

## Lignin-Polyethylene Glycol Matrices and Ethylcellulose to Encapsulate Highly Soluble Herbicides

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**ABSTRACT:** The blending of lignin with polyethylene glycol (PEG) allowed us to obtain formulations with controlled release properties in which metribuzin have been successfully trapped with encapsulation efficiency higher than 85%. Moreover, the modification of the lignin's viscoelastic properties by the addition of PEG led to obtain herbicide formulations with active ingredient contents lower than 15%, suitable for its application in soil. Fourier transformed infrared spectroscopy and differential scanning calorimetry studies indicated the compatibility between polymers and metribuzin in lignin-based controlled release formulations (CRFs). Lignin-based formulations were coated in a Wurster-type fluidized-bed equipment using ethylcellulose and dibutylsebacate. Scanning electron microscope pictures showed a homogeneous film in ethylcellulose-coated CRFs. The kinetic release studies showed that the release rate of metribuzin was mainly controlled either by selecting the granule size of controlled release lignin-PEG matrixes, or by changing the thickness of coating film for ethylcellulose coated CRFs. These results could help to increase the efficiency of delivery of the highly soluble herbicide metribuzin and prevent the environmental pollution derived from its use. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41422.

**KEYWORDS:** biopolymers and renewable polymers; cellulose and other wood products; coatings; drug delivery systems

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### INTRODUCTION

Metribuzin [4-amino-3-methylthio-6-ter-butyl-1,2,4-triazin-5(4H)-one] is used as selective herbicide for the control of annual broad-leaved weeds in field and vegetable crops. This herbicide is absorbed predominantly by the roots, with translocation to all plant parts. Metribuzin is highly soluble in water (water solubility = 1050 mg L<sup>-1</sup> at 20°C) and has a low tendency to adsorb to most soils.<sup>1</sup> The United States Environmental Protection Agency considers metribuzin as being one of the groups of pesticide compounds that has the greatest potential for leaching into and contaminating groundwater.<sup>2</sup>

The application of polymeric materials to obtain controlled release formulations (CRFs) can be used as a way to avoid the losses caused by leaching of highly soluble herbicides. The primary objective of controlled release technology is the regulation of the supply of herbicides, allowing a lower and continued concentration of them in soil. In CRFs, herbicides are trapped, that is, they are integrated into a polymer matrix, where they are dissolved or linked to it physically or chemically.<sup>3</sup>

Although there are plenty of polymers used to prepare CRFs of herbicides with low solubility,<sup>4,5</sup> is necessary to optimize and

develop new methods to encapsulate herbicides with high solubility in water, and also increase the release efficiency to minimize the risk of environmental pollution. In this research, polymers such as lignin, polyethylene glycol, and ethylcellulose (EC) have been used to prepare new monolithic matrixes and coated CRFs of the herbicide metribuzin.

Lignin polymer is a low-cost waste product in the paper pulp manufacturing process, which is readily available, cheap, and an underutilized resource nowadays. The use of the lignin by-product, produced in the pulping of soft wood (kraft lignin), has been reported in other papers.<sup>6,7</sup> Some papers have reported the use of lignin to obtain CRFs in which this polymer was solvated or plasticized by the pesticide.<sup>8,9</sup> Nevertheless, active ingredient contents lower than 50% have not been obtained by plasticization of lignin with pesticides.

In this study as novelty, the polymer polyethylene glycol (PEG), suitability for melting,<sup>10</sup> has been added to lignin-based formulation to achieve a better plasticization of herbicides highly soluble in water such as metribuzin. The blending of lignin with PEG can modify the lignin's viscoelastic properties,<sup>11</sup> allowing

**Table I.** Coating Solutions Composition for the Preparation of CR Granules Containing Metribuzin

CR granules	Weight of MPEL granules (g)	Coating solution composition			EC (%) <sup>a</sup>	DBS (%) <sup>b</sup>
		EC (g)	DBS (g)	Ethanol (mL)		
MPEL+EC <sub>10</sub>	20	2	-	100	10	-
MPEL+EC <sub>20</sub>	20	4	-	200	20	-
MPEL+EC <sub>20</sub> +DBS	20	4	0.45	200	20	2.25

$${}^a \text{EC}(\%) = \frac{\text{EC}(\text{g})}{\text{weight of MPEL granules (g)}} \times 100.$$

$${}^b \text{DBS}(\%) = \frac{\text{DBS}(\text{g})}{\text{weight of MPEL granules (g)}} \times 100.$$

MPEL+EC<sub>10</sub>: Metribuzin-PEG-lignin-EC 10%.

MPEL+EC<sub>20</sub>: Metribuzin-PEG-lignin-EC 20%.

MPEL+EC<sub>20</sub>+DBS: Metribuzin-PEG-lignin-EC 20%- dibutyl sebacate 2.25%.

us to obtain formulations with active ingredients contents lower than 50% which is suitable for its use in agronomic practices.

EC is one of the most widely used polymers in film coating because of many advantages it offers as formulator, such as good film formability, excellent physical-chemical stability and minimum toxicity.<sup>12</sup>

The aims of this study were to design, prepare, and characterize CRFs of metribuzin using polymers like EC, PEG, and lignin. Moreover, metribuzin CRFs were evaluated in water through kinetic studies.

In order to investigate the physical and chemical compatibility of the materials used in the preparation of the formulations, pure polymers, metribuzin, and blends were analyzed by Fourier transformed infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Materials

Technical grade metribuzin (93.0%) was kindly supplied by Afrasa, S. A. (Valencia, Spain). Its molecular formula and selected properties are as follows<sup>13,14</sup>: molecular formula, C<sub>8</sub>H<sub>14</sub>N<sub>4</sub>OS; molecular weight, 214.3 g mol<sup>-1</sup>; melting point, 126.2°C; vapor pressure (20°C), 0.058 mPa; water solubility (20°C), 1.05 g L<sup>-1</sup>; octanol/water partitioning (log K<sub>ow</sub>)(pH 5.6, 20 °C), 1.6.

The lignin used in this study was a commercially available pine kraft lignin, Indulin AT (Westvaco, Charleston, SC). To improve the properties of homogeneity of the formulation, PEG (molecular weight, 1000 g mol<sup>-1</sup>) was used; the film-forming material of polymer coating was EC (Ethocel®; ethoxy content, 48.0–49.5%; viscosity, 9–11 cp); and the plasticizer selected for the study was dibutylsebacate (DBS) (≥97%, *d* = 0.936 g mL<sup>-1</sup>). These products were supplied by Fluka Chemie AG (Buchs, Switzerland).

### Monolithic Lignin-Based Formulations

Using a glass reactor inserted in a thermostatic bath (model Tectron L by Selecta S. A., Barcelona, Spain) filled with silicone oil, the CR granules were formed by mixing lignin, PEG and metribuzin in the optimized ratio [65 : 20 : 15 (w/w)]. The mixture was heated under melting conditions at 126 ± 1°C for 20 min. On cooling, the matrixes were crushed in a hammer

mill and then sieved to obtain granules of size between: 0–0.2 mm; 0.2–0.5 mm; 0.5–1 mm; 1–2 mm, and 2–3 mm. The resulting products are labelled in the text as MPEL (0 < *d* < 0.2 mm), MPEL (0.2 mm < *d* < 0.5 mm), MPEL (0.5 mm < *d* < 1 mm), MPEL (1 mm < *d* < 2 mm) and MPEL (2 mm < *d* < 3 mm). The numbers in brackets represent the size range (mm). Additionally, lignin-based granules without metribuzin (PEL) were also prepared to evaluate compatibility and interactions through DSC and FT-IR studies.

### EC-Coated Granules

**Coating Solutions Preparation.** Appropriate quantities of EC and plasticizer were combined and dissolved in ethanol (Table I) to obtain the coating solutions with two different polymer levels and, in one case, with a plasticizer. The coating film consists of 10% and 20% EC of the weight of the dry granules (20 g) and, for the coating solution containing a plasticizer, the coating film consist of 20% EC and 2.25% DBS of the weight of the dry granules.

**Coated Granules Preparation.** To prepare coated granules, 20 g of MPEL formulation, granules of size between 0.2 mm < *d* < 1 mm were loaded into a fluidized-bed coater (Mini-Glatt, Glatt AG, Pratteln I, Switzerland) assembled with a Wurster insert. The bed temperature was adjusted to 40 ± 2°C. The granules were preheated at this temperature for 10 min, after that the coating solution was delivered with a peristaltic pump (Watson-Marlow, Model 1B-1003/R) and sprayed into the fluidized-bed via spray nozzle at the atomizing pressure of 1.2 bars. The coating solutions were pumped with a flow rate of 2.5 mL min<sup>-1</sup> to prepare MPEL+EC<sub>10</sub> and with a flow rate of 5 mL min<sup>-1</sup> for both MPEL+EC<sub>20</sub> and MPEL+EC<sub>20</sub>+DBS granules. The total spraying time was 40 min. The coated granules were then dried in the same device at 40°C for 10 min and sieved, selecting the granules of size between 0.2 mm < *d* < 1 mm.

### Granules Characterization

**Metribuzin Content in CRFs.** The actual concentration of metribuzin in the granules was determined by dissolving 20 mg of the granules in 50 mL of methanol in an ultrasound bath for 15 min, which led to the complete disintegration of the granules. The volume was made up to 100 mL with ultra-pure water. This solution was placed in stoppered conical flasks and shaken in a thermostatic bath at 25°C ± 1°C for 24 hours, then the

**Table II.** Characteristics of Controlled Release Granules (0.2 mm < *d* < 1 mm) Containing Metribuzin

Formulation	Theoretical metribuzin loading (%) <sup>a</sup>	Practical metribuzin loading (%)	Solids recovery (%) <sup>b</sup>	EE (%)	Mean thickness of film (μm)
MPEL	13.29	11.38 (0.13)		85.64	
MPEL+EC <sub>10</sub>	11.03	10.91 (0.52)	94.86	98.87	8.54 (0.94)
MPEL+EC <sub>20</sub>	10.12	9.99 (0.26)	99.31	98.69	19.98 (1.43)
MPEL+EC <sub>20</sub> +DBS	9.29	9.24 (0.23)	98.91	99.41	16.69 (0.77)

<sup>a</sup>Theoretical metribuzin loading (%) = (total amount of metribuzin used to prepare the formulations / total amount of solid components used in the formulation process) × 100.

<sup>b</sup>Solids recovery (%) = (total amount of formulation recovered / total amount of solid components used in the formulation process) × 100.

<sup>c</sup>Values in parentheses represent the standard deviation.

resulting extract was filtered using nylon filters (0.20 μm). The concentration of metribuzin in the solution was determined by high-performance liquid chromatography (HPLC) using a Beckman Coulter, System Gold HPLC (Fullerton, CA, USA) equipped with a diode-array detector and 32 Karat data station.

HPLC operating conditions to analyze metribuzin were described previously by the authors<sup>15,16</sup> and were as follows: the separation, by isocratic elution, was performed on a 150 mm × 3.9 mm Nova-Pack LC-18 bonded-phase column from Waters (Milford, USA); flow rate, 1.0 mL min<sup>-1</sup>; sample volume 50 μL; and the mobile phase, an acetonitrile-aqueous solution of 5 mM KH<sub>2</sub>PO<sub>4</sub> mixture 40 : 60. The herbicide was analyzed at its wavelength of maximum absorption, 229 nm. External standard calibration was used, and three replicates were carried out for each formulation.

**Mean Particle Size.** The average diameter of CR granules was determined using a Stereoscopic Zoom Microscope from Nikon, model SMZ1000, provided with a camera PixelLINK (Megapixel FireWire Camera) model PL-A662. Each measure was taken through the analysis of a basis of 200 particles using the software Image Pro-Plus 6.0.

**Differential Scanning Calorimetry.** DSC scans of metribuzin, lignin, PEG, PEL, and MPEL were taken with a DSC from TA Instruments, model DSC Q20. The samples (6 mg) were pre-heated to 120°C for water evaporation. The heat evolved during the heating process (10°C/min) from room temperature to 300°C was recorded as a function of temperature. Nitrogen atmosphere was used at a steam of 20 mL/min.

**Fourier Transform Infrared Measurements.** FT-IR spectra of the PEG, lignin, empty lignin-based granules (PEL), and metribuzin lignin-based granules (MPEL) were taken with a FT-IR Raman Vertex 70 from Bruker. FT-IR spectra of samples [5% (w/w) sample in KBr] were recorded between 400 and 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

**Scanning Electron Microscopy.** Morphological and structural surface of lignin matrix and EC-coated granules was examined with the aid of a Hitachi S-3500-N scanning electron microscope (SEM) from Hitachi Instruments (Tokyo, Japan) at the required magnification at room temperature. The granules were deposited on a brass hold and sputtered with a thin coat of gold under vacuum. The acceleration voltage used was 10 kV with secondary electron image as a detector. To examine the

internal morphology of the polymeric films and to measure their thickness, coated granules were carefully cut with the aid of a chisel and their cross sections were photomicrographed. Each film sample was measured at 10 different points.

#### Water Release Kinetics

For each formulation and technical metribuzin (two replicates), an accurately weighed quantity of granules containing 8 mg of metribuzin was added to 500 mL of distilled water and placed into stoppered conical flasks. Flasks were kept in a thermostatic bath at 25 ± 1°C. At different time intervals, aliquots of 0.5 mL were removed to determine metribuzin concentration and 0.5 mL fresh water was added to the flasks to maintain sinking conditions.

## RESULTS AND DISCUSSION

### Granules Characterization

The results of practical metribuzin loading and encapsulation efficiency (EE) were calculated using the following equations. These results are shown in Table II:

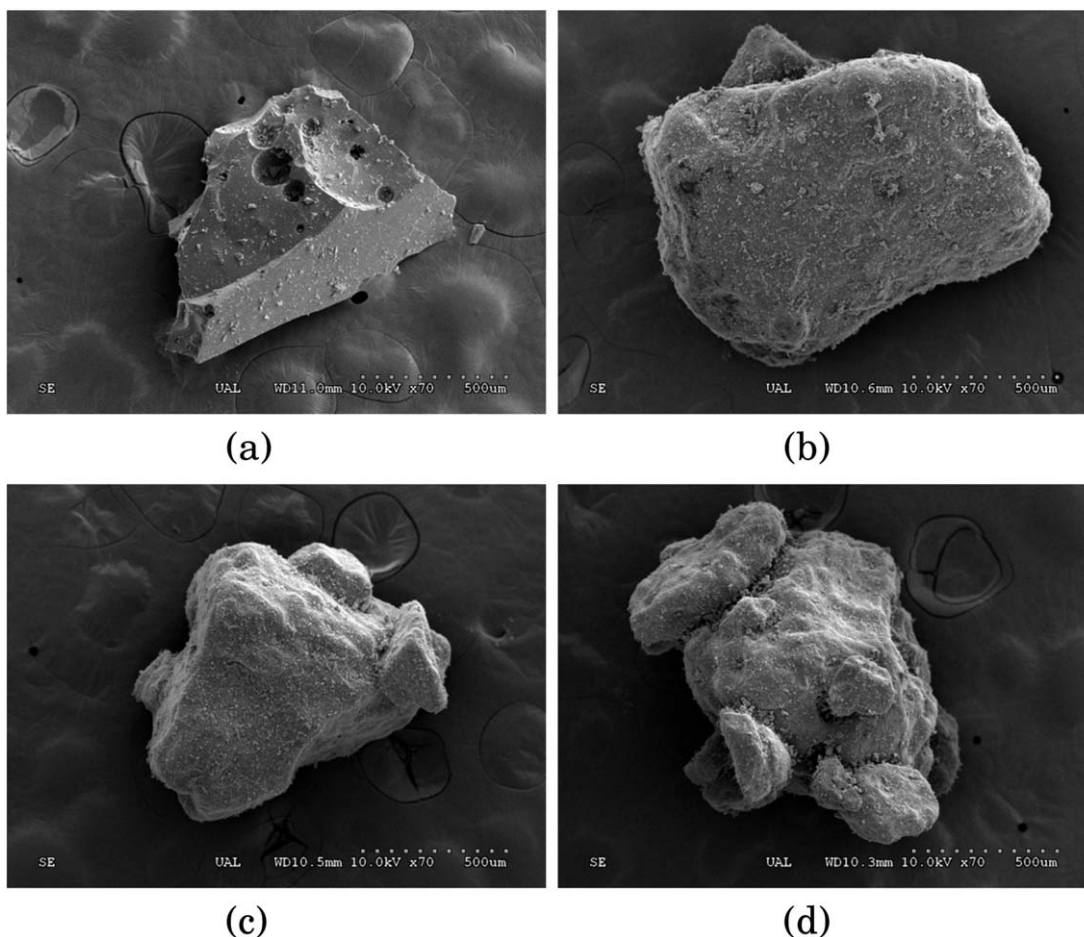
$$\begin{aligned} \text{Practical metribuzin loading (\%)} \\ = \left( \frac{\text{weight of metribuzin CR granules}}{\text{weight of CR granules}} \right) \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Encapsulation efficiency (\%)} \\ = \left( \frac{\text{Practical metribuzin loading}}{\text{Theoretical metribuzin loading}} \right) \times 100 \end{aligned} \quad (2)$$

The value of EE for the MPEL system is 85.64%, which highlights the efficacy of melting process using lignin and PEG to formulate metribuzin. For EC coated granules, the EE values ranged between 98.69% for the MPEL+EC<sub>20</sub> system and 99.41% for the MPEL+EC<sub>20</sub>+DBS formulation.

The practical metribuzin loading ranged between 9.29% for the MPEL+EC<sub>20</sub>+DBS system and 11.38% for the MPEL system, being the active ingredient of the granules suitable for agricultural practices. The addition of PEG to lignin-based formulations allows us to obtain formulations with active ingredient contents lower than 50%, which have not been achieved previously by plasticization of lignin by agrochemicals.<sup>8,9</sup>

SEM pictures from CR granules (Figure 1) show the disappearance of the wrinkled aspect that the external surface of MPEL granules possesses [Figure 1(a)] and the existence of a uniform and intact film in the coated formulations [Figure 1(b-d)]. The



**Figure 1.** SEM of shape and external morphology ( $\times 70$  magnifications): (a) MPEL, (b) MPEL+EC<sub>10</sub>, (c) MPEL+EC<sub>20</sub>, and (d) MPEL+EC<sub>20</sub>DBS.

cross-section on coated formulations (Figure 2) shows the porous core structure with a coherent film at the boundary, observing a bigger homogeneity and adherence in the coating film for the system that contains the plasticizer. This fact is also observed by other authors, who explain that the plasticizer, incorporated normally with polymers, modifying the properties of adhesion, flexibility, and tensile strength of the coating.<sup>17,18</sup>

The thickness of the coating film was estimated using SEM photographs (Table II). The thickness of the coating film ranged between 8.54  $\mu\text{m}$  for the MPEL+EC<sub>10</sub> system and 19.98  $\mu\text{m}$  for the MPEL+EC<sub>20</sub> system.

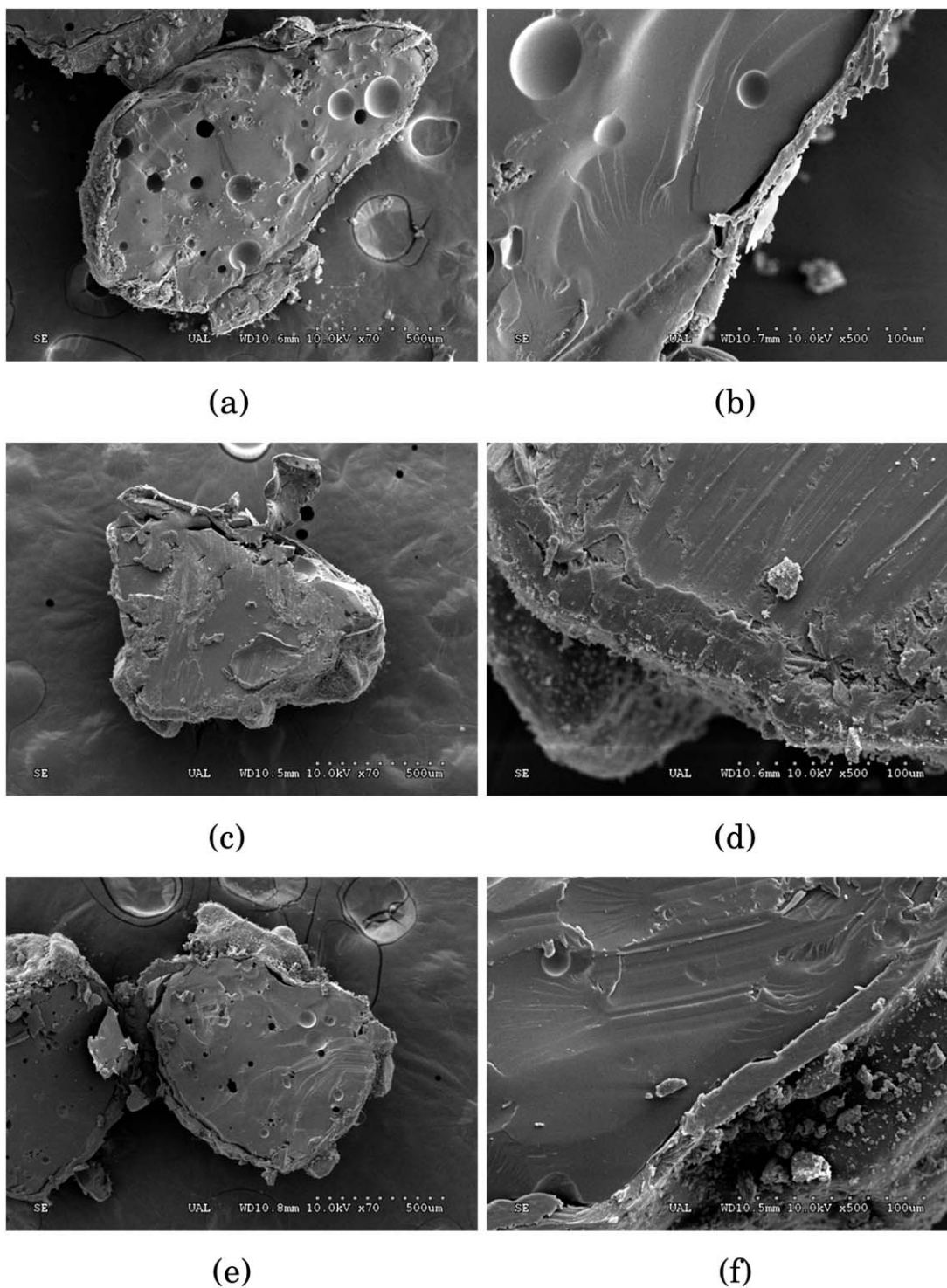
As expected, the highest amount of EC in the coating solution applied for the MPEL+EC<sub>20</sub> system increases the thickness of the membrane in relation to the MPEL+EC<sub>10</sub> system. The presence of the plasticizer in the MPEL+EC<sub>20</sub>+DBS system leads to a decrease in the thickness of the film compared to the MPEL+EC<sub>20</sub> system.

DSC curves of metribuzin, lignin, PEG, PEL, and MPEL are shown in Figure 3. DSC thermogram of metribuzin showed a clear endothermic peak at 124°C, which is associated with the melting point of the technical product of metribuzin. DSC curve of lignin shows both  $T_g$  and  $T_m$  which means that lignin

has a partially crystalline structure as is also showed by Corradini et al.<sup>19</sup> in lignin-poly (vinyl alcohol) blends studied by thermal analysis. For PEG no  $T_g$  has been appreciated, which indicates a crystalline structure. As it is observed in the DSC curve of PEL granules, the end point temperature of endothermic peak is shifted to higher temperature, in relation to the  $T_m$  of pure components, because of the blending and crosslinking of PEG and lignin. The detection of a single  $T_g$  value in PEL granules higher than that corresponding to lignin, can be attributed to the formation of a more rigid polymer matrix because of the interaction between the ether groups of PEG and the hydroxyl and carbonyl groups of lignin as is discussed below in FT-IR studies. DSC thermogram of MPEL showed a sharp endothermic peak at 235.37°C corresponding to the melting point of the formulation. The shift to a higher temperature of the melting point of the formulation in relation to the  $T_m$  of pure components and PEL granules indicates metribuzin-polymer interaction. Besides, no characteristic peak of metribuzin was observed in DSC curves of the MPEL granules, suggesting that the metribuzin is molecularly dispersed in the polymer matrix.

FT-IR spectra of (a) lignin, (b) PEG, (c) PEL, and (d) MPEL were shown in Figure 4. FT-IR spectra for lignin and PEG



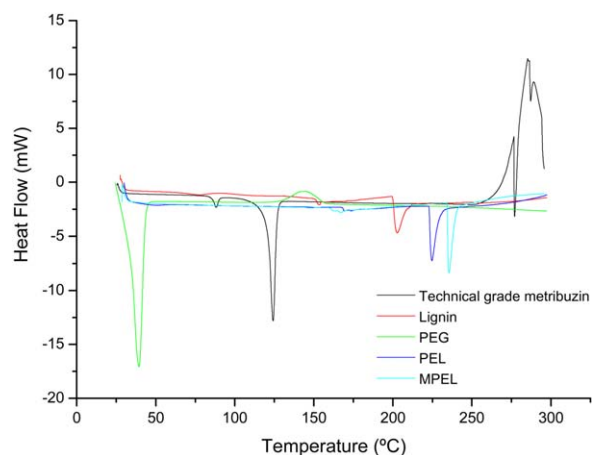


**Figure 2.** SEM of the internal morphology ( $\times 70$  magnifications): (a) MPEL+EC<sub>10</sub>, (c) MPEL+EC<sub>20</sub>, and (e) MPEL+EC<sub>20</sub>+DBS. The other ones show the detail of the coating film ( $\times 500$  magnifications): (b) MPEL+EC<sub>10</sub>, (d) MPEL+EC<sub>20</sub>, and (f) MPEL+EC<sub>20</sub>+DBS.

[Figure 4(a,b)] were similar to those described previously by others for kraft lignin<sup>20,21</sup> and PEG.<sup>22</sup>

FT-IR spectrum for PEL granules shows a little shift of the broad center band at  $3398\text{ cm}^{-1}$ , attributed to the hydroxyl groups in phenolic and aliphatic structures of lignin, which leads to a lower wavenumber in presence of PEG ( $3392\text{ cm}^{-1}$ ).

A related effect is observed in the asymmetric C–O–C stretching ( $\nu_{\text{asC-O-C}}$ ) region ( $1050\text{--}1150\text{ cm}^{-1}$ ). For PEG this band appears at  $1106\text{ cm}^{-1}$ , whereas this band shifted to a lower wavenumber region when PEG is blended with lignin, as shown in Figure 4(c). This is consistent with the observed effect in the  $\nu_{\text{O-H}}$  region and can be because of the fact that new specific



**Figure 3.** DSC curves of metribuzin, lignin, PEG, PEL granules, and MPEL granules. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

hydrogen-bonding interactions are formed between the ether group of PEG and the hydroxyl groups of lignin when thermal blending of PEG with lignin is carried out. The existence of hydrogen-bonding interactions is an important factor in the formation of miscible lignin-based polymer blends.<sup>23</sup> FT-IR spectrum of MPEL granules showed only an additional band at  $1677\text{ cm}^{-1}$  which is characteristic of C=O vibration in metribuzin,<sup>24,25</sup> along with all the characteristics bands of PEL granules. The observed changes in the vibrational frequencies of these functional groups demonstrate the existence of specific interactions between the components of the mixture. The magnitude of the displacement in the wavenumber depends on the intensity of intermolecular interactions occurring.

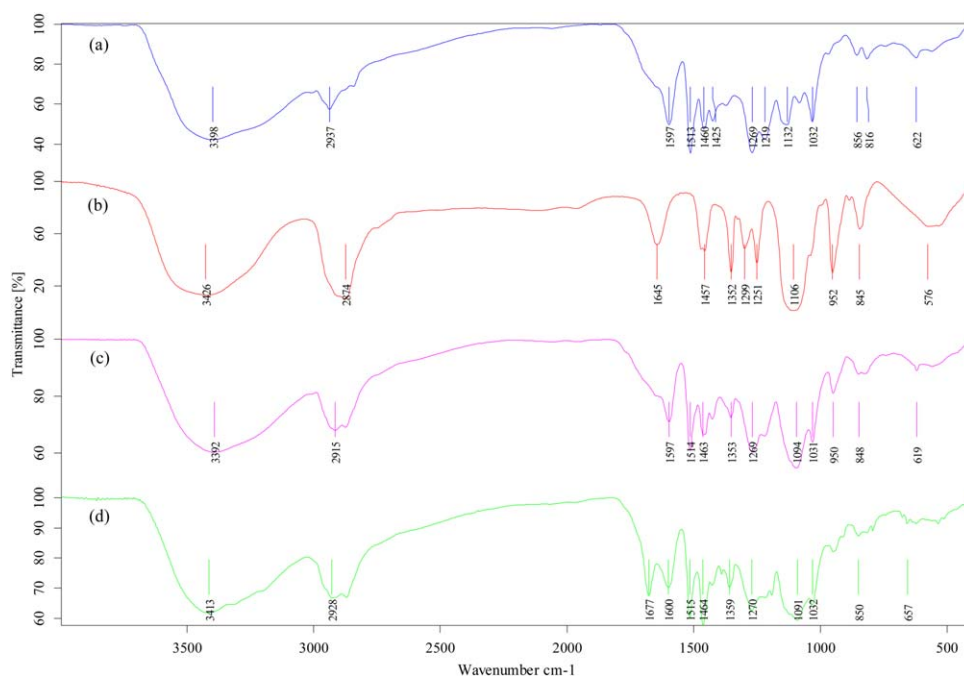
### Water Release Kinetics

The cumulative release of metribuzin from MPEL granules with different particle size and the solubility curve of technical grade metribuzin are shown in Figure 5(a). For the technical grade product, 99% of the metribuzin was dissolved in less than 0.5 h. The rate of metribuzin release from MPEL granules diminished in all cases in relation to the technical grade product, being necessary at least 48 h to release 90% of metribuzin from MPEL ( $2\text{ mm} < d < 3\text{ mm}$ ) granules. This is because the lignin formulations contain metribuzin particles uniformly dispersed, as has been shown by SEM studies [Figure 1(a)]. For all formulations, a decrease in the release of metribuzin over time was observed. This result is because of an increase in the distance where dissolved molecules have to diffuse as the depleted zone advances to the centre of the matrix. As can be seen in Figure 5(a), a decrease in the release rate of metribuzin is observed as the size of MPEL matrixes increases from MPEL ( $d < 0.2\text{ mm}$ ) up to MPEL ( $2\text{ mm} < d < 3\text{ mm}$ ). This happened as expected because of a lower surface area of the matrix being exposed to water, along with a longer distance over which metribuzin must be diffused from the center of the matrix. Similar results were obtained for the release of different pesticides from granules based on a lignin matrix system.<sup>8,26,27</sup>

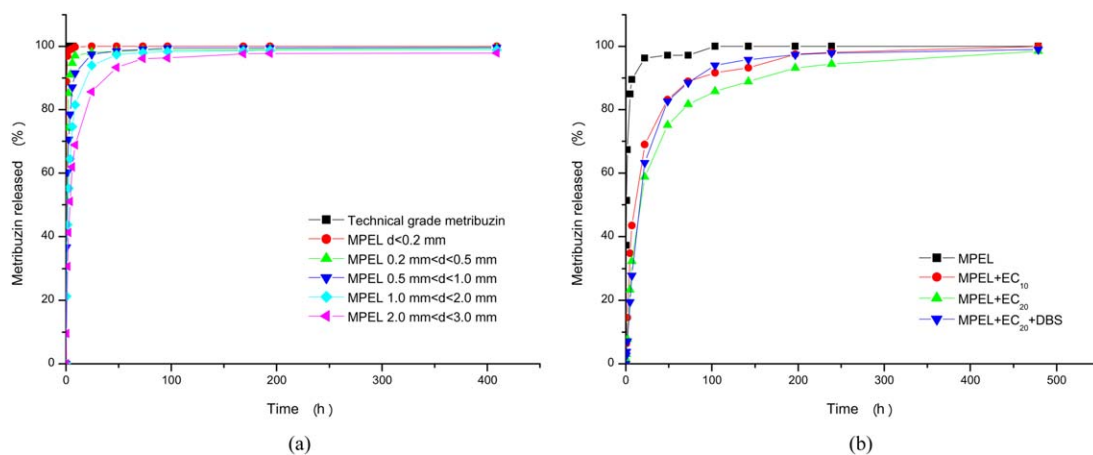
In order to obtain a parameter to compare the behavior of CR granules prepared as lignin matrix, the kinetics release data of metribuzin in water were analyzed using the empirical equation proposed by Ritger and Peppas:<sup>28</sup>

$$\frac{M_t}{M_\infty} = K_1 t^n \quad (3)$$

$M_t / M_\infty$  is the percentage of active ingredient released at time  $t$ ,  $K_1$  is a constant that incorporates characteristics of the



**Figure 4.** FT-IR spectra of (a) lignin, (b) PEG, (c) PEL granules, and (d) MPEL granules. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Water release kinetics from different size fractions of (a) MPEL and from (b) EC-coated granules containing metribuzin and MPEL (0.2 mm  $< d < 1.0$  mm) granules. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

macromolecular network system and the active ingredient, and  $n$  is a diffusional parameter which is indicative of the transportation mechanism.

The values of  $K_1$  and  $n$  obtained from the initial 90% of metribuzin released in water are presented in Table III. There was a good correlation of the release profiles of CR matrixes of metribuzin with the empirical equation, being the correlation coefficient ( $r$ ) greater than 0.92.

The time corresponding to release 50% of metribuzin,  $T_{50}$ , was calculated for the matrixes using the constants from Table III. For uncoated granules (different fraction sizes),  $T_{50}$  values ranged from  $3.34 \times 10^{-4}$  h for MPEL ( $d < 0.2$  mm) granules up to 5.98 h for MPEL (2 mm  $< d < 3$  mm) granules. By observing the  $T_{50}$  values obtained for lignin CR matrixes, is possible to notice that the  $T_{50}$  value increases as the matrix size increases, showing MPEL (2 mm  $< d < 3$  mm) granules the highest  $T_{50}$  value, which means the slowest metribuzin release. This behavior is related to the results of studying imidacloprid, urea, and chloridazon release from lignin matrix,<sup>8,27,29</sup> where the  $T_{50}$  values increase as the diameter of the matrixes grows.

As commented above, it seems that the size of noncoated lignin matrixes is the most influential factor that affects the release rate of metribuzin. So,  $T_{50}$  values of lignin CR granules (Table III) were related to the average diameter of granules ( $D$ ) which are 0.02, 0.34, 0.83, 1.52, and 2.78 mm for MPEL (0  $< d < 0.2$  mm), MPEL (0.2 mm  $< d < 0.5$  mm), MPEL (0.5 mm  $< d < 1$  mm), MPEL (1 mm  $< d < 2$  mm), and MPEL (2 mm  $< d < 3$  mm), respectively. The equation of linear correlation and correlation coefficient were obtained by applying the least-squares method to the data:

$$T_{50} = 2.19 \times D - 0.40 \quad (r = 0.989) \quad (P = 0.001) \quad (4)$$

This proves that the release of active ingredient from the systems based on lignin polymeric matrix is notably depleted through the increase of the granule size (average diameter,  $D$ ). In this way, it can be stated that is possible to foresee, under an early approach and an acceptable degree of reliability,  $T_{50}$  values for metribuzin formulations from the average granule diameter.

In Figure 5(b), the cumulative release curves of metribuzin from MPEL granules, size fraction between 0.2 mm  $< d < 1$  mm, and EC coated granules are shown. Coated CR granules MPEL+EC<sub>10</sub>, MPEL+EC<sub>20</sub> and MPEL+EC<sub>20</sub>+DBS produce a decrease in the

**Table III.** Constants from Fitting the Empirical Equations the Release Data of Controlled Release Systems into Static Water

Equation	Formulation	$K_1 \times 10^2$ ( $h^{-n}$ )	$n$	$r$	$T_{50}$ (h)
$M_t / M_\infty = K_1 t^n$	MPEL $d < 0.2$ mm	93.97	0.08	0.99	$3.39 \times 10^{-4}$
	MPEL 0.2 mm $< d < 0.5$ mm	63.97	0.30	0.99	0.43
	MPEL 0.5 mm $< d < 1$ mm	49.66	0.32	0.98	1.02
	MPEL 1 mm $< d < 2$ mm	34.67	0.38	0.95	2.62
	MPEL 2 mm $< d < 3$ mm	21.98	0.46	0.92	5.98
	MPEL <sup>a</sup> 0.2 mm $< d < 1$ mm	49.89	0.33	0.99	1.01
$M_t / M_\infty = 1 - e^{-K_2 t}$	Formulation	$K_2 \times 10^2$ ( $h^{-1}$ )		$r$	$T_{50}$ (h)
	MPEL+EC <sub>10</sub>	6.30		0.98	11.01
	MPEL+EC <sub>20</sub>	3.39		0.98	20.44
	MPEL+EC <sub>20</sub> +DBS	4.09		0.99	16.94

<sup>a</sup>This fraction is used to compare the lignin-based formulation with EC-coated formulations.



process of dissolution of the active ingredient in relation to MPEL granules. From the release curves of the coated CR granules, we can observe a short initial part of the curve during which a constant release rate is observed, followed by an extended stage of gradual decay of release rate. Similar behavior was reported by other authors with polymer coated chemicals.<sup>30,31</sup> The highest delay in the release rate is observed in MPEL+EC<sub>20</sub> system. Besides, as expected, the highest quantity of EC in MPEL+EC<sub>20</sub> formulation compared to MPEL+EC<sub>10</sub> causes a delay in the release rate of metribuzin. This fact can be explained if we take into account that the diffusion of water through the membrane is slowed down as the thickness of the membrane increases. This behavior has also been observed by other authors.<sup>12,32,33</sup>

To compare the behavior of EC-coated granules, the following first-order mathematical model was used for evaluation of the dissolution profiles of the nondisintegrating coated pellets. The herbicide quantity within the reservoir is assumed to decline exponentially and the release rate is proportional to the residual quantity<sup>34</sup>:

$$\frac{M_t}{M_\infty} = 1 - e^{-K_2 t} \quad (5)$$

Where,  $M_t$  is the dissolved amount (%) at time “ $t$ ” (h),  $M_\infty$  is the dissolved amount (%) at infinite time and  $K_2$  is the dissolution rate constant ( $\text{h}^{-1}$ ).

The values of  $K_2$  obtained from initial 90% metribuzin released in water are presented in Table III, beside  $K_1$  and  $n$  values for MPEL granules obtained by applying eq. (3). There was a good correlation between the release profiles of CR matrixes of metribuzin and the empirical equation, correlation coefficients ( $r$ ) were greater than 0.98.  $T_{50}$  values were also calculated using the constants from Table III. The values ranged from 1.01 h for MPEL ( $0.2 \text{ mm} < d < 1.0 \text{ mm}$ ) granules up to 20.44 h for MPEL+EC<sub>20</sub> granules. The variation order is

$$\text{MPEL} < \text{MPEL}+\text{EC}_{10} < \text{MPEL}+\text{EC}_{20}+\text{DBS} < \text{MPEL} + \text{EC}_{20}$$

The presence of a uniform film of EC and/or plasticizer in the coated granules causes a delay in metribuzin release rate. When the data of  $T_{50}$  referring to the coated systems without plasticizer, MPEL+EC<sub>10</sub> and MPEL+EC<sub>20</sub>, are assessed, it can be seen that  $T_{50}$  value is slightly higher in the system with a greater EC percentage (MPEL+EC<sub>20</sub>), which is in agreement with the low difference in the thickness of the coating.  $T_{50}$  value of MPEL+EC<sub>20</sub>+DBS formulation ( $T_{50} = 16.94 \text{ h}$ ) showed that the addition of plasticizer in the coating process produces a moderate decrease on the release rate of metribuzin compared to MPEL+EC<sub>10</sub> formulation. This may be because the coating process is performed by at 40°C, which gives rise to a slight cross-linking between the EC and the plasticizer.<sup>35</sup>

## CONCLUSIONS

Polymeric materials like lignin, PEG, and EC have been used to prepare and optimize CRFs for the herbicide metribuzin. High EE values for metribuzin have been obtained using lignin and PEG in monolithic systems and EC in coated granules. The blending of lignin with PEG led to obtain herbicide formulations with active ingredient contents lower than 15%, suitable

for its application in soil. FT-IR and DSC studies indicate the miscibility between lignin and PEG mainly through hydrogen-bonding and compatibility between polymers and metribuzin in lignin-based CRFs. SEM studies demonstrate the existence of a uniform film in the CR-coated formulations prepared. An important retard in the release rate of metribuzin was achieved with the use of EC in coated CRFs. Metribuzin release rate can be controlled by adjusting the EC content for EC-coated granules and selecting the granule size for uncoated CR lignin matrixes. So, delivery of the highly soluble herbicide can be controlled using polymers, such as lignin, PEG, and EC in CRFs.

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