Low Molecular Weight Polylactic Acid as a Matrix for the Delayed Release of Pesticides

JING ZHAO[†,§] AND RICHARD M. WILKINS*[,†]

*School of Biology, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom, and
School of Materials Science and Engineering, Beijing University of Chemical Technology,
Beijing 100029, China*

Low molecular weight polylactic acid (LMW PLA) was used as a matrix to formulate biodegradable matrix granules and films with bromacil using a melt process. The compatibility of the PLA with bromacil was evaluated. The release characteristics of the formulations were investigated in vitro. The degradation and erosion of the formulations were monitored by pH and gravimetric analysis during the course of release. Various granules and films had similar biphasic release patterns, a delayed release followed by an explosive release. The release rates were independent of bromacil content in the matrix, but varied with the geometry of matrices. The mechanisms of diffusion and erosion were involved in the release. The delayed release of the formulations was dominantly governed by the degradation and erosion of PLA. LMW PLA underwent bulk erosion. LMW PLA-based matrix formulations could thus be useful for the application of pesticides to sensitive targets such as seed treatment.

KEYWORDS: Delayed release; polylactic acid; matrix; pesticides; diffusion; degradation; erosion

INTRODUCTION

Biodegradable polymers have been extensively used as a matrix for the controlled release (CR) of a variety of pesticides. The main focuses have been on the naturally occurring biodegradable polymers such as starch, cellulose, chitosan, alginate, and lignins and their derivatives due to their low cost and ease of processing as well as nontoxicity to the environment (*1−7*). The release mechanism is primarily dominated by diffusion in such biodegradable polymer-based matrix formulations, which is characterized by the decrease of the overall release rate with time. However, there remain many applications in agriculture where a rapid burst of release of active agent after a certain time lag is required or, in other words, where initial release is not desirable. For example, as a result of plant growth and other losses there is actually a need for more active agent at later periods after application. Seed treatment is one such scenario, where protection is needed for the emergent seedling and where pesticide delivery needs to match the growing plant. However, if release occurs too soon, the germinating seed itself may be harmed, hence, the need for a delay. Low molecular weight (LMW) polylactic acid (PLA) could be used as carrier material in a matrix system to potentially provide such release characteristics. In comparison to the extensive study of naturally occurring biodegradable polymers in pesticide CR formulations, the use of synthetic biodegradable polymers such as PLA and other polylactide polymers (and related polyesters) for the controlled release of agrochemicals has been rather limited due to their high cost. High molecular weight (HMW) PLA (formed by catalyzed addition of D,L-lactide dimers) has been evaluated for the controlled release of a fertilizer (urea) and herbicides (sodium salt of 2,4-D and diuron) (*8, 9*). The release of the entrapped active agent from HMW PLA-based CR formulations is typically controlled by the rate of diffusion of the active agent through the PLA matrix. The attractiveness of polylactic acid as a matrix lies in hydrolytic degradation under aqueous conditions and its breakdown to lactic acid—a metabolite widely distributed in nature and hence very safe in environmental terms. The hydrolytic degradation products of oligomeric and monomeric lactic acids were also found to contribute to the plant growth regulation of LMW PLA (3500 Da) for soybean (*10*). More importantly, the use of LMW PLA as a matrix for the controlled release of agrochemicals could be justified by a reduction in the cost of PLA production using thermal polycondensation (via dehydration) of lactic acid (*11*) or with the aid of microorganisms. However, LMW PLA has been little studied as a matrix in pesticide CR formulations, but it has been shown to undergo autocatalytic hydrolysis (*12*), and thus a film of LMW PLA can be used as a degradable barrier (*13, 14*). In this paper, we report the use of LMW PLA as a matrix for the delayed release formulations. The release characteristics and the release mechanisms of the model compound bromacil were investigated for the matrix formulations based on LMW PLA in the forms of granules and films, representing the two most likely used formulation configurations relevant to seed treatments or other applications.

* Author to whom correspondence should be addressed (telephone 44-191-2226945; fax 44-091-2225228; e-mail richard.wilkins@ncl.ac.uk).
† Newcastle University.
§ Beijing University of Chemical Engineering.

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Table 1. Composition and Characterization of Bromacil–PLA Matrix Formulations

composition (%)	bromacil content (% ± SD)		solubility	physical property	
bromacil/PLA	granule	film		appearance	handling
10/90	10.4 ± 0.10	10.3 ± 0.13	soluble	glassy, clear	good
20/80	19.3 ± 0.15	19.7 ± 1.72	mostly soluble	glassy, clear	good
30/70	28.7 ± 0.30	29.0 ± 1.29	crystallizes	glassy, milky	good
40/60	37.9 ± 0.68	37.1 ± 0.70	crystallizes	glassy, opaque	good
50/50	48.1 ± 0.18	46.3 ± 0.79	crystallizes	glassy, opaque	good

MATERIALS AND METHODS

Materials. Polylactic acid (MW = 900 by end-group analysis) was kindly provided by Croda Bowmans Chemicals Ltd. Lactic acid was of analytical grade and purchased from BDH, Poole, U.K. Bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H)-pyrimidine] (purity = 97%) was obtained from Griffin Corp. (Valdosta, GA). Bromacil standard (purity = 98%) was purchased from Greyhound (Birkenhead, U.K.). All analytical grade solvents were obtained from Fisher Scientific, U.K., and used as received without further purification.

Methods. *Preparation of LMW PLA-Based Matrix Formulations.* Bromacil and PLA powder (total amount of 5 g; the proportions of the two ingredients are listed in **Table 1**) were thoroughly mixed and then melted on a hot plate at 150 °C for 10 min. After it was cooled, the blend was either granulated and sieved to the granule size of 2.4−2.8 mm or recast into the films with a dimension of 10 × 10 × 1 mm. F-*X* or G-*X* was used as the code for the formulations, where F and G represent film and granule, respectively, and *X* was the percentage of bromacil by weight (w/w) in the formulations. The formulations were analyzed for bromacil (ai) content by extraction with acetone (sonicated) in quadruplicate, filtered through a nylon membrane, and analyzed on GC-FID (Perkin-Elmer AutoSystem) using a SUP-Herb fused silica capillary column (column i.d. = 0.53 mm, column length = 15 m, film thickness = 0.50 μm) (Supelco U.K., Dorset, U.K.). The conditions were as follows: He carrier gas, 15.7 mL/min; air, 450 mL/min; hydrogen, 45 mL/min; injector temperature, 250 °C; column temperature, 210 °C; and detector temperature, 280 °C. A split mode was used at the ratio of carrier gas flow to split vent flow of 1/20. The retention time for bromacil was 1.6 min.

Measurement of Pesticide Release. Bromacil release from matrix granular formulations (50 mg, ai) was studied at 30 °C in 250 mL of deionized water. Bromacil release from matrix film formulations (100 mg) was investigated at 30 °C in 50, 100, 150, 200, and 250 mL of deionized water for 10, 20, 30, 40, and 50% bromacil contents, respectively. All of the release studies were performed in an environmentally controlled incubator shaker at 150 rpm. Immersion water was collected at intervals and replaced with fresh deionized to maintain "sink" conditions. The samples collected were analyzed using a UV− vis spectrophotometer at 278 nm. Three replicates were used for granules and four replicates for film. The average values were used for further data treatment and plotting.

Degradation of LMW PLA-Based Matrix Formulations. The degradation of bromacil−PLA matrices was investigated by analyzing the amount of lactic acid end product appearing in the immersion water by means of the change in pH values. The amount of PLA degradation products was calculated using eq 1 on the assumption that the hydrolysis of polylactic acid is irreversible, resulting in lactic acid end product and oligomers

$$D\,(\%) = \frac{m_P \times W_L}{m_L \times n \times W_P} \times 100 \tag{1}$$

where *D* is the percent of polylactic acid degraded, m_p is the molecular weight of polylactic acid, W_L is the amount of lactic acid released into the immersion water, *n* is the degree of polymerization of polylactic acid, m_L is the molecular weight of lactic acid, and W_P is the initial amount of polylactic acid in the matrix.

Erosion of LMW PLA-Based Matrix Formulations. The erosion of bromacil−PLA matrices was characterized by the PLA weight loss due to degradation. The weight loss due to the degradation of PLA was investigated by weighing the dried matrix formulations. A separate experiment was performed using a bromacil−PLA matrix (100 mg) coated on a microscope slide cover slip (*d* = 19 mm) to establish the relationship between PLA erosion determined by gravimetric analysis and PLA degradation determined by pH analysis. The PLA weight loss was calculated according to eq 2

$$W_{Loss} = \frac{W_I - (W_R + W_D)}{W_I \times (1 - C)} \tag{2}$$

where W_I is the initial weight of matrix (mg), W_R is the amount of bromacil released, W_D is the dry weight of the matrix at each sampling time (mg), and *C* is the bromacil (ai) content of the matrix.

Observation of LMW PLA-Based Matrix Formulations. The morphology of various bromacil−PLA matrices before the release of bromacil and the matrix formulations collected at the end of the release experiment was observed with light microscopy (Wild M5 stereomicroscope, ×100 magnification).

RESULTS AND DISCUSSION

Characterization of LMW PLA-Based Matrix Formulations. The characteristics of various matrix formulations are summarized in **Table 1**. Microscopic study of the morphology of the matrices indicated that the matrix formulations were homogeneous at the 10 and 20% levels. No crystals were observed for 10% formulations, and some very fine crystals were seen for 20% formulations. With increasing bromacil content of the formulations (ai > 30%), more and larger crystals were suspended in the matrix (**Figure 1**). The handling property was good for all five matrices. The actual percentage of bromacil (ai) in the formulations was used when the percentage of bromacil released in water was calculated.

Release of Bromacil from LMW PLA-Based Matrix Formulations. *Effect of Bromacil Content.* The release profiles of bromacil from various LMW PLA-based matrix granules and films are shown in **Figures 2** and **3**, respectively. The release patterns were similar for both granules and films with various bromacil contents, being a slow release followed by a rapid release. The cumulative release of bromacil was low at the early stage of release, with 8−17% of bromacil released in 23 days and 16−21% of bromacil released in 16 days for granules and films with bromacil contents ranging from 10 to 50%, respectively. Then, the release rate was dramatically increased and kept almost constant until the device was exhausted of active agent.

To investigate the release mechanisms, the release data were respectively fitted to Fickian and zero-order models for the early and late stages of release, with the resulting constants shown in **Table 2**. The correlation coefficients of fitting data to models were high, suggesting that the release was governed by two independent mechanisms: diffusion followed by erosion. Some variation in the release rate constants was found for various formulations with different bromacil contents at the early stage of release. However, as the cumulative release of bromacil was very low in all cases (<20%), the influence of bromacil (ai)
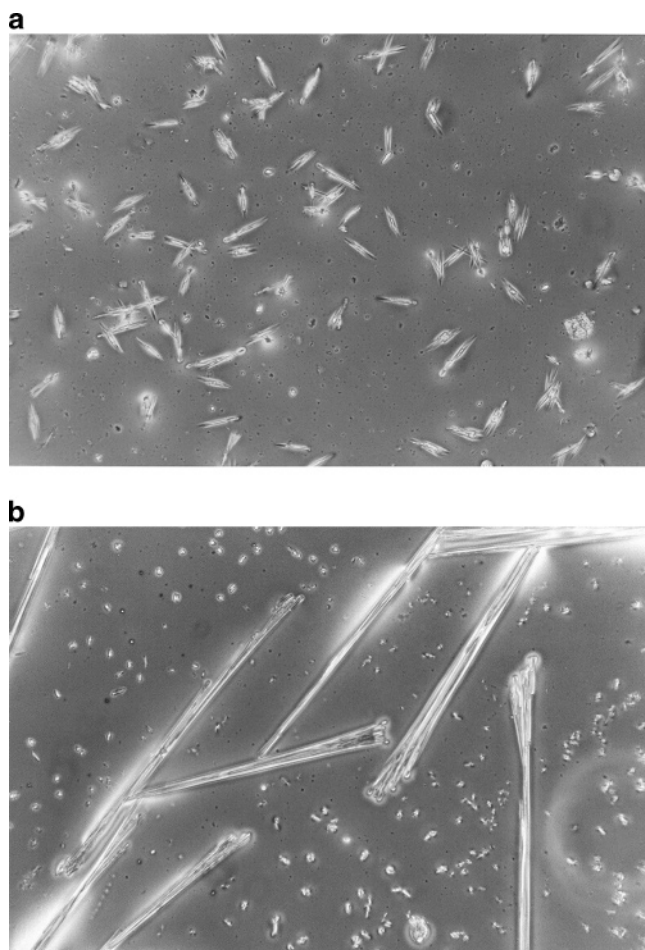
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Figure 1. Photomicrographs of (**a**) 30% bromacil–PLA matrix and (**b**) 50% bromacil–PLA matrix (×100 magnification).
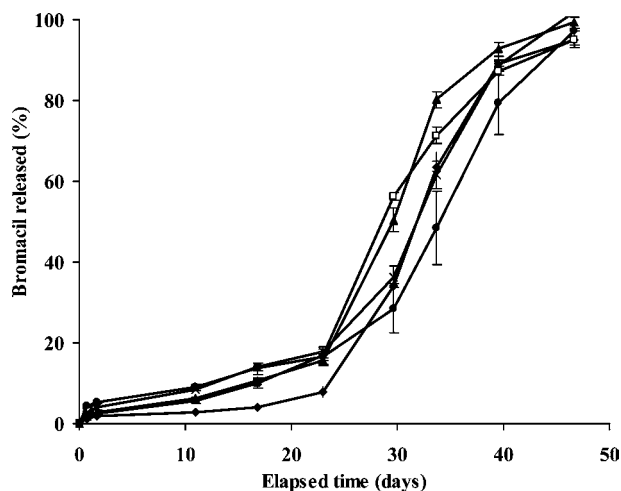
Figure 2. Release of bromacil from various bromacil–PLA matrix granules: G-10 (◆); G-20 (□); G-30 (▲); G-40 (×); G-50 (●). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where the bars are not shown.)

contents on the overall release could be minimal. The release rates were independent of bromacil content for both LMW PLA-based granules and films at the late stage of release (23−40 days), as indicated by the similar release rate constants. The release rates, therefore, might be mainly controlled by erosion at the late stage of release. The results suggested that bromacil content in the matrices had little influence on the release rates of bromacil from LMW PLA-based matrix formulations.
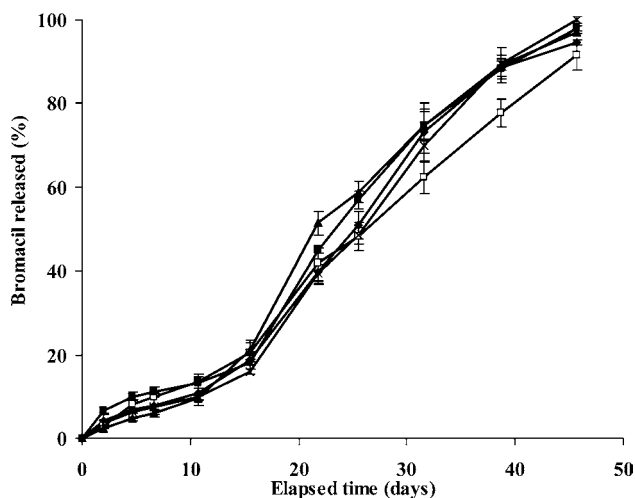

Figure 3. Release of bromacil from various bromacil–PLA matrix films: F-10 (◆); F-20 (□); F-30 (▲); F-40 (×); F-50 (■). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where the bars are not shown.)

Table 2. Constants from Fitting Fickian and Zero-Order Models to the Release Data

	Fickian model $(M_t/M_\infty = k_{1/2} t^{0.5})^a$		zero-order model $(M_t/M_\infty = A + k_0 t)^b$		
matrix	$k_{1/2} \pm$ SE	r^c	$k_0 \pm$ SE	$A \pm$ SE	r^d
G-10	1.31 ± 0.05	0.933	3.59 ± 0.06	−70.72 ± 2.39	0.966
G-20	1.89 ± 0.10	0.997	3.51 ± 0.09	−58.41 ± 2.98	0.951
G-30	2.02 ± 0.05	0.998	3.80 ± 0.09	−65.71 ± 2.98	0.943
G-40	3.02 ± 0.05	0.994	3.60 ± 0.07	−63.13 ± 2.71	0.984
G-50	3.37 ± 0.10	0.962	3.42 ± 0.16	−62.50 ± 5.00	0.984
F-10	3.16 ± 0.52	0.998	2.39 ± 0.06	−14.43 ± 2.62	0.981
F-20	2.77 ± 0.22	0.976	2.37 ± 0.12	−14.25 ± 3.66	0.995
F-30	1.86 ± 0.04	0.973	2.19 ± 0.06	−2.98 ± 2.68	0.971
F-40	2.82 ± 0.07	0.997	2.86 ± 0.04	−27.10 ± 1.11	0.992
F-50	4.41 ± 0.23	0.994	2.46 ± 0.03	−13.41 ± 0.99	0.978

[a] The release of bromacil at the early stage (<16 days) was fitted to the square root of time model, where $k_{1/2}$ is the release rate constant. [b] The release of bromacil at the late stage (>16 days) was fitted to the zero-order model, where A is a constant and k_0 is a release rate constant. [c] The correlation of data versus model was significant at $P = 0.001$ except for G-10 at $P = 0.02$. [d] The correlation of data versus model was significant at $P = 0.01$ for the granules and significant at $P = 0.001$ for the films.

Varying Geometry of the Matrices. The release profiles of bromacil from 50% bromacil−PLA granules and films are compared in **Figure 4**. At the early stage of release (<16 days), bromacil released slightly more quickly from the film (10 × 10 × 0.89 mm) than from granules (2.36−2.80 mm), as indicated by its higher $k_{1/2}$ of 4.41units compared to the lower $k_{1/2}$ of 3.37 units (**Table 2**). However, the release rates of the granules were ∼1.4 times that of the film in the following release period as indicated by the k_0 values. Similar results were also found for the other films from which the release of bromacil was slower compared to the granules with the same bromacil content during the late release stage (**Table 2**). The results suggested that the geometry of the LMW PLA-based formulations had a considerable effect on the release rates of bromacil at different release stages.

Degradation of LMW PLA-Based Matrix Formulations. The degradation profiles of PLA, which were obtained by pH analysis, are compared for various bromacil−PLA granules and films in **Figures 5** and **6**, respectively. Not surprisingly, biphasic degradation patterns were obtained for granules and films with
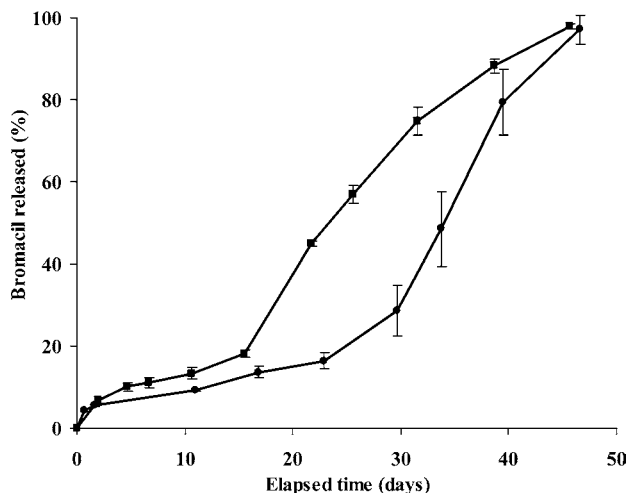
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Figure 4. Release of bromacil from 50% bromacil–PLA matrix granules and film: G-50 (●); F-50 (■). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where the bars are not shown.)
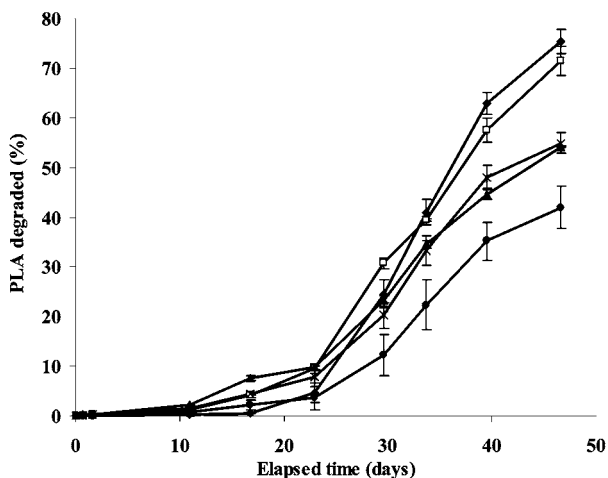

Figure 5. Degradation of PLA from various bromacil–PLA matrix granules: G-10 (◆); G-20 (□); G-30 (▲); G-40 (×); G-50 (●). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where the bars are not shown.)

Figure 6. Degradation of PLA from various bromacil–PLA matrix films: F-10 (◆); F-20 (□); F-30 (▲); F-40 (×); F-50 (■). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where they are not shown.)

various bromacil contents, being a very slow initial degradation followed by a dramatic increase in degradation, which would account for the biphasic release profiles discussed above. The cumulative amounts of PLA degraded were small and ranged from 0.77 to 9.61% and from 6.26 to 11.05% of initial PLA being degraded in 16 days of immersion for granules and films, respectively. Thus, the release of bromacil from the matrices was primarily governed by diffusion at this release stage. This was followed by the beginning of the rapid degradation of the matrix at 16 days, resulting in the replacement of the diffusion-controlling with the degradation-controlling step.

The results of the PLA degradation after 23 days of immersion showed that the PLA degradation decreased with increasing bromacil content in the matrix. This reduction may be due to reduced water uptake of the bromacil−PLA matrices (observed for 10, 30, and 50% bromacil−PLA matrices, data not shown) and the inhibitory effect of bromacil on the autocatalytic hydrolysis of PLA, with increasing bromacil content. The reduction in water uptake could retard the hydrolysis of PLA in the matrices.
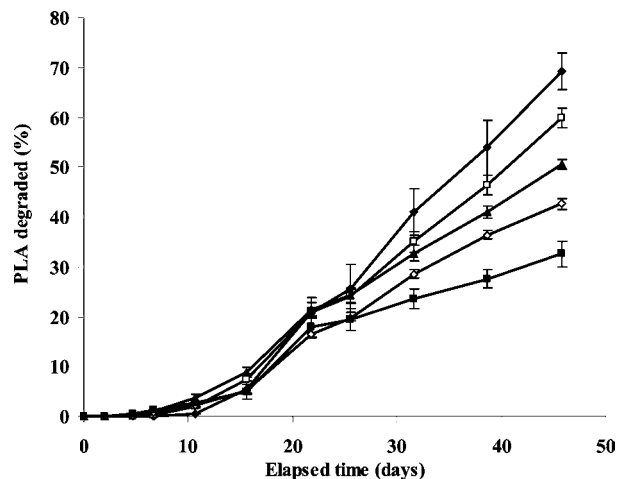
As PLA degradation is autocatalytic, the hydrolysis rate of PLA was found to be inversely proportional to the pH of the degradation medium (*15*). The lactic acid end products formed during chain cleavage and then entrapped in the matrix may result in relatively strong acidic conditions inside the matrix, thus accelerating the hydrolytic degradation. The acidity of bromacil was weaker than that of lactic acid, as indicated by the pK_a values of 9.27 for bromacil (*16*) and 3.86 (25 °C) for lactic acid (*17*). The presence of dissolved bromacil in the imbibed water could probably dilute the concentrated solution of lactic acid and oligomer degradation products inside the matrix, slowing further degradation of PLA. As a result, more oligomers could be produced as major degradation products in the matrix with higher bromacil content than with lower bromacil content. The release of degraded PLA oligomers from the matrices was facilitated by the developing porous structure, which was formed after bromacil crystals dissolved and were released from the matrix, due to the presence of bromacil crystals in the PLA-based matrix with high bromacil content (**Figure 1**). This release of more oligomers into water would result in a lowered reduction in pH values of the immersion water, leading to lower cumulative amount of degraded PLA obtained from the pH analysis (**Figures 5** and **6**).

Degradation of PLA from 50% bromacil−PLA matrix granules (2.36−2.80 mm) is compared with that from 50% bromacil−PLA matrix films (10 × 10 × 0.89 mm) in **Figure 7**. The degradation of PLA was slow at the early stage (<16 days), being faster for the films than for the granules (4.97% compared to 2.18% of PLA degraded). In addition, the slow degradation operated for a longer period of time for the granules than for the film, with only 3.59% of degraded PLA being released into water at ∼23 days. This slow degradation suggested that diffusion dominated a longer period of release for the granules than for the films. At the late stage of release (degradation-dependent release), however, the degradation of PLA was faster in the granules than in the films, which was probably due to the carboxylic end groups of PLA chains that are entrapped in the matrix and thus accelerated the cleavage of the main-chain ester bonds by autocatalysis (*15*). In the case of large devices, autocatalytic cleavage of ester bonds is greater inside than outside, leading to the formation of a highly degraded center surrounded by a slowly degrading membrane (*18*). The diffusion of hydrolytically degraded fragments is slow compared to ester hydrolysis (*19*). The distance from the highly degraded

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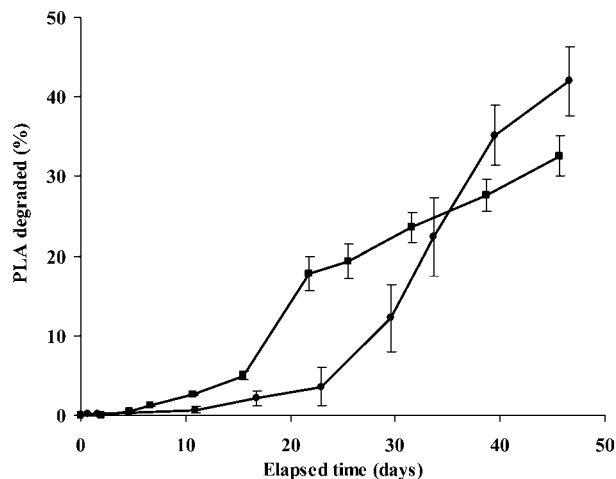
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Figure 7. Degradation of PLA from 50% bromacil–PLA matrix granules and film: G-50 (●); F-50 (■). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where the bars are not shown.)

Figure 8. Comparison of the cumulative amount of PLA degraded and eroded for the bromacil–PLA matrix granules and films. PLA erosion was determined by gravimetric analysis (GA) for bromacil–PLA matrix G-GA (●) granules and F-GA (■) films. PLA degradation was determined by pH analysis for bromacil–PLA matrix G-pH (○) granules and F-pH (□) films (F). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where they are not shown.)

center to the slowly degraded surface is smaller for the film (10 × 10 × 1 mm) than for the granules (2.36−2.80 mm). In addition, the surface area of the film was slightly higher than that of the granules, being 236 mm^2 for film (thickness = 0.89 ± 0.01 mm, 97.6 ± 0.60 mg) compared to 200 mm^2 for granules (diameter = 2.51 ± 0.04 mm, 100.6 ± 0.55 mg). Due to the short diffusion pathway and large surface area of the film, the release of oligomers and even parts of the polymer bulk could be facilitated provided the degradation products are sufficiently small to be soluble. The pH value in the immersion water would be higher that that of the highly degraded center in the matrix. The degradation of oligomers could be slowed after they release from the matrix into the immersion water. Therefore, less rapid degradation was found for the films than for the granules.

Erosion of LMW PLA-Based Matrix Formulations. Degradation of polymers is followed by the release of degradation products, leading to the weight losses of the matrices that are characteristic for erosion (*15*). In this study, the PLA weight losses (in percentage of the original amount of PLA in the matrix) were defined as the cumulative erosion of PLA.

The cumulative amount of PLA eroded was measured for various bromacil−PLA granules and films at the end of the release experiment and compared with the cumulative amount of PLA degradation products calculated on the pH of immersion water collected during the course of release (**Figures 5**−**7**). **Figure 8** shows the plots of the PLA degraded or eroded versus the bromacil content of the granules and films. The cumulative amounts of PLA eroded were very similar for the granules or films with various bromacil contents. Interestingly, the cumulative amounts of PLA degraded were remarkably lower than that of the cumulative amounts of PLA eroded. Moreover, as indicated by the ratio of PLA erosion to PLA degradation (**Table 3**), the difference between the PLA erosion and PLA degradation increased with increasing bromacil content, and the greater difference was found for films than for granules. The results supported the previously proposed contention that the degradation of PLA and release of PLA degradation products could be associated with the bromacil content and the geometry of the matrices. As previously discussed, more PLA oligomers would release from the matrices with greater bromacil content, or more from films than from granules, leading to the similarity in PLA erosion of various bromacil−PLA matrices. However, the cumulative amounts of PLA degraded, which were determined
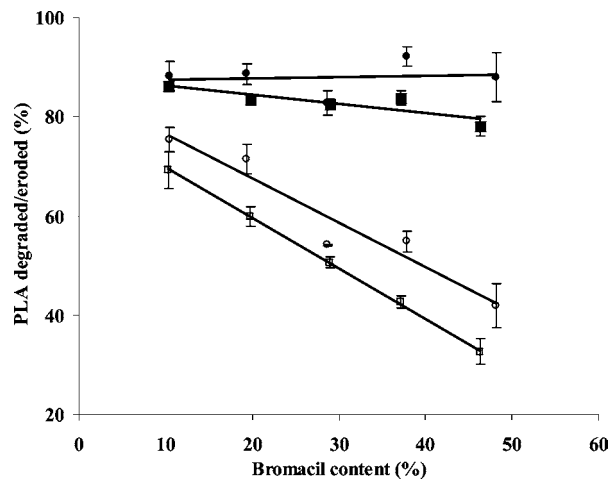
Table 3. Ratios of PLA Erosion to PLA Degradation for Bromacil–PLA Matrix Granules and Films

matrix	ratio of PLA erosion to PLA degradation[a]	matrix	ratio of PLA erosion to PLA degradation[a]
G-10	1.17 ± 0.01	F-10	1.25 ± 0.08
G-20	1.24 ± 0.08	F-20	1.39 ± 0.03
G-30	1.53 ± 0.04	F-30	1.63 ± 0.03
G-40	1.68 ± 0.09	F-40	1.97 ± 0.06
G-50	2.10 ± 0.11	F-50	2.40 ± 0.13

[a] The ratio was calculated by dividing the cumulative amount of PLA eroded by the cumulative amount of PLA degraded (data taken from **Figure 8**).

by the reduction of pH values resulting from the end degradation products (lactic acid) in the immersion water, would be underestimated in such cases because of dimers or oligomers of PLA rather than lactic acid released into the water. The results imply that incomplete degradation of PLA would likely occur for the matrices with high bromacil content and for films rather than granules.

To confirm the assumption of incomplete degradation of PLA and to establish the relationship between the PLA erosion and the PLA degradation, an independent experiment was conducted to determine PLA erosion by gravimetric analysis and PLA degradation by pH analysis during the course of bromacil release. The cumulative amount of PLA eroded was plotted against the cumulative amount of PLA degraded at the same time intervals in **Figure 9**, with the curve-fitting results in **Table 4**. As shown by the slopes, the erosion of PLA was faster than the degradation of PLA, and the difference in rates between PLA erosion and degradation increased with bromacil content. The results here are in agreement with the previous findings that the PLA degradation decreased with bromacil content, whereas the PLA erosion remained almost constant for the granules and films (**Figure 8**; **Table 3**).

The erosion of PLA correlated very well with the degradation in a linear relationship, as indicated by the high correlation coefficient (**Table 4**), suggesting that the ratio of PLA eroded to PLA degraded was constant for each bromacil−PLA matrix but varied with the bromacil content in the matrix. Therefore, the PLA erosion could be predicted from the PLA degradation
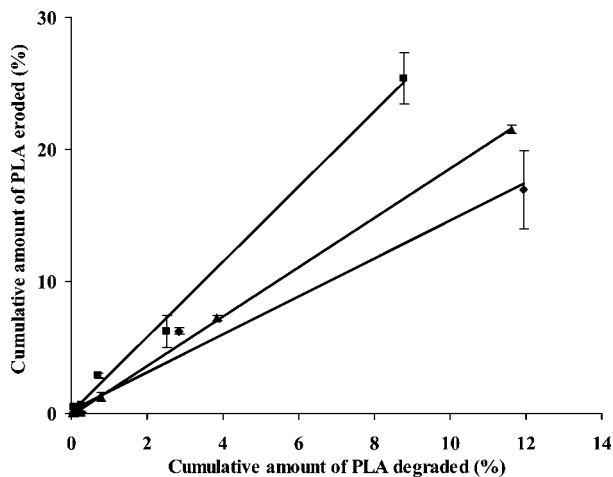
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Figure 9. Plots of the cumulative amount of PLA eroded versus the cumulative amount of PLA degraded for bromacil–PLA coatings: C-50 (■); C-30 (▲); C-10 (◆). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where they are not shown.)
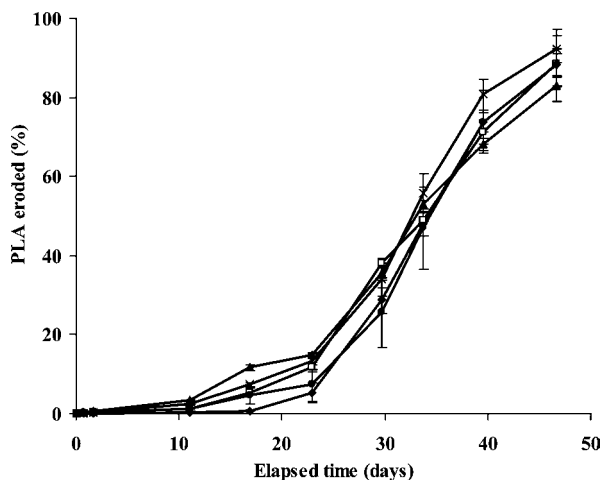

Figure 11. Erosion of PLA in various bromacil–PLA matrix films: F-10 (◆); F-20 (□); F-30 (▲); F-40 (×); F-50 (■). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where they are not shown.)

Figure 10. Erosion of PLA in various bromacil–PLA matrix granules: G-10 (◆); G-20 (□); G-30 (▲); G-40 (×); G-50 (●). (Error bars represent the standard deviation of three replicates. The error bars are smaller than the symbols where they are not shown.)

Table 4. Constants from Fitting a Linear Regression Equation, $y = mx + c$, to the Plots of the Erosion Data of PLA versus the Degradation Data of PLA for Bromacil–PLA Matrix Coatings

	$y = mx + c$		
code	$m \pm$ SE	$c \pm$ SE	r^a
C-PLA	1.40 ± 0.03	−0.34 ± 0.19	0.9991
C-10	1.44 ± 0.10	0.27 ± 0.49	0.9908
C-30	1.87 ± 0.02	−0.16 ± 0.09	0.9998
C-50	2.85 ± 0.09	0.08 ± 0.34	0.9980

by calculating the product of the cumulative amount of PLA degraded and the ratio of PLA eroded to PLA degraded.

The erosion profiles of PLA (**Figure 10** and **11**) were obtained by using the ratios of PLA eroded to PLA degraded (**Table 3**) and degradation data (**Figure 5** and **6**). Not surprisingly, the erosion profiles of granules and films containing various bromacil contents were biphasic, showing very slow initial erosion followed by a dramatic increase in erosion. The erosion rates did not significantly vary with bromacil content at the rapid erosion stage. However, the erosion rates of PLA were greater for the granules than for the films at this stage.
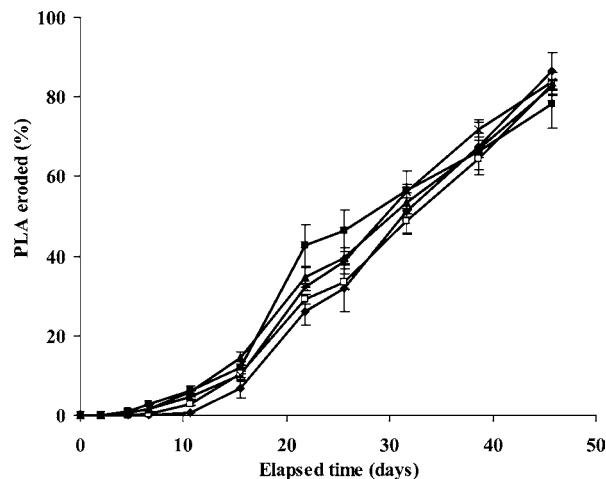
The morphological changes of eroding polymers occur concomitantly with erosion but vary with the type of either surface (or heterogeneous) or bulk (or homogeneous) erosion (*15*). The matrix geometry of bulk eroding polymers normally does not change for a substantial time period (*20*). For bromacil−PLA matrices, the extent of change in geometry varied with the bromacil content in the matrix. The higher the bromacil content, the longer the geometry remained intact. For 40 and 50% bromacil−PLA films, the matrix geometry remained intact at 46 days when bromacil was almost completely released. The photomicrographs of the matrix morphology (**Figure 12**) suggest that the LMW PLA underwent bulk erosion.

Conclusions: Correlation of Degradation and Erosion of PLA with Release of Bromacil. The degradation and erosion characteristics of LMW PLA-based films were correlated well to the biphasic release profiles of those formulations, indicating that two release mechanisms are involved, that is, diffusion and erosion. The very slow PLA degradation and erosion at the early stage of bromacil release suggested that the release was governed by diffusion, which was in good agreement in the curve-fitting results of bromacil release (**Table 2**). The significant weight losses of PLA from the matrices indicated the beginning of rapid erosion as a result of rapid degradation of PLA and release of degradation products, suggesting that the release is mainly controlled by erosion at the late stage of release. PLA started rapid degradation and erosion at 23 and 16 days from the bromacil−PLA matrix granules and films, respectively, implying that the diffusion-controlling step operated for a longer time in the granules than in the films. The similarity of the rates of PLA erosion strongly supported the evidence that release of bromacil was independent of bromacil content of LMW PLA-based granules and films at the late stage of release. Similarly, the rates of PLA erosion of granules were greater than that of films and accounted for the faster release of bromacil from granules than from films at this stage. It should be mentioned that there were some variations in the release of bromacil at the early stage of release for LMW PLA-based matrices. However, the cumulative release of bromacil was much lower at the early diffusion-controlling stage than at the late erosion-controlling stage (**Figures 2** and **3**). Therefore, the release of bromacil was dominantly controlled by degradation and erosion of PLA for the matrix formulations based on LMW PLA.

In conclusion, LMW PLA was proved to be a promising matrix for the delayed release of pesticides in both particle
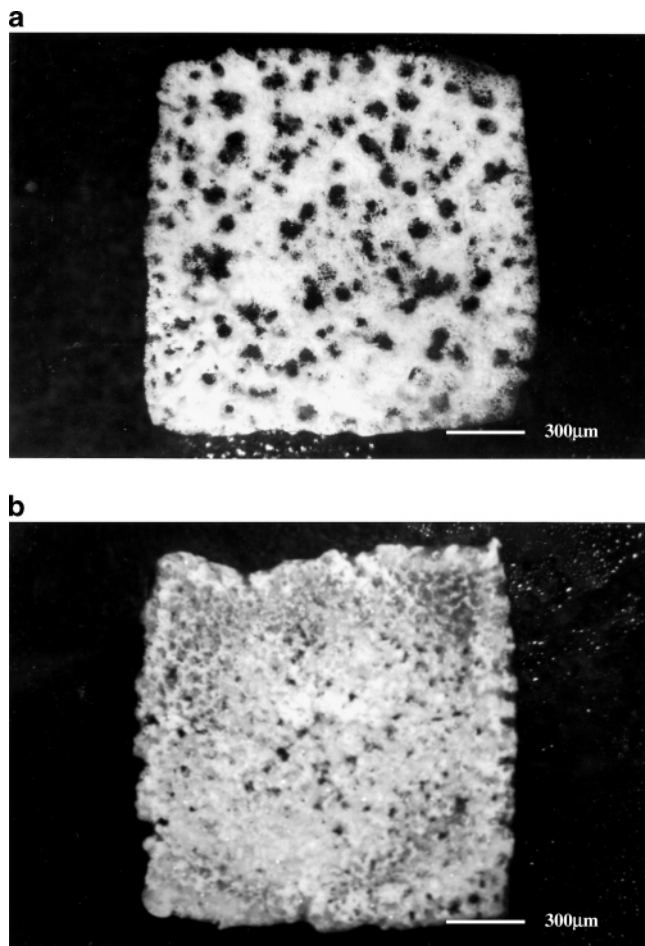
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Figure 12. Photomicrographs of (**a**) 40% bromacil–PLA film and (**b**) 50% bromacil–PLA film after 39 days of release (×60 magnification). The porous morphology of the bromacil–PLA matrix indicated the erosion of the PLA polymer.

(granule) and film conformers. The properties of initially slow followed by rapid release (delayed or lag-burst release) is not common in polymeric pesticide formulations but has been demonstrated for lignin matrix granules, where there is also release of a low molecular weight fraction (*6*). The unique biphasic release pattern of the LMW PLA-based matrices could find application to sensitive targets such as seed treatments based on both particulate and film geometries.

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