be complex involving partitioning of the imidacloprid into the PLA layer as well as diffusion in of water from the environment. An important feature, however, is the increasing hydrolysis of the PLA, which initially forms a barrier but rapidly degrades to release the active ingredient (Zhao, 2005).

Temperature and the release of imidacloprid. The role of temperature on the release of imidacloprid from encapsulated seed was investigated by carrying out static immersion tests at two temperatures in addition to the first study. Figures 2 and 3 show the release of imidacloprid at 20 and 30°C respectively.

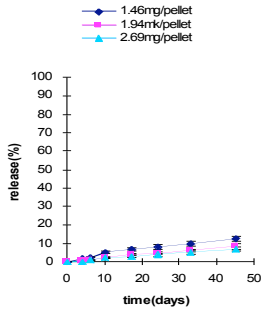

Figure 2: Release of imidacloprid at 20ºC

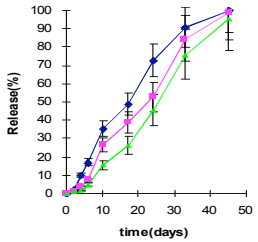

Figure 3: Release of imidacloprid at 30ºC

Over the 45 days of the release study only 7.1-12.5% of imidacloprid was released at 20°C while at 30°C the rate was much higher, about 77.8-100% and the delay step was shortened. At 20°C the slow delay step continues with no burst effect thus water uptake and hydrolysis are depressed. Clearly, a phase change occurred between these 2 temperatures, indicating that diffusion becomes a more important step at low temperatures (Amy 2004). Thus, the low molecular weight PLA is a temperature sensitive release system and it is likely that the temperature of the phase change can be altered by incorporation of other polymers. This process could also allow for other changes such as rate of water uptake, hydrolysis rate and the solubility of the active agent in the wall, affecting the diffusion.

Scanning electron micrography (SEM). Surface and cross-section images of uncoated and coated Cauliflower seed pellets obtained by using scanning electronic microscope (SEM) with the type JEOL JSM5300LV, revealed that the surface of the capsule wall was smooth but after exposure to water became cracked and porous. The initial integrity of the wall can be seen in Figures 4 and 5 showing comparative wall thicknesses. There was close contact with the seed pellet showing little opportunity for direct entry of water.

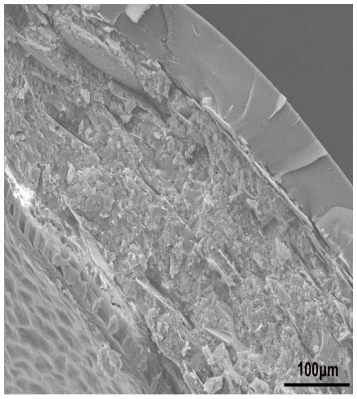

Figure 4 : SEM images of fractured wall of encapsulated seed, 1.03mg PLA

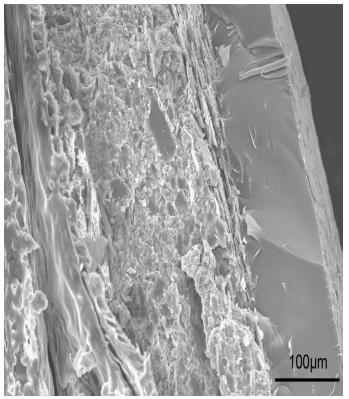

Figure 5: SEM images of fractured wall of encapsulated seed, 1.46 mg PLA

CONCLUSIONS

Low molecular weight PLA was proved to have a controlled lag-burst release for the active ingredient imidacloprid when encapsulation had a suitable thickness, under limited conditions in vitro. The rates were controllable by varying wall thickness. The rapid release following a delay was possibly caused by autocatalytic hydrolysis, converting the PLA wall from a barrier to a porous hydrated medium. The process was temperature sensitive, varying substantially the profile and rate over the range 20-30°C, giving a very slow release or a continuous complete release with a fairly linear profile.

REFERENCES

- Amy C. et al. (2004) *Biomaterials* 26, 2137–2145
- Baskaran, S., et al (1997) *Journal of Chromatography* A.787, 271-275
- Chang, Y. N. et al (1996). *Plant Growth Regulation*. 19, 223-232.
- Ester, A., et al, *Crop Protection* 22, 761–768
- Hiltunen, K. et al (1997) *Macromolecules* 30, 373-379.
- Sinclair, R. G. (1973) *Environm. Sci. Technol.* 7, 955-956.
- Taki, S. et al. (2001) *J. Supercrit. Fluids* 21, 61-70.
- Tomlin, C. The Pesticide Manual. British Crop Protection Council, Surrey, UK. 1999.
- Wilkins, R. M. (1999) In Controlled Release Delivery Systems for Pesticides; Scher H. B., Ed; Marcel Dekker: N.Y. pp195-224.
- Zhao J. et al, (2005) *J. Agric Food Chem*, 53 (11), 4076-4082.