

Preparation and Characterization of Imidacloprid Lignin–Polyethylene Glycol Matrices Coated with Ethylcellulose

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ABSTRACT: Imidacloprid, a systemic insecticide that has a water solubility of 610 mg L⁻¹, has been formulated in lignin–polyethylene glycol matrices by a melting process. This formulation was coated in a Wurster type fluidized-bed equipment using ethylcellulose and dibutyl sebacate. Imidacloprid has been entrapped, with an entrapment efficiency higher than 87% in all cases. Thermogravimetric analysis, differential scanning calorimetry, and Fourier transformed infrared spectroscopy studies indicate the stability and compatibility of polymers and imidacloprid. Scanning electron microscopy images show a homogeneous film of ethylcellulose in coated formulations. From T_{50} values (the time taken for 50% of the active ingredient to be released into water), the release rate of imidacloprid is controlled by changing the thickness of the coating film and modifying its surface properties by adding a plasticizer. T_{50} values, ranging from 3.02 to 168.6 h, allow supplying the appropriate amount of imidacloprid in each specific agronomic practice to increase the efficiency of this bioactive material and minimize the risk of environmental pollution.

KEYWORDS: imidacloprid, controlled release, lignin, polyethylene glycol, ethylcellulose

■ INTRODUCTION

Imidacloprid [1-(6-chloro-3-pyridinylmethyl)-*N*-nitro-2-imidazolidinimine] is a neonicotinoid systemic insecticide having a mode of action based on interference of the transmission of impulses in insect nerve systems and has excellent systemic properties.¹ The uptake of the active substance via the roots is an important prerequisite for soil-directed application, for example, via irrigation systems, in-furrow application, granular application including seedling-box application in rice, or seed treatment. Because of the excellent systemic activity and the low application rates (0.05–0.075% w/v), imidacloprid can be used as a seed dressing as well as for foliar, soil, and stem treatments. Nevertheless, previous studies have shown that this pesticide has the potential to leach especially in areas where soils are permeable and water tables are shallow.^{2,3} This fact could result in a risk of pollution of groundwater with imidacloprid, which can be reduced by using polymeric controlled release formulations (CRFs).

CRFs regulate the supply of pesticides, allowing a lower and continued concentration of them in soil. Therefore, they reduce the losses caused by leaching and evaporation,⁴ always maintaining their concentration between the limits of toxicity and effectiveness. In CRFs, pesticides are trapped; that is, they are integrated into a polymer matrix, where they are dissolved or linked to it physically or chemically. In this way, the active ingredient is released through controlled diffusion processes, achieving minimal losses.

Polymeric matrices (PM) have been extensively used in various applications: as drug delivery vehicles, in the protection of functional ingredients, as sensing devices, in biomaterials, and for catalysis. The PM can be made of either synthetic or natural polymers. Natural polymers such as dextrans, gelatin, chitosan, sodium alginate, lignin, and cellulose derivatives are more interesting than synthetic polymers for food and

biomedical applications due to their higher biodegradability and biocompatibility.⁵ Natural PM can be also used to prepare CRFs of pesticides.

Lignin is a low-cost waste product in the paper pulp manufacturing process, which is readily available, cheap, and an underutilized resource nowadays. Lignin has been used as a carrier polymer since the 1970s to prepare pesticide CRFs.⁶ The original source and extraction method used can vary noticeably the physicochemical characteristics of the lignin. The kraft lignin, which is nonwater-soluble, produced in the pulping of soft wood has been already reported for pesticide CRFs preparation.^{7–9} To overcome the technical limitations and constraints imposed by lignin when directly used, alkylene oxides polymer derivatives, especially polyethylene glycol (PEG), can be used to produce chemical modifications such as esterification and etherification.¹⁰ PEG was used in some of the formulations due to its characteristics such as hydrophobicity, low density, lack of reactivity with the other components within the system, and suitability for melting and low cost.¹¹ Ethylcellulose (EC) is one of the most widely used polymers in film coating because of the many advantages it offers as a formulator, such as good film formability, excellent physical–chemical stability, and minimum toxicity.¹² Plasticizers are commonly incorporated with the polymeric film, to change the flexibility, tensile strength, and adhesion properties of the resulting film.¹³ Dibutyl sebacate (DBS) is a plasticizer permitted in the food packaging industry, in plastics used for medical devices, and for pharmaceutical applications, for example, as a plasticizer for film coatings of tablets, beads,

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and granules. DBS provides excellent compatibility with a range of polymeric materials.¹⁴ DBS has been used in previous agrochemicals CRFs researches due to a minimum pollution potential risk for the environment.¹⁵ DBS is a water-insoluble plasticizer and, when combined with the EC, can control the release rate of the active ingredient from the CRFs.

A set of alginate and lignin-based imidacloprid CRFs have been described in previous papers related to the study presented here.^{16,17} In water release studies, the authors reported that the use of sorbents with different sorption capacity in alginate-based formulations and the granule size in lignin-based formulations are the main factors to control the imidacloprid release rate. So, with this paper, we try to continue advancing in the development of more effective imidacloprid formulations through the design, preparation and testing of CR based on lignin-PEG matrices coated with polymeric films. The use of coated CRFs can be a way to control the release rate of highly water-soluble agrochemicals such as imidacloprid.

The objectives of this study were, first, to design, prepare, and characterize new CRFs of imidacloprid using biodegradable polymers like EC, lignin, and PEG and, second, to evaluate imidacloprid CRFs in water through kinetic studies. The lignin-based CR granules were prepared by mixing the insecticide with kraft lignin and PEG under melting conditions. The EC-coated granules were prepared by coating lignin-based granules in Wurster type fluidized-bed equipment.^{18–20}

Fourier transformed infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) studies of pure polymers, imidacloprid, and blends were carried out to investigate the physical and chemical compatibility of the materials used in the preparation of the CRFs, and scanning electron microscopy (SEM) was used to examine the morphological and structural surface of lignin matrix and EC-coated granules.

MATERIALS AND METHODS

Materials. The lignin used in this study was a commercially available pine kraft lignin, Indulin AT (Westvaco Corp., Charleston, SC). To improve the properties of homogeneity of the formulation, PEG (molecular weight, 1000 g mol⁻¹) 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 dibutyl sebacate (DBS) ($\geq 97\%$, $d = 0.936$ g mL⁻¹). These products were supplied by FlukaChemie AG (Buchs, Switzerland).

Imidacloprid technical grade (99.0%) was provided by Laboratorios Alcotán (Sevilla, Spain). Its molecular formula and selected properties are as follows:^{21,22} molecular formula, C₉H₁₀ClN₅O₂; melting point, 144 °C; water solubility (20 °C), 610 mg L⁻¹; octanol/water partitioning (log *K_{ow}*) (20 °C), 0.57; and stable in aqueous media at pH 5–11.

Lignin-Based Formulations. CR granules were formed by mixing the lignin (L), PEG, and imidacloprid (Im) in the optimized ratio [65:20:15 (w/w)] using a glass reactor inserted in a thermostatic bath (model Tectron L by Selecta S. A., Barcelona, Spain) filled with silicone oil. The mixture was heated under melting conditions at 144 °C for 20 min. After they cooled, the matrixes were crushed in a hammer mill and then sieved to obtain granules of sizes between 0.2 and 1.0 mm. The resulting product was labeled in the text as ImPEL. Additionally, lignin-based granules without imidacloprid (PEL) were also prepared to evaluate compatibility and interactions through DSC and FT-IR studies.

Preparation of Coating Solutions. Appropriate quantities of EC and plasticizer were combined and dissolved in ethanol (Table 1) to obtain the coating solutions with two polymer levels and, in one case, with a plasticizer. The coating film consisted of 10 and 20% EC of the dry granules weight (20 g), and for the coating solution containing the

Table 1. Coating Solutions Composition for the Preparation of CR Granules Containing Imidacloprid^a

CR granules	weight of ImPEL granules (g)	coating solution composition				
		EC (g)	DBS (g)	ethanol (mL)	EC (%) ^b	DBS (%) ^c
ImPEL + EC ₁₀	20	2		100	10	
ImPEL + EC ₂₀	20	4		200	20	
ImPEL + EC ₂₀ + DBS	20	4	0.45	200	20	2.25

^aImPEL + EC₁₀, imidacloprid-PEG-lignin-10% EC; ImPEL + EC₂₀, imidacloprid-PEG-lignin-20% EC; and ImPEL + EC₂₀ + DBS, imidacloprid-PEG-lignin-20% EC-2.25% DBS. ^bEC (%) = [EC (g)/weight of ImPEL granules (g)] × 100. ^cDBS (%) = [DBS (g)/weight of ImPEL granules (g)] × 100.

plasticizer, the coating film consisted of 20% EC and 2.25% DBS of the weight of the dry granules.

Preparation of Coated Granules. To prepare coated granules, 20 g of ImPEL formulation, granules of size between 0.2 mm < *d* < 1 mm, were loaded into a fluidized-bed coater (Mini-Glatt, Glatt AG, Pratteln, Switzerland) assembled with a Wurster insert. The bed temperature was adjusted to 60 ± 2 °C. The granules were preheated at this temperature for 10 min. 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 bar. The coating solutions were pumped with a flow rate of 2.5 mL min⁻¹ to prepare ImPEL + EC₁₀ and a flow rate of 5 mL min⁻¹ for both ImPEL + EC₂₀ and ImPEL + EC₂₀ + DBS granules. The total spraying time was 40 min. The coated granules were then dried in the same device at 60 °C for 10 min and sieved, selecting the granules of size between 0.2 mm < *d* < 1 mm.

Determination of Imidacloprid Content in the CRFs. The actual concentration of imidacloprid 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 ultrapure water. This solution was placed in stoppered conical flasks and shaken in a thermostatic bath at 25 ± 0.1 °C for 24 h, and then, the resulting extract was filtered using 0.20 μm syringe nylon filters (Milllex GN, Millipore Co., Billerica, MA). The concentration of imidacloprid in the solution was determined by high-performance liquid chromatography (HPLC). Analysis was conducted with a Beckman Coulter Inc., System Gold HPLC (Fullerton, CA) equipped with a solvent delivery module, model 126; diode array detector, model 168; and 32 Karat data station.

The HPLC operating conditions to analyze imidacloprid were described previously by other authors.^{23,24} The mobile phase consisted of acetonitrile–water (HPLC grade) mixture 35:65 at a flow rate of 1 mL min⁻¹. Imidacloprid was analyzed at its maximal absorption wavelength of maximum absorption, 270 nm, by injecting a volume of 20 μL. Isocratic separation was performed on a 150 mm × 3.9 mm NOVA PACK C18 column (catalog no. WAT037520, Waters, Wexford, Ireland). Three replications were carried out for each formulation. Under these chromatographic conditions, imidacloprid was eluted at approximately 1.9 min.

TGA. The thermal stability of formulation components and formulation was analyzed using a thermogravimetric analyzer from TA Instruments, model TGA Q50 (New Castle, DE). The experiments were performed under synthetic air atmosphere. Experiments were conducted at 10 °C min⁻¹, with the sample (6.0 ± 0.1 mg) being heated from 20 to 900 °C, due to the degradation of the polymers in this range. The used sample holder was a platinum pan.

DSC. DSC scans of imidacloprid, lignin, PEG, PEL, and ImPEL were taken with a DSC from TA Instruments, model DSC Q20 (New Castle, DE). The samples (6.0 ± 0.1 mg) were preheated to 120 °C

Table 2. Characteristics of Controlled Release Granules ($0.2 \text{ mm} < d < 1 \text{ mm}$) Containing Imidacloprid

formulation	theoretical imidacloprid loading (%)	practical imidacloprid loading (%)	EE (%)	solids recovery ^a (%)	mean thickness of film (μm) ^b
ImPEL	15.00	14.64	97.60		
ImPEL + EC ₁₀	13.30	11.48	86.31	94.04	8.28 (2.02)
ImPEL + EC ₂₀	12.20	11.28	92.46	90.73	20.35 (4.51)
ImPEL + EC ₂₀ + DBS	11.97	12.13	101.33	95.44	14.75 (2.45)

^aSolids recovery (%) = (total amount of formulation recovered/total amount of solid components used in the formulation process) \times 100. ^bValues in parentheses represent the standard deviation.

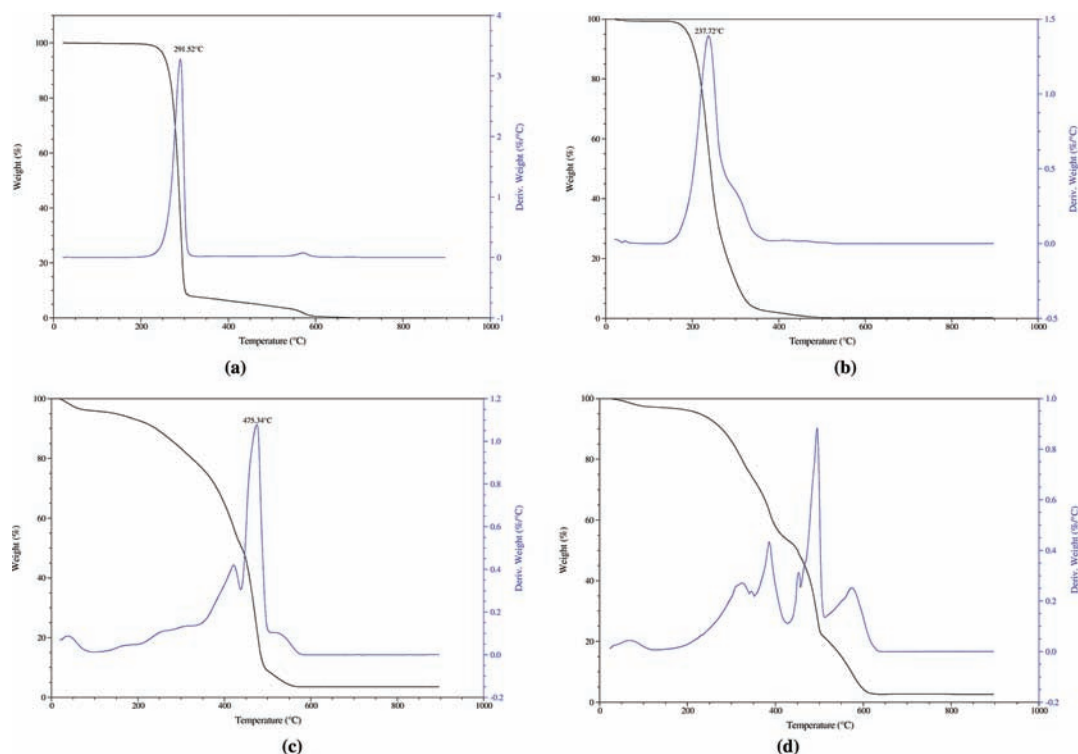


Figure 1. TGA–DTG curves of imidacloprid (a), PEG (b), lignin (c), and PEL granules (d).

for water evaporation. The heat evolved during the heating process ($10 \text{ }^\circ\text{C min}^{-1}$) from room temperature to $300 \text{ }^\circ\text{C}$ was recorded as a function of temperature. Nitrogen atmosphere was used at a stream of 20 mL min^{-1} .

Fourier Transform Infrared (FT-IR) Measurements. FT-IR spectra of the PEG, lignin, empty lignin-based granules (PEL), and imidacloprid lignin-based granules (ImPEL) were taken with a FT-IR Raman Vertex 70 from Bruker Optics (Billerica, MA). FT-IR spectra of samples [5% (w/w) sample in KBr] were recorded between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} .

SEM. The morphological and structural surface of lignin matrix and EC-coated granules were examined with the aid of a Hitachi S-3500-N SEM at the required magnification at room temperature. The granules were deposited on brass hold and sputtered with a thin coat of gold under vacuum. The acceleration voltage used was 10 kV with a 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 least at 10 locations across the film.

Water Release Kinetics. For each formulation and technical imidacloprid (two replicates), an accurately weighed quantity of granules containing 8 mg of imidacloprid was added to 500 mL of distilled water and placed into stoppered conical flasks. Flasks were kept in a thermostatic bath at $25 \pm 0.1 \text{ }^\circ\text{C}$. At time intervals, aliquots of 0.5 mL were removed to determine imidacloprid, and 0.5 mL of fresh water was added to the flasks to maintain sink conditions.

RESULTS AND DISCUSSION

Entrapment Efficiency (EE). The results of practical imidacloprid loading and EE (see Table 2) were calculated using eqs 1–3.

$$\begin{aligned} &\text{theoretical imidacloprid loading (\%)} \\ &= (\text{total amount of imidacloprid used to prepare} \\ &\quad \text{the formulation/total amount of solid} \\ &\quad \text{components used in the formulation process}) \\ &\quad \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} &\text{practical imidacloprid loading (\%)} \\ &= \left(\frac{\text{amount of imidacloprid in CR granules}}{\text{amount of CR granules}} \right) \\ &\quad \times 100 \end{aligned} \quad (2)$$

$$\begin{aligned} &\text{entrapment efficiency (\%)} \\ &= \left(\frac{\text{practical imidacloprid loading}}{\text{theoretical imidacloprid loading}} \right) \times 100 \end{aligned} \quad (3)$$

The value of EE for the ImPEL system is 97.60%, which highlights the efficacy of the melting process using lignin and PEG to formulate imidacloprid. For EC-coated granules, the EE values ranged between 86.31% for the ImPEL + EC₁₀ formulation and 101.33% for the ImPEL + EC₂₀ + DBS formulation. The practical imidacloprid loadings range between 11.28% for the ImPEL + EC₂₀ formulation and 14.64% for the ImPEL formulation, being the active ingredient of the granules suitable for agricultural practices.

TGA, DSC, and FT-IR Studies. The interactions of imidacloprid and polymers in the lignin-based matrices have been studied through TGA, DSC, and FT-IR analysis to obtain further information about the compatibility of polymeric blends and imidacloprid. The thermal stability of imidacloprid, PEG, lignin, PEL, and ImPEL was evaluated by TGA (Figures 1 and 2). The TGA of imidacloprid and PEG (Figure 1a,b) shows only a step weight loss due to their decomposition. For the lignin (Figure 1c), three stages were observed during the degradation process. Initially, the loss of weight is due to the moisture present in the sample. Furthermore, lost weight is

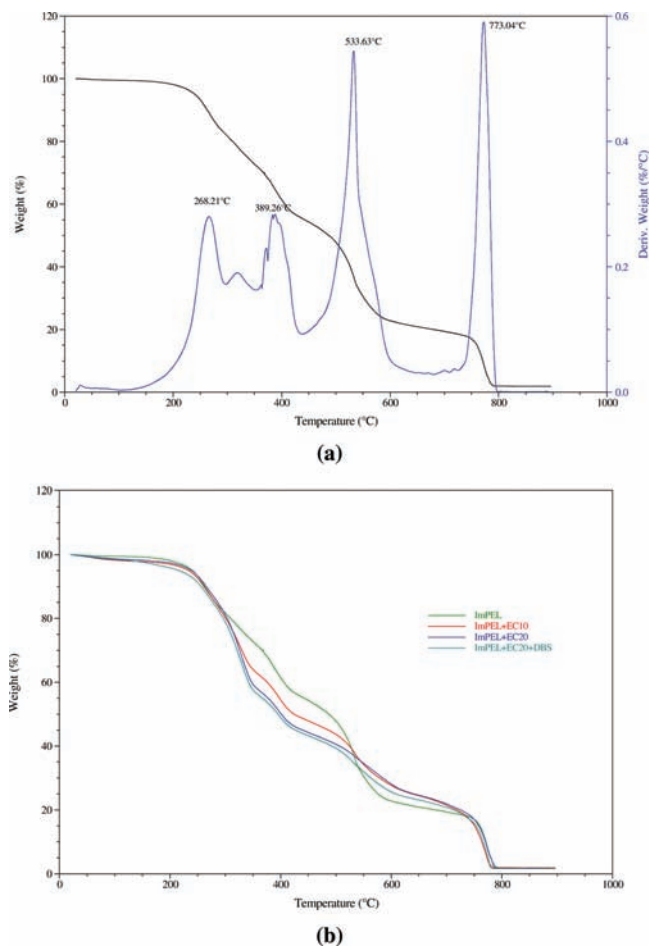


Figure 2. TGA–DTG curve of ImPEL formulation (a) and TGA curves corresponding to ImPEL, ImPEL + EC₁₀, ImPEL + EC₂₀, and ImPEL + EC₂₀ + DBS formulations (b).

attributable to the evaporation of carbon dioxide, carbon monoxide, and other pyrolysis products. The degradation of lignin within a wide range of temperatures (200–450 °C) can be explained by the fact that lignin presents a complex structure made up of phenolic hydroxyl, carbonyl groups, and benzylic

hydroxyl, which are connected by direct links.²⁵ At higher temperatures (>450 °C), decomposition reactions and condensation reactions of aromatic rings are possible during the lignin pyrolytic process. The steps in the lignin thermogram described above (Figure 1c) were similar to those described in other papers.^{26,27} Given that the preparation of CRFs was carried out at 144 °C (melting point of imidacloprid), it can be concluded that no thermal decomposition occurred for either imidacloprid or polymers used.

Figure 2a shows the thermal degradation profile of the ImPEL formulation where the thermal decomposition of the formulation occurred in four stages. Coated formulation TGA curves (Figure 2b) showed the existence of the four stages of degradation as it was the case for the ImPEL formulation. As shown in Figure 2b, at temperatures below 500 °C, the curves for the formulations coated with EC suffer a greater loss of mass than uncoated formulation at the same temperature and also increased with the percentage of EC in the samples.

Table 3 shows the degradation temperature intervals, mass loss percentages, and the maximum values of DTG curves. From this table, the next is observed; first, the mass loss is higher in the first stage for coated formulations than for uncoated formulations, which suggests that during this stage EC degradation occurs. Second, in the second stage, the value of mass loss decreases in the order ImPEL > ImPEL + EC₁₀ > ImPEL + EC₂₀ > ImPEL + EC₂₀ + DBS. Finally, the temperature at which it reaches a mass loss of 50% decreases with the increase of EC content of the formulation.

DSC curves of imidacloprid, lignin, PEG, PEL, and ImPEL are shown in Figure 3. The DSC thermogram of imidacloprid (Figure 3a) showed two clear endothermic peaks at a temperature of 132.70 and 141.54 °C, which are associated with melting point (T_m) of the two crystalline forms of the technical product of imidacloprid.²⁸ Figure 3b shows both T_m and glass transition temperature (T_g), which means that lignin has a partially crystalline structure as shown by Corradini et al.²⁹ in lignin-poly(vinyl alcohol) blends studied by thermal analysis. For PEG (Figure 3c), no T_g was appreciated, which indicates a crystalline structure. As it is observed in Figure 3d, the end point temperature of endothermic peak of the PEL granules shifted to higher temperature, in relation to the T_m of pure components, due to the blending and cross-linking of PEG and lignin. The detection of a single T_g value in PEL granule higher than that corresponding to lignin can be attributed to the formation of a more rigid polymer matrix due to the interaction between the ether groups of the PEG and the hydroxyl and carbonyl groups of lignin as it is discussed below in FT-IR studies. The DSC thermogram of ImPEL showed a sharp endothermic peak at 253.56 °C (Figure 3e) corresponding to the melting point of the formulation. The shift of the melting point of the formulation to higher temperature in relation to the T_m of pure components and PEL granules indicates imidacloprid–polymer interactions. Besides, no characteristic peak of imidacloprid was observed in DSC curves of the ImPEL granules, which suggests that imidacloprid is molecularly dispersed in the polymer matrix.

FT-IR spectra of lignin (a), PEG (b), PEL (c), and ImPEL (d) are shown in Figure 4. The FT-IR spectra for lignin and PEG (Figure 4a,b) were similar to those described previously by others for kraft lignin^{30,31} and PEG.³²

The FT-IR spectrum for PEL granules shows a little shift of the broad center band at 3398 cm⁻¹, attributed to the hydroxyl groups in phenolic and aliphatic structures of lignin, which

Table 3. Degradation Temperatures and Mass Loss Percentages of Formulations Containing Imidacloprid

		ImPEL	ImPEL + EC ₁₀	ImPEL + EC ₂₀	ImPEL + EC ₂₀ + DBS
stage 1	degradation temp (°C)	150–350	150–360	150–360	150–360
	mass loss (%)	27.0	35.2	41.1	41.4
	DTG max. (°C)	268.1	327.4	330.0	328.3
stage 2	degradation temp (°C)	350–437	360–450	360–450	360–450
	mass loss (%)	16.9	14.6	13.1	12.7
	DTG max. (°C)	389.2	398.2	398.2	401.0
stage 3	degradation temp (°C)	437–640	450–650	450–650	450–650
	mass loss (%)	34.1	23.2	19.4	19.6
	DTG max. (°C)	533.6	535.4	537.2	530.9
stage 4	degradation temp (°C)	640–800	650–800	650–800	650–800
	mass loss (%)	19.6	22.7	22.7	21.5
	DTG max. (°C)	773.0	771.2	773.0	744.8
T mass loss 50% (°C)		486.7	424.5	400.8	394.8

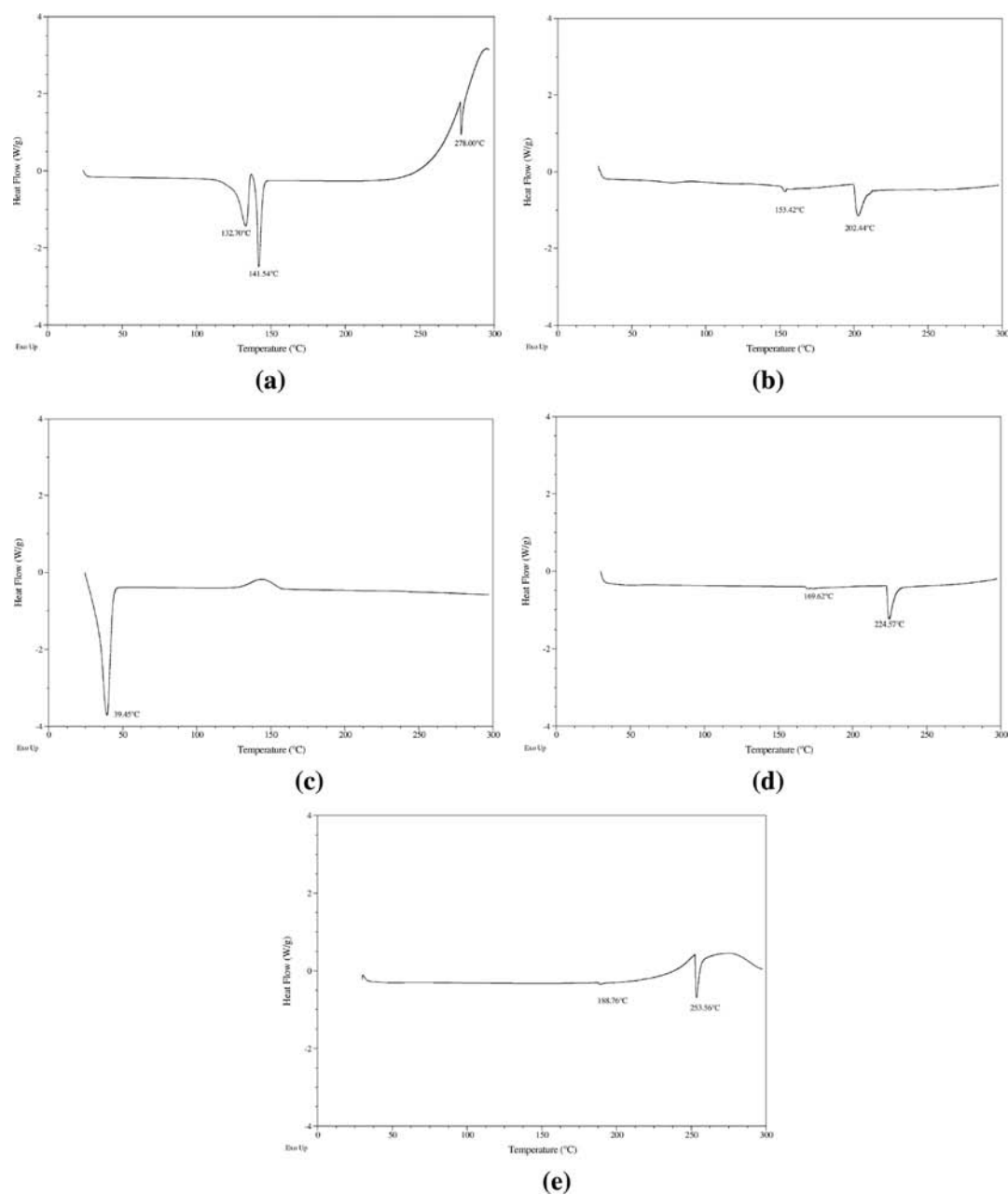


Figure 3. DSC curves imidacloprid (a), lignin (b), PEG (c), PEL (d), and ImPEL (e).

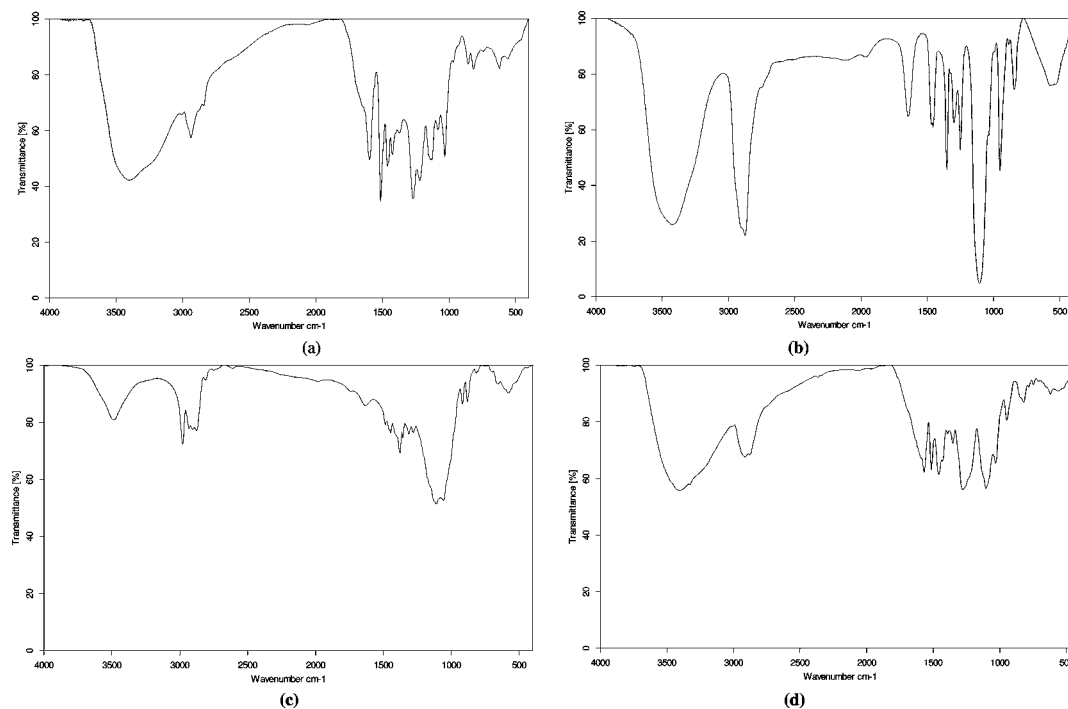


Figure 4. FT-IR spectra of lignin (a), PEG (b), PEL granules (c), and ImPEL granules (d).

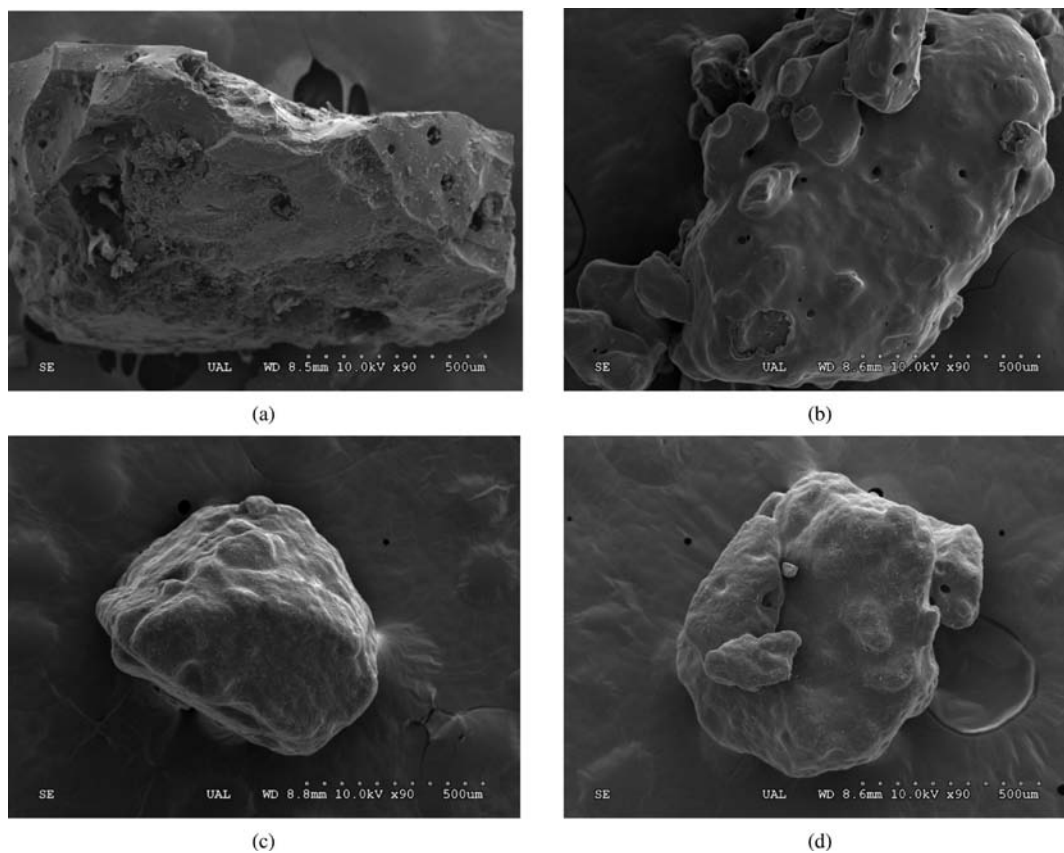


Figure 5. SEM of shape and external morphology ($\times 90$ magnifications) (a) ImPEL, (b) ImPEL + EC₁₀, (c) ImPEL + EC₂₀, and (d) ImPEL + EC₂₀ + DBS.

leads to a lower wavenumber in presence of PEG (3392 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 PE, this band appears at 1106 cm^{-1} , whereas this band shifted to a lower

wavenumber region when PEG is blended with lignin, as shown in Figure 4c. This is consistent with the observed effect in the $\nu_{\text{O-H}}$ region and can be due to the fact that new specific hydrogen-bonding interactions occur between the ether group

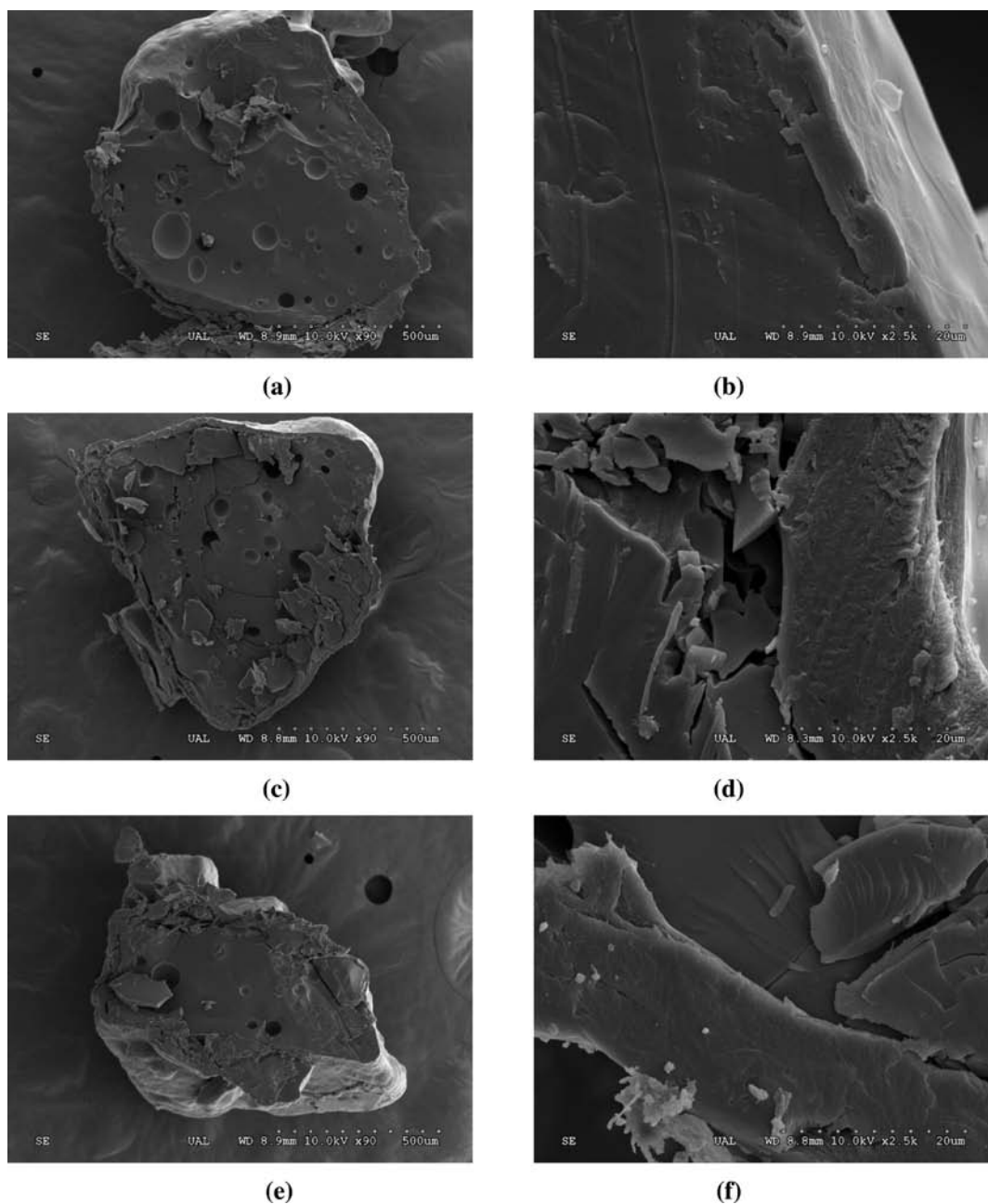


Figure 6. SEM of the internal morphology ($\times 90$ magnifications): (a) ImPEL + EC₁₀, (c), ImPEL + EC₂₀, and (e) ImPEL + EC₂₀ + DBS. The other ones show the detail of the coating film ($\times 2500$ magnifications): (b) ImPEL + EC₁₀, (d) ImPEL + EC₂₀, and (f) ImPEL + EC₂₀ + DBS.

of the PEG and the hydroxyl groups of the 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.³³ The FT-IR spectrum of ImPEL granules showed additional bands at 1567 and 1278 cm^{-1} , which are characteristic of the stretching vibration of C=N bond and the symmetric stretching vibration of the NO₂ group of the molecule of imidacloprid, respectively, along with all of the characteristic bands of the PEL granules.

Morphological Study. SEM pictures from CR granules (Figure 5) show the disappearance of the wrinkled aspect that the external surface of ImPEL granules possesses (Figure 5a) and the existence of a uniform and intact film in the coated formulations (Figure 5b–d). The cross-section of coated formulations (Figure 6) 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 a plasticizer. This fact is also observed by other authors, who explain that the plasticizer, incorporated normally with polymers, modifies the properties of adhesion, flexibility, and tensile strength of the coating film.^{13,34}

The thickness of the coating film was estimated using SEM photographs (Table 2). The thickness of the coating film ranged between 8.28 μm for the ImPEL + EC₁₀ system and 20.35 μm for the ImPEL + EC₂₀ system.

As expected, the highest amount of EC in the coating solution applied for the ImPEL + EC₂₀ system increases the thickness of the membrane in relation to the ImPEL + EC₁₀ system. The presence of the plasticizer in the ImPEL + EC₂₀ +

DBS system leads to a decrease in the thickness of the film as compared to the ImPEL + EC₂₀ system.

Water Release Kinetics. In Figure 7, the cumulative release curves of imidacloprid from ImPEL granules size fraction between 0.2 mm < *d* < 1 mm, EC-coated granules, and the solubility curve of technical grade imidacloprid are shown. For the technical grade product, 90% of the imidacloprid was dissolved in less than 0.5 h. The rate of imidacloprid release from ImPEL granules diminished in relation to the technical grade product, being necessary at least 48 h to release 90% of

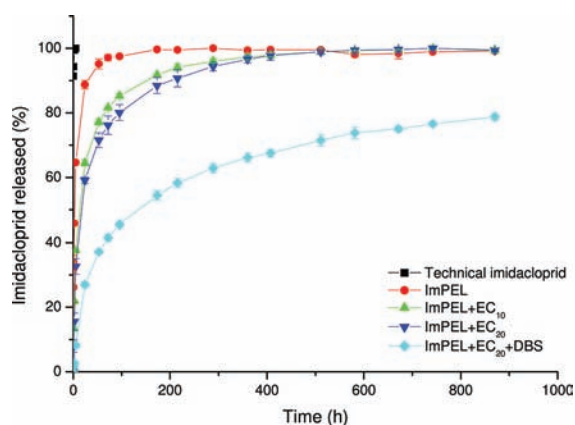


Figure 7. Water release kinetics from of ImPEL and from EC-coated granules containing imidacloprid.

imidacloprid from ImPEL granules. This fact is due to interactions between polymers and imidacloprid deduced from DSC and FT-IR studies. The coated CR granules ImPEL + EC₁₀, ImPEL + EC₂₀, and ImPEL + EC₂₀ + DBS produced a decrease in the process of dissolution of the active ingredient in relation to the ImPEL granules. From the release curves of the coated CR granules, we observed 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.^{15,35} The highest delay in release rate is observed in the ImPEL + EC₂₀ + DBS system. Besides, as expected, the highest quantity of EC in the ImPEL + EC₂₀ formulation as compared to ImPEL + EC₁₀ caused a delay in the release rate of imidacloprid. 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.^{12,36,37}

To obtain a parameter to compare the behavior of CR granules prepared as lignin matrix and EC-coated granules, the kinetics release data of imidacloprid in water were analyzed applying the empirical equation proposed by Ritger and Peppas.³⁸

$$\frac{M_t}{M_\infty} = Kt^n \quad (4)$$

M_t/M_∞ is the percentage of active ingredient released at time *t*, *K* is a constant that incorporates characteristics of the macromolecular network system and the active ingredient, and *n* is a diffusional parameter that is indicative of the transportation mechanism.

The values of *K* and *n* obtained from initial 90% imidacloprid released in water are presented in Table 4. There was good

correlation of the release profiles of CR matrices of imidacloprid with the empirical equation, with the correlation coefficient (*r*) greater than 0.97. The *n* values range from 0.146 for ImPEL formulation to 0.318 for ImPEL + EC₂₀ + DBS formulation. Values of *n* close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrices.³⁸ The complexity of the heterogeneous system involved together with the capacity

Table 4. Constants from Fitting the Empirical Equation the Release Data of Controlled Release Systems into Static Water

formulation	$K \times 10^2 \text{ (h}^{-n}\text{)}$	<i>n</i>	<i>r</i>	<i>T</i> ₅₀ (h)
ImPEL	0.381	0.246	0.977	3.02
ImPEL + EC ₁₀	0.227	0.288	0.976	15.40
ImPEL + EC ₂₀	0.196	0.300	0.972	22.64
ImPEL + EC ₂₀ + DBS	0.098	0.318	0.984	168.60

of the lignin and PEG to interact with the diffusion agent and the irregular shape of granules could explain some deviation from the *n* value above indicated.

The time corresponding to release 50% of imidacloprid, *T*₅₀, was calculated for the matrices using the constants from Table 4. *T*₅₀ values were also calculated using the constants from Table 4. The values ranged from 3.02 h for ImPEL granules and up to 168.60 h for ImPEL + EC₂₀ + DBS granules. The variation order is

$$\begin{aligned} \text{ImPEL} &< \text{ImPEL} + \text{EC}_{10} \\ &< \text{ImPEL} + \text{EC}_{20} \\ &< \text{ImPEL} + \text{EC}_{20} + \text{DBS} \end{aligned}$$

The presence of a uniform film of EC and/or plasticizer in the coated granules caused a delay in imidacloprid release rate. When the data of *T*₅₀ referring to the coated systems without plasticizer, ImPEL + EC₁₀ and ImPEL + EC₂₀, are assessed, it can be seen that the *T*₅₀ value is slightly higher in the system with a greater EC percentage (ImPEL + EC₂₀), which is in agreement with the low difference in the thickness of the coating. The addition of plasticizer in the coating process produces an increase of *T*₅₀ values, which can be due to the higher homogeneity, less porosity, and more hydrophobicity of the coating film in the ImPEL + EC₂₀ + DBS formulation.^{14,36}

*T*₅₀ values obtained for imidacloprid-coated lignin-PEG-matrix were between 3 and 50 times higher than those obtained for imidacloprid lignin granules previously reported.¹⁷ These results provide a higher *T*₅₀ values range, which allow selection of the most appropriate CRF in each particular agronomic situation.

In conclusion, imidacloprid has been successfully entrapped using lignin-PEG and EC to obtain imidacloprid monolithic systems and coated granules, respectively. In both, high EE values for imidacloprid have been obtained. From TGA studies, it can be concluded that no thermal decomposition occurs for either imidacloprid or polymers used. FT-IR and DSC studies indicate the miscibility between lignin and PEG mainly through hydrogen bonding and the compatibility between polymers and imidacloprid in lignin-based CRFs. SEM studies demonstrate the existence of a uniform film in the CR-coated formulations prepared, observing a higher homogeneity and adherence in the coating film for the system that contains a plasticizer.

Kinetic water release experiments show that the use of CR granules reduces the release rate of imidacloprid in comparison with the technical grade product, showing the EC-coated granules release profiles slower than lignin matrix. The release rate of imidacloprid can be controlled by adjusting the EC content but mainly by adding a plasticizer as DBS. The set of release profiles obtained can be useful to select the appropriate imidacloprid CRF in each agronomic practice.

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