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Novel Aphid-Repellent Fiber Mats Based on Poly(lactic acid)-Containing Ionic Liquids

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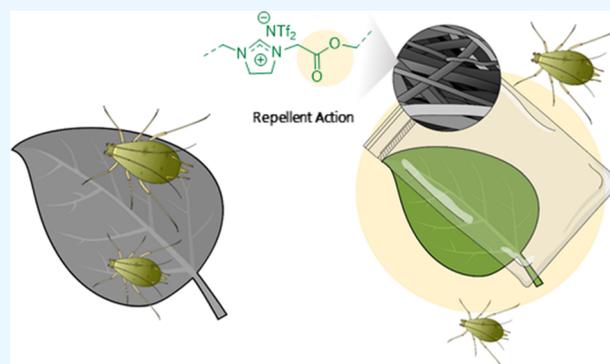
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ABSTRACT: To protect crops as well as human and animal health, the development of novel repellents based on biopolymers is critical for a growing world population. Here, novel aphid-repellent electrospun mats containing epoxidized ionic liquids (ILs) covalently bonded to the carboxyl or hydroxyl groups of poly(lactic acid) (PLA) were designed to produce nonwoven mats. First, di-, tri-, and tetra-epoxidized imidazolium ILs were synthesized and incorporated in different weight fractions (3, 5, and 10 wt %) into the PLA solution. Then, the effect of ILs' microstructure, thermal properties, mechanical performance, and hydrophobic behavior were investigated. It was found that the incorporation of ILs resulted in a reduction of the fiber diameters while the mechanical properties of the mats, i.e., the three-dimensional fibrous porous structure, were maintained. Finally, the effect of these three ILs against the pea aphid *Acyrtosiphon pisum* (Harris) was evaluated for the first time, showing an attractive effect for the diepoxidized IL and a repellent effect for the tri- and tetra-epoxidized ILs. By exploiting the chemical nature of ILs, an environmentally friendly strategy can be developed to limit the need for chemical pesticides and petroleum-based polymers.

KEYWORDS: ionic liquids, biopolymers, fiber mats, aphid repellent, poly(lactic acid)



1. INTRODUCTION

Aphids, such as the pea aphid *Acyrtosiphon pisum* (Harris), are one of the most important pests of crops causing an estimated loss of millions of dollars worldwide.^{1–5} Up until now, most aphid control strategies have relied on the use of systemic chemical pesticides, with alarming public health, environmental, and even economic consequences.^{3,6,7} One study shows that the exposure of the European population to endocrine-disrupting pesticides alone cost up to 120 billion euros in 2015.⁸ The class of neonicotinoids, pesticides responsible for the deaths of 300,000 bee colonies every year, has been banned.⁹ In its “Ecophyto” plan, the French government has decided to reduce the use of pesticides by 50% by 2018. Unfortunately, due to a lack of alternatives to pesticides, the target has been postponed until 2025.¹⁰ This creates a need to develop innovative pest management solutions that exclude the use of chemical pesticides.

Various synthetic or natural substances have been used as insecticides and repellents against aphids.^{3,11–13} Repellents preserve the balance between the populations of harmful and beneficial insects and limit the risks of side effects.¹⁴ Synthetic substances are usually more effective but can be harmful to a wide range of nontarget organisms.^{3,11,15–17} On the other hand, botanical pesticides such as plant extracts, essential oils,

or pure compounds (flavonoids, alkaloids, glycosides, esters, and fatty acids) are an environmentally friendly, nontoxic, and safer alternative to synthetic chemicals.^{11,13,14,17–21} All these botanical pesticides contain active, volatile organic compounds, but their purity and concentration are different depending on the extraction process. However, they have some drawbacks due to their natural origin. Indeed, the commercial application of botanical pesticides requires a sufficient and continuous supply of raw materials.^{11,22} In addition, the chemical composition of the plant extracts can vary depending on the conditions of cultivation and extraction. Thus, the production of botanical pesticides relies on standardization all along the production chain to ensure a right mixture of active compounds, which remains difficult and costly.^{11,22} Furthermore, their application to crops remains complex. Essential oils require a lot of solvents and emulsifiers to be sprayed on crops as aqueous emulsions.¹⁵ More generally, botanical pesticides

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usually degrade within a few days due to their volatile properties and need to be applied more frequently, considerably increasing the cost of treatment.^{11,15,23} Furthermore, the idea of combining natural substances and biopolymers for sustainable agricultural applications has been raised several times with promising results, demonstrating that biopolymers can protect active compounds from early degradation and enable their controlled release into the environment.^{23–26}

Most mixtures of insecticides and biopolymers for agricultural applications are micro or nanocapsules spread on crops.^{23,24,26,27} Nowadays, there is growing interest in the idea of incorporating active substances into plasticulture to develop a new physical–chemical barrier against insects. Therefore, some studies investigated the use of insecticide-treated nets²⁸ and insect-repellent films as mulch²⁹ or greenhouse cover materials^{30–32} with promising results. However, there has only been limited work on the incorporation of active substances against insects in plasticulture, and most of them rely on chemical pesticides^{28,30} and petropolymers,^{28,30–32} which is not a sustainable solution for crop protection. Thus, it is crucial to develop a new solution to control aphids that excludes the use of chemical pesticides and overcomes the drawbacks of botanical pesticides. This solution could be the use of a new effective repellent that can be incorporated into a biopolymer matrix for use as an insect-repellent film in agricultural crop protection.

In view of the growth of the world's population, the last few decades have seen a rapid development in the production of polymers, especially those based on petroleum, which has led to increased environmental concerns for the future of the planet. For these reasons, the European countries are encouraging industry to rethink production methods in order to reduce the use of fossil resources and minimize the environmental impact of the products throughout their life cycle. To this end, biobased polymers, which are mainly based on crop-based components, i.e., from annually renewable sources such as sugar cane, corn, castor oil, etc., have recently received great attention as one of the relevant solutions for the development of more environmentally friendly polymer materials.^{33,34} Due to its unique properties such as its biodegradability, biocompatibility combined with transparency, high modulus, and high strength at break, poly(lactic acid) (PLA), derived from the ring-opening polymerization of lactide, is the most widely studied aliphatic polyester in recent decades.^{35,36} However, PLA has some disadvantages, including low thermal stability, low melt strength, a narrow processing window, brittle behavior, and a slow crystallization rate, which makes it difficult to process by means that require melt stretching, such as the melt spinning process, blow molding, and foaming. Like other polyesters, PLA begins to degrade at temperatures close to its melting point through degradation reactions such as interchain transesterification, hydrolysis, or depolymerization by backbiting. These degradation mechanisms lead to chain scissions, resulting in a significant decrease in molecular weight and consequently to lower melt viscosities.^{37,38} According to the literature, a promising way to increase the melt strength and molecular weight of linear polymers is to use chain extenders with functional groups.^{39,40} Typically, PLA chain extension can be achieved by the reaction of multifunctional modifiers that react with carboxyl or hydroxyl reactive groups of these polymers resulting from their partial hydrolysis during melt processing. Much research

has therefore focused on the use of chain extenders such as dianhydrides, diisocyanates, and di- or multifunctional epoxides such as Joncryl, leading to a significant improvement in the physical properties.^{39,40} Other authors have also confirmed these results by showing that the use of Joncryl plays a key role in the degradation over a wide range of processing temperatures.^{41,42} It has also been shown that the formation of chemical bonds between PLA chains and chain extenders containing epoxy groups does not affect biodegradability. In addition, the degradation time for PLA is approximately six months to two years, which is much shorter than the degradation time of conventional plastics.^{43–45}

More recently, the use of ionic liquids (ILs) could be a promising alternative due to their excellent thermal and chemical stability, nonflammability, and low saturated vapor pressure (volatility), which make them suitable for the development of insect repellents with long-term efficacy.^{46–48} According to the literature, ILs have demonstrated repellent and antifeedant activity against stored product pests,^{49,50} as well as mosquito larvae of *Culex pipiens* L.⁵¹ and *Aedes aegypti* (L.).⁴⁶ Varying the cationic and anionic components can alter the properties of ILs allowing the design of effective insect repellents.^{49,50} Moreover, the multitude of cation–anion combinations offered by ILs can make it possible to modulate their biodegradability. According to the literature, the biodegradability of ILs depends on many factors, such as the chemical nature of the cation and the counteranion. In fact, it is well-known that the use of ILs bearing short alkyl chains is more biodegradable compared with ILs containing long alkyl chains. We also know that higher biodegradability can be attained by a suitable modification of the cation architecture. For example, integrating a cleavable ester function can help with biodegradation.⁵² Furthermore, in a recent publication on the design and the use of tri- and tetra-epoxidized imidazolium ILs containing cleavable ester bonds and used as chain extenders, we have highlighted that these ILs prevent a reduction in PLA molecular weight during the extrusion process and are covalently attached to PLA, avoiding the migration of these ILs.⁵³

In addition to the intrinsic properties of the repellent substance, it is important to consider the microstructure of the manufactured film and the polymer used to provide water resistance and avoid swelling, without losing water vapor and air permeability for the proper development of plants. Electrospinning is an interesting and versatile process that allows the production of electrospun mats with different hierarchical structures, such as aligned or randomly distributed, hollow, or core–shell fibers obtained by manipulating the solution or process parameters. Typically, the electrospun fibers exhibit 3D porous structures, with random fibers having submicron diameters, controllable pore structures, a high surface-to-volume ratio, and structural flexibility.^{54,55} Because of their unique structure electrospun mats, they can provide chemical protection without compromising the water vapor or air permeability of the material.⁵⁶ In addition, they also provide a high surface area that can be functionalized with ILs, improving the release of these agents to the environment and the protection against various hazards, such as insects. Typically, when these agents are incorporated into the polymer (inside the fibers), they are more effective because they are not easily removed by surface abrasion or washing, for example, so the effectiveness can be increased. Moreover, the surface roughness of electrospun mats is a promising property that

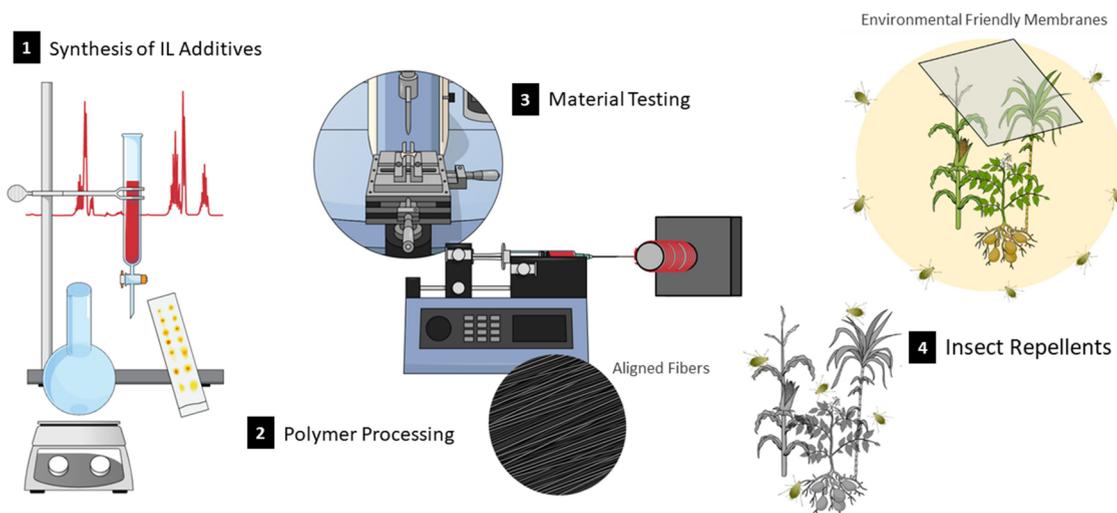


Figure 1. Illustrative overview of the development of repellent PLA-fiber mats using ILs.

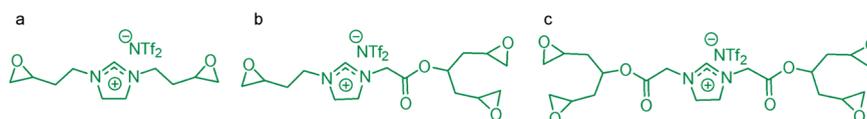


Figure 2. Chemical structures of (a) di-, (b) tri-, and (c) tetra-epoxidized ILs.

reduces insect adhesion.⁵⁷ For these reasons, functionalized electrospun fibers have been widely investigated for food packaging with antimicrobial activity.⁵⁸ However, the application of the electrospinning process in agriculture remains largely unexplored, with only a few studies evaluating their potential against insects, like mosquito repellents^{59,60} or even insect-traps⁶¹ with promising results. More recently, some papers reported the use of electrospun nanofibers as a seed coating.^{62,63} Therefore, electrospun mats could be well suited to incorporate ILs as new aphid-repellents for crop protection.

To reduce the environmental impact related to the accumulation of nonbiodegradable plastic waste and the risks of chemical pesticides to soil, groundwater, and human health, this study proposes to develop biodegradable and insect-repellent polymers as an alternative to conventional chemical pesticides. The objective of this work is to investigate the effect of epoxidized ILs against aphids as well as the effects of ILs on the physical properties of the PLA matrix prepared by electrospinning.

2. EXPERIMENTAL METHODS

Figure 1 presents an illustrative overview of the development of repellent PLA-fiber mats using ILs. First, (1) the synthesis of epoxidized ILs were carried out, which were later (2) integrated into the PLA fiber through electrospinning processing. Subsequently, (3) the fiber mats underwent comprehensive analysis to evaluate their morphology, thermal stability, mechanical strength, and surface properties. Lastly, (4) the repellent efficacy was examined, uncovering encouraging prospects.

2.1. Materials. Poly(lactic acid) (Ingeo Biopolymer 4043D) in the pellet form, with a density of 1.24 g cm^{-3} and a melt flow rate of $6 \text{ g } 10 \text{ min}^{-1}$ ($210 \text{ }^\circ\text{C}$, 2.16 kg), was purchased from NatureWorks LLC (Plymouth, MN, USA). Solvents used to prepare PLA solutions were dimethylforma-

mid (DMF) and dichloroethane (DCE), both purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

2.2. Synthesis of ILs. The synthesis of di-, tri-, and tetra-epoxidized imidazolium ILs used in this work was carried out following the methodology outlined in recent publications from our research group.^{64–66} **Figure 2** presents the chemical structures of the different ILs prepared in this work. Moreover, these salts combined with a fluorinated counteranion named bis(trifluoromethyl-sulfonyl)imide anions $[\text{NTf}_2^-]$ have been designed due to their excellent thermal stability in order to withstand extrusion temperatures ($170\text{--}180 \text{ }^\circ\text{C}$) and to avoid a possible homopolymerization reaction corresponding to the opening of the epoxy groups (see **Figures S1 and S2** in the Supporting Information).

2.3. Preparation of Polymer–IL Mixtures by Extrusion Process. Before the preparation of the electrospun mats, an extrusion step of the PLA/IL mixtures is required. In fact, the ILs corresponding to the di-, tri-, and tetra-epoxidized were used as chain extenders, inducing an increase of the PLA molecular weight due to the reaction of the acidic or hydroxyl functions of the PLA and the epoxy rings.⁵³ The data values of the PLA molecular weight are summarized in the Supporting Information (**Table S1**).

The PLA pellets were dried at $70 \text{ }^\circ\text{C}$ overnight before extrusion. The PLA pellets were mixed manually with IL and then incorporated into a twin-screw extruder, DSM Micro 15 (Xplore, Sittard, The Netherlands), with a screw speed of 70 rpm . During processing, the extrusion barrel temperature profile was fixed at 170 , 180 , and $180 \text{ }^\circ\text{C}$ for the feeding zone, compression zone, and die, respectively. The mixture was prepared after 3 min of mixing at 70 rpm . The melted compounds were extruded into filaments, which were cut into pellets. Mixtures were prepared using neat PLA, and PLA with 3 , 5 , and $10 \text{ wt } \%$ of different ILs: di-, tri-, and tetra-epoxidized ILs.

2.4. Preparation of Electrospun Mats. Pellets of PLA/ILs previously mixed by extrusion were added in DCE/DMF 3:1 v/v (4.5 mL of DCE/1.5 mL of DMF) and stirred for 24 h at 50 °C until the complete solubilization. Samples were prepared using a concentration of 14 wt % of PLA in the solution, with 3, 5, and 10 wt % (related to PLA mass) of different ILs: di-, tri-, and tetra-epoxidized. Thereafter, PLA/IL solution was added into a 5 mL syringe with a 22 s gauge needle, spinneret with an inner diameter of 0.168 mm, to be electrospun. Electrospun mats were obtained using a NANON-01A electrospinning setup from MECC Nanofiber (Fukuoka, Japan). The electrospinning process was carried out with optimized parameters: at 24 kV, a needle-collector distance of 12 cm, and a flow rate of 0.5 mL h⁻¹. The samples have been denoted as PLA/*xy*, where *x* represents the weight fraction of IL (3, 5, or 10 wt %) and *y* is the type (di-, tri-, or tetra-epoxidized).

2.5. Insects. The insects used in this study were parthenogenetic females of the pea aphid *A. pisum* from field originated line LL01. The pea aphid is one of the most important aphid species, feeding on *Fabaceae* crops such as peas or broad beans and causing considerable economic losses.³ Aphid rearing was conducted on broad beans (*Vicia faba* L. “Aquadulce”) under controlled conditions (temperature 20 ± 2 °C, relative humidity RH 65% ± 5%, and 16 h light: 8 h dark photoperiod). The lighting was a combination of cold white LED tubes (Philips, Amsterdam, The Netherlands) and Fluora fluorescent tubes (Osram Lighting, Munich, Germany). Organic broad bean seeds (Graines-Voltz, Loire-Authion, France) were grown in a peat substrate (TRH400, Florentaise, Saint-Mars-du-Désert, France) to the two-leaf stage before aphid infestation. The aphids used for the insect-repellent test were synchronized one-day-old apterous nymphs (N1) from alate adults, according to a standard method previously described.⁶⁷

2.6. Insect-Repellent Test. The insect-repellent test was carried out for 24 h in a climate room at 20 ± 2 °C and 65% ± 5% RH in the dark to avoid any possible light bias. Indeed, aphids also rely on visual cues to find their host plant, implying light, colors, and shapes.⁶⁸ A black box allows aphids to focus only on the olfactory aspect and thus interpret the results without the influence of other factors. Pea aphid nymphs (N1) were placed in the center of a tube (8.33 cm³) sealed on both sides with an artificial diet specifically developed for their feeding and development⁶⁹ coupled to a strip (30 × 5 mm) of PLA mat for the control side and PLA/IL mat for the treatment side (Figure 3). Aphids picked a direction by olfaction and passed beyond the PLA electrospun mat before settling on an artificial diet. The next day, the number of aphids settled on the diet was counted on each side of the tube.

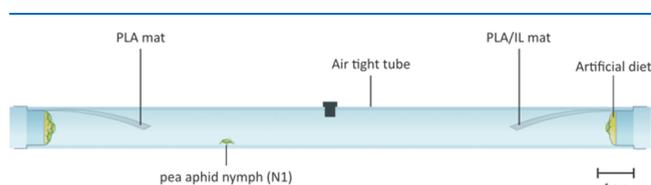


Figure 3. Device of the insect-repellent choice test. Pea aphid nymphs (N1) have 24 h to choose between the control side with a PLA mat or the treatment side with a PLA/IL mat and to settle on the artificial diet. Figure reproduced from Lacotte et al.¹⁴ with permission from Elsevier, copyright 2023.

For each one of the nine combinations of PLA/*xy* IL, a repellent test was repeated 18 times with 6 aphids per tube, for a total of 108 aphids.

The difference between the total number of aphids settled on the control side (C) and on the treatment side (T) was analyzed statistically with a 2-to-2 proportion comparison test of Chi², with a significance level of 5% (0.05) for each pair of PLA/*xy* IL combinations. Finally, a Repellency Index (%) (RI) was calculated to assign a final repellency rate to each combination of PLA/*xy* IL tested according to the following formula:⁷⁰

$$RI = [(C - T)/(C + T)] \times 100$$

Positive and negative values indicate repellent and attractive effects, respectively.

2.7. Characterization. Scanning Electron Microscopy (SEM) analyses were performed using a Tescan Vega microscope (Kohoutovice, Czech Republic). The samples were coated with gold and analyzed under an accelerating voltage of 10 kV. From the SEM images, the fiber diameters were estimated by ImageJ software (National Institutes of Health, Bethesda, MD, USA).

The contact angle measurement was performed using the sessile drop technique in a Contact Angle System OCA (Dataphysics Instruments, Filderstadt, Germany). A water droplet (6 μL) was deposited on a PLA or PLA/IL surface, and the contact angle was measured within 10 s. For each sample, 20 drops were put on the specimen's surface, and the droplet arc and the angle of contact at the interface were traced and recorded.

The mechanical properties were conducted using an MTS 2/M universal testing machine (Eden Prairie, MN, USA). The tests were performed using specimens with dimensions of 10 × 30 × 0.04 mm at room temperature (23 ± 1 °C) with a constant crosshead displacement of 5 mm min⁻¹.

Differential Scanning Calorimetry (DSC) analyses were carried out on Q20 TA Instruments (New Castle, DE, USA). Samples of approximately 5 mg were sealed in standard aluminum pans and heated from 25 to 200 °C (1st heating), followed by a cooling scan from 200 to 25 °C and then reheated to 200 °C (2nd heating), at a rate of 10 °C min⁻¹, under nitrogen flow (60 mL min⁻¹). The crystallinity content (*X_c*) was calculated from eq 1, where Δ*H_f* is the sample enthalpy of fusion, Δ*H_f*^{*} is the heat of fusion of perfectly crystalline PLA (93.7 J g⁻¹),⁷¹ and φ is the weight fraction of PLA.

$$X_c = \frac{\Delta H_f}{\Delta H_f^* \phi} \quad (1)$$

The number-average molecular weight and average molecular weight were determined by gel permeation chromatography (GPC) on a light scattering instrument TREOS, Cell Type K5. Chloroform was used as the eluent at a flow rate of 1.0 mL min⁻¹.

3. RESULTS AND DISCUSSION

3.1. Impact of ILs on the Morphology of PLA Electrospun Mats. The primary aim of this study is to explore the impact of PLA-fiber mats based on ILs on aphid repellency for safeguarding agricultural lands, alongside assessing the influence of ILs on the physical characteristics

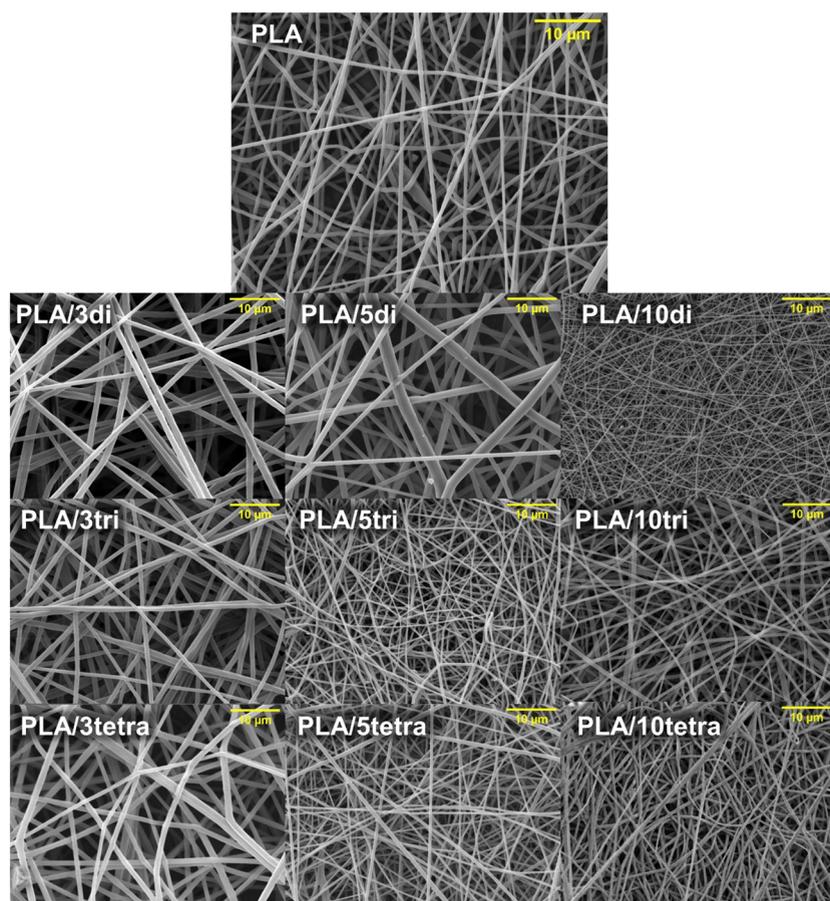


Figure 4. SEM micrographs of neat PLA and PLA electrospun mats containing 3, 5, and 10 wt % di-, tri-, and tetra-epoxidized ILs.

and processing of the PLA matrix fabricated via electrospinning.

Figure 4 presents the SEM micrographs of the neat PLA and the PLA electrospun mats containing different amounts of ILs (3, 5, and 10 wt %). In all cases, the PLA electrospun mats display a 3D structure with randomly oriented continuous fibers, high porosity, and rough fibers, giving the fiber-based polymer material a high surface area and excellent ductility. However, some differences were observed in the morphology of the fibers in the presence of ILs. Thus, the incorporation of 3 wt % of di-, tri-, and tetra-epoxidized ILs induced an increase of the fibers' diameter from $0.55 \pm 0.13 \mu\text{m}$ (pure PLA) to around $1.00 \pm 0.20 \mu\text{m}$ (Figure 5). This phenomenon can be explained by the role of chain extenders of the epoxidized ILs, leading to an increase of the average molecular weight (M_w) as well as the number-average molecular weight (M_n) of PLA, as demonstrated in a previous paper.⁵³ In contrast, an increase in the concentration of ILs led to a reduction in fibers' diameters. This result can be associated with an increase of the ionic conductivity of the solution by adding a larger quantity of ILs,⁷² which enhanced the polymer stretching during electrospinning process. The presence of additional ether groups in the tri- and tetra-epoxidized ILs facilitates the ionic conduction mechanisms, which enhances ionic conductivity, explaining the lowest fiber diameters.⁷³ Thus, reducing fiber diameter increases the surface area available for IL interaction with insects and could improve the efficiency of electrospun mats compared to a nonporous film. The small fiber diameters can also improve the elongation and elasticity of the mat.

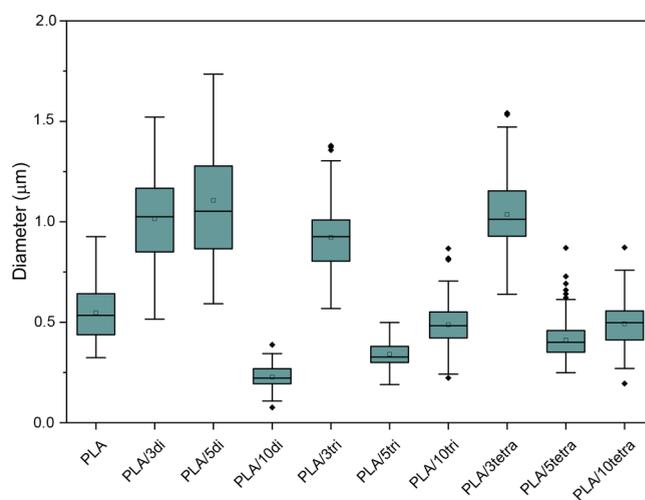


Figure 5. Fiber distribution of PLA and PLA/IL electrospun mats.

3.2. Impact of ILs on the Thermal Behavior of PLA Electrospun Mats. The thermal transitions were determined by DSC, as can be seen in the curves of the second heating scans shown in Figure 6 and Table 1. In the first heating scan, the PLA exhibits a glass transition temperature at ca. $T_g = 59 \text{ }^\circ\text{C}$, followed by a not clearly observed cold crystallization peak exothermic at ca. $T_{cc} = 94 \text{ }^\circ\text{C}$, and then a melting endotherm at ca. $T_m = 151 \text{ }^\circ\text{C}$. The T_g value was gradually reduced with increasing IL fractions, indicating a slight plasticizing effect. In all cases, this behavior was observed when di-, tri-, and tetra-

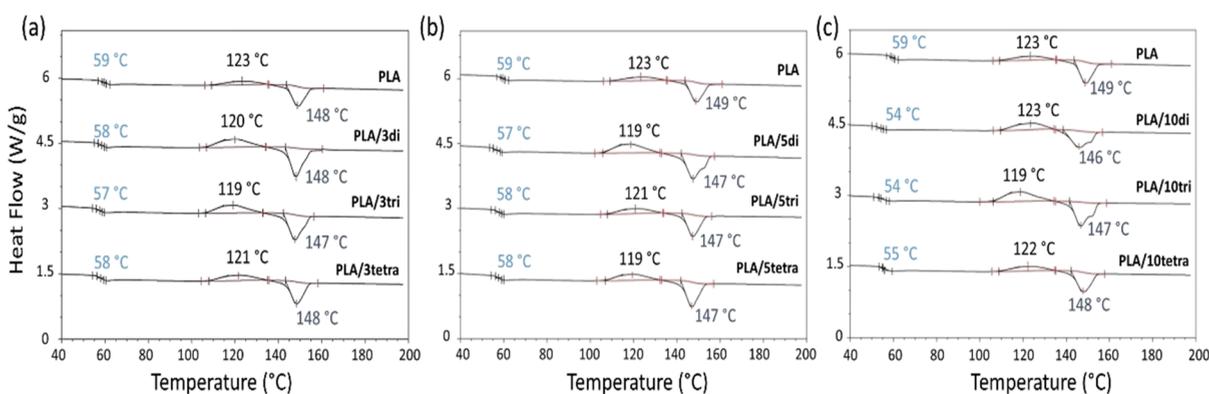


Figure 6. DSC curves (2nd heating) of PLA with different ILs: (a) di-, (b) tri-, and (c) tetra-epoxidized.

Table 1. Thermal Properties of PLA and PLA/ILs in the 1st and 2nd Heating Cycles

samples	1st heating					2nd heating					
	T_g	T_{cc}	T_m	ΔH_m	X_c (%)	T_g	T_{cc}	T_m	ΔH_m	X_c (%)	
PLA	59.2 ± 0.2	94.3 ± 0.5	150.8 ± 0.3	26.2 ± 0.5	27.9 ± 0.5	59.5 ± 0.2	123.3 ± 0.3	148.7 ± 0.4	19.5 ± 0.6	20.8 ± 0.3	
PLA/3di	60.0 ± 0.2	87.7 ± 0.4	149.0 ± 0.5	29.1 ± 0.4	32.0 ± 0.4	58.4 ± 0.3	120.0 ± 0.4	148.1 ± 0.2	30.1 ± 0.4	33.1 ± 0.4	
PLA/5di	56.0 ± 0.3	87.5 ± 0.4	150.3 ± 0.4	32.7 ± 0.3	36.7 ± 0.3	56.9 ± 0.3	118.7 ± 0.5	147.4 ± 0.3	29.2 ± 0.5	32.8 ± 0.5	
PLA/10di	54.6 ± 0.4	85.8 ± 0.5	150.2 ± 0.2	31.2 ± 0.2	37.0 ± 0.2	54.2 ± 0.5	123.5 ± 0.6	145.9 ± 0.7	21.0 ± 0.7	24.9 ± 0.7	
PLA/3tri	59.4 ± 0.3	86.7 ± 0.4	150.1 ± 0.3	32.1 ± 0.6	35.3 ± 0.6	57.4 ± 0.2	119.1 ± 0.7	147.6 ± 0.4	27.1 ± 0.3	29.8 ± 0.3	
PLA/5tri	57.6 ± 0.3	87.5 ± 0.2	150.2 ± 0.2	31.0 ± 0.3	34.8 ± 0.3	58.0 ± 0.2	120.8 ± 0.5	147.3 ± 0.3	21.1 ± 0.6	23.7 ± 0.6	
PLA/10tri	55.0 ± 0.5	101.4 ± 0.5	149.9 ± 0.4	31.5 ± 0.2	37.3 ± 0.2	54.1 ± 0.4	118.8 ± 0.3	146.7 ± 0.4	25.7 ± 0.4	30.5 ± 0.4	
PLA/3tetra	57.7 ± 0.3	88.1 ± 0.6	150.9 ± 0.5	34.2 ± 0.4	37.6 ± 0.4	58.1 ± 0.3	121.6 ± 0.4	148.3 ± 0.2	21.7 ± 0.5	23.9 ± 0.5	
PLA/5tetra	57.4 ± 0.1	87.9 ± 0.5	150.1 ± 0.5	31.1 ± 0.5	34.9 ± 0.5	57.5 ± 0.2	119.4 ± 0.4	146.8 ± 0.5	24.6 ± 0.3	27.6 ± 0.3	
PLA/10tetra	55.1 ± 0.4	90.8 ± 0.7	150.1 ± 0.3	29.7 ± 0.3	35.2 ± 0.3	55.1 ± 0.5	122.3 ± 0.2	147.8 ± 0.2	19.5 ± 0.2	23.1 ± 0.2	

epoxidized ILs were used. In terms of melting temperature, the presence of ILs has no influence, whatever their chemical nature. Indeed, as the IL seems to be preferentially located in the amorphous phase due to the reduction in the glass transition temperature, the melting temperature is similar in all cases, i.e., 150 °C. The presence of the cold crystallization of PLA indicates a rapid cooling during the electrospinning process due to the fast solvent evaporation, which prevented the maximum polymer crystallization. The large number of crystal nuclei formed during the process can grow during further heating of the sample, giving rise to rapid recrystallization observed at temperatures lower than the melting of the polymer. However, the addition of ILs led to a more defined and lower cold crystallization peak around 85–90 °C which can be explained by the plasticizing effect as well as the nucleating effect of ILs into the PLA matrix.⁷⁴ For these reasons, the crystallinity degrees of the PLA/IL electrospun mats were higher than those reported for neat PLA mats.

In the second heating, the thermal transitions were similar to those observed in the first heating; however, differences can be observed in T_{cc} and T_m . The first difference can be seen in the cold crystallization temperature, where this transition is detected at higher temperatures when compared to the first heating. This behavior can be related to the slower crystallization during cooling, which despite not allowing full crystallization, results in larger nuclei. Thus, during heating, higher temperatures are needed for these nuclei to grow. The T_m of PLA/ILs tends to decrease with the increment of the amount of ILs due to the reduction of intermolecular interaction in the crystalline phase caused by the ILs. Moreover, especially for the electrospun mats with higher

concentrations of di- and triepoxide, there are double melting transitions, due to the PLA polymorphic structure, indicating that ILs can induce the formation of different crystalline phases. The β -form melts at lower temperatures, while the α -form melts at a higher temperature.^{75,76} This behavior has also been associated by some authors with the crystal reorganization upon melting of imperfect crystals, formed in cold crystallization.^{75,77} These crystals would have a high tendency to reorganize into more ordered structures and melt at a higher temperature. The crystallinity degrees display similar results in the first heating, increasing with the increase of the amount of ILs.

3.3. Impact of ILs on the Hydrophobic Behavior of PLA Electrospun Mats. The contact angles for the PLA electrospun mats were measured at 132° (Figure 7), indicating a hydrophobic behavior of PLA ($90^\circ < \theta_e < 150^\circ$). It is interesting to notice that the neat PLA electrospun mats induce a higher contact angle, compared to the nonporous PLA film ($\sim 76^\circ$). This increase in contact angle can be generated by different factors, such as porosity, pore diameter, and surface roughness. In fact, increasing the roughness on the fiber surface can trap more air in the interfiber space, improving the possibility that a droplet sitting on air leads to a hydrophobic behavior. This behavior was reported by Cho et al.⁷⁸ for polypropylene electrospun mats. In the case of PLA/IL electrospun mats, the contact angle was not significantly modified by incorporating different types and amounts of ILs, and the mats continued to display hydrophobic behavior. Hydrophobicity is particularly important when using electrospun mats as insect-repellent materials to develop protective films for agricultural land that do not absorb water. Indeed, the protective films applied on crops are frequently exposed to rain

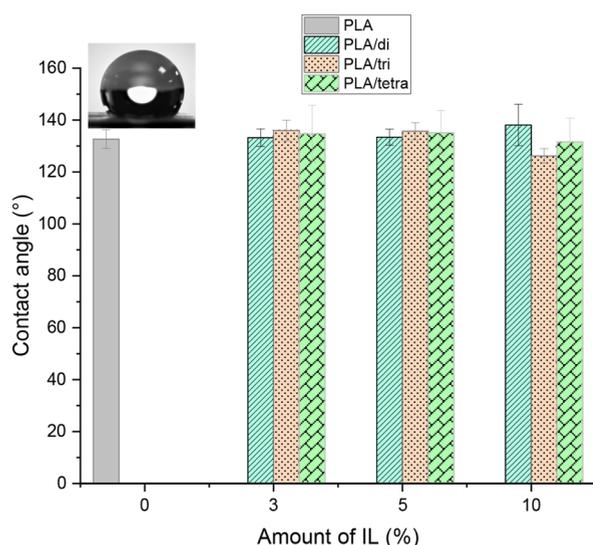


Figure 7. Contact angle of the electrospun mats of PLA and PLA/ILs with water.

and watering, which could accelerate the degradation of a hydrophilic material and considerably reduce its efficacy. In our case, the hydrophobicity of PLA/IL electrospun mats can limit the hydrolytic degradation of PLA and the effects of weathering.^{37,38,79,80} Moreover, according to the work reported by England et al.,⁵⁷ the general trend is that hydrophobic surfaces tend to reduce the attachment forces of insects. It turns out that the active flight of aphids is very energy-consuming and should be used with moderation.⁸¹ Thus, after a migratory flight (wind, etc.) toward crops, aphids generally land on agricultural films and then walk in search of a host plant using olfactory, visual, and tactile cues.⁶⁸ With hydrophobic films, aphids will have difficulties settling and will be forced to fly in search of a crop more suitable for colonization.

3.4. Mechanical Performances of the PLA Electrospun Mats. To highlight the impact of the chemical nature of the di-, tri-, and tetra-epoxidized ILs on the mechanical properties of PLA electrospun mats, the tensile properties of neat PLA and PLA/IL blends are presented in Figure 8. As it can be seen, all the PLA electrospun mats presents a good ability to sustain large deformations (strain at break) ranging from 50 to 90%. This is a very promising result, considering that one of the main disadvantages that have been reported in the literature^{82,83} is the inherent brittleness and poor toughness of PLA, which prevent its use for many applications.

Concerning the neat PLA, a Young's modulus of 60 MPa and a strain at break of 90% was determined. These values are quite similar to those reported by Lins et al., who investigated the mechanical properties of PLA scaffolds (40 MPa, 100%) produced by the electrospinning process.⁸⁴ However, several differences depending on the ILs used are clearly demonstrated. In fact, the incorporation of 3, 5, and 10 wt % of the tetra-epoxidized ILs into the PLA matrix led to a continuous increase in Young's modulus (50 to 100 MPa) combined at a constant deformation of around 60%. These results can be explained by the increase in the crystallinity percentage as a function of the amount of tetra-epoxidized IL (23–30% for 3 and 10 wt % of ILs, respectively). Regarding the strain at break, no plasticizing effect of the IL was observed by DSC, which explains a similar deformation. In the case of the diepoxidized IL, a slight increase in Young's modulus is obtained from 60 to

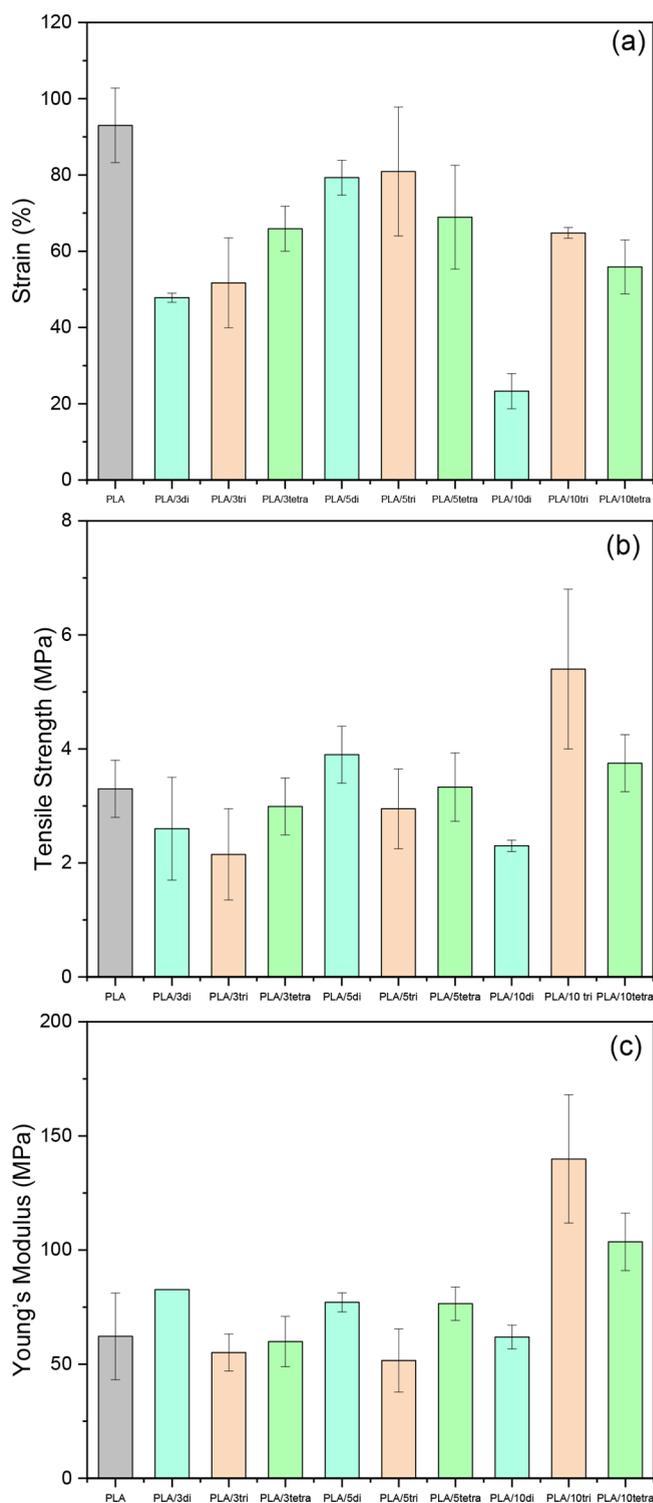


Figure 8. Mechanical property of PLA and PLA/IL electrospun mats. (a) Strain, (b) tensile strength at break, and (c) Young's modulus.

80 MPa when 3 and 5 wt % of IL are used. This phenomenon can be explained by the size of the fibers (1 μm) compared to 0.55 μm for the neat PLA but also by the significant increase of the crystallinity rate, which rises from 20% (neat PLA) to 33% for both compositions. On the other hand, the plasticizing effect observed by DSC for PLA containing 5 wt % of the diepoxidized IL induced a significant improvement of the strain at break from 50 to 80%. Only the PLA electrospun mat

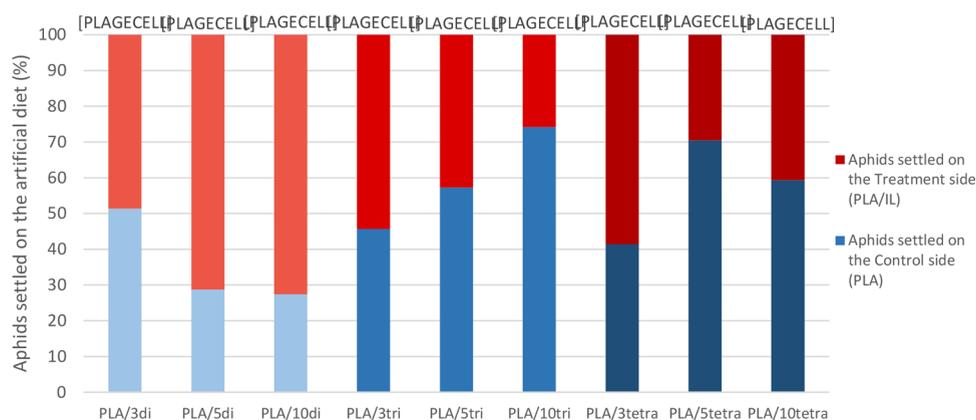


Figure 9. Repellent activity of epoxidized ionic liquids (ILs) on the pea aphid after 24 h in a two-choice test between samples of PLA on the control side and PLA/IL on the treatment side. Comparison of proportion of aphids settled on each side using a χ^2 statistical test ($P \geq 0.05$), with letters assigned according to significant differences.

Table 2. Repellency Index (RI) of PLA/IL Samples against the Pea Aphid according to the Two-Choice Test^a

samples	PLA/3di	PLA/5di	PLA/10di	PLA/3tri	PLA/5tri	PLA/10tri	PLA/3tetra	PLA/5tetra	PLA/10tetra
RI (%)	2.8	-42.6	-45.1	-8.6	14.6	48.4	-17.2	41.0	18.8

^aRI (%) = $[(C - T)/(C + T)] \times 100$ where C is the total number of aphids on the control side, and T is the total number of aphids on the treatment side. Positive and negative values indicate repellent and attractive effects, respectively.

containing 10 wt % of this IL presented a different behavior characterized by a reduction in Young's modulus and the strain at break, which is attributed to the small diameter of the fibers obtained (220 nm compared to 1 μm). Finally, the introduction of 10 wt % of the triepoxidized IL reached the best rigidity/deformation compromise.

In summary, even if there is a tendency to reduce deformation after adding ILs, the deformation of the electrospun mats with tri- and tetra-epoxidized ILs remains high (>50%), opening promising prospects for the application of these films on agricultural lands.

3.5. Repellent Activity of Epoxidized ILs on the Pea Aphid. As previously described, the incorporation of epoxidized ILs led to good mechanical performances in terms of stiffness and strain at break, hydrophobic behavior, and similar morphologies of neat PLA with average diameter sizes of $1.00 \pm 0.20 \mu\text{m}$. In addition, no significant impact of these ILs was observed on the thermal properties of PLA except for an increase in crystallinity and a slight plasticizing effect. After studying the impact of di-, tri-, and tetra-epoxidized ILs on the physical properties of PLA electrospun mats, their repellent activity was evaluated against the pea aphid *A. pisum* to understand the effectiveness of such a blend as an environmentally friendly repellent material against crop pests. According to Figure 9, the three types of epoxidized ILs have a significant effect on pea aphids at the highest concentrations (5 and 10 wt %). The ILs incorporated at 3 wt % do not have a significant effect on aphids (RI close to neutral in Table 2). The diepoxidized IL shows an attractive effect on the pea aphid at 5 and 10 wt % (Figure 9), with a negative RI of -42.6 and -45.1, respectively (Table 2). Tri- and tetra-epoxidized ILs have a repellent effect against the pea aphid at 5 and 10 wt %. The triepoxidized IL is slightly repellent at 5 wt %, with a positive RI of 14.6% (Table 2), but not significantly different from the concentration at 3 wt % (Figure 9). Triepoxidized IL is more repellent at 10 wt % with a RI of 48.44% (Figure 9 and Table 2). Finally, the tetra-

epoxidized IL is repellent at 5 wt % with a RI of 41.0% (Table 2). It shows a lower repellency at 10 wt % with a RI of 18.8% (Table 2), but not significantly different from the concentration at 5 wt % (Figure 9). Some agitated, underweight, and dead aphids were observed during counting with tri- and tetra-epoxidized ILs at 10 wt %, which could be a toxic response that could explain the variable results obtained with tetra-epoxidized IL at this high concentration.

Therefore, PLA electrospun mats with epoxidized ILs have an effect on the pea aphid *A. pisum* starting at 5 wt % concentration. Diepoxidized IL showed an attractive effect, while tri- and tetra-epoxidized ILs were repellent and even potentially toxic at 10 wt %. To our knowledge, this is the first investigation of ILs as insect repellents on agricultural crops, focusing on aphids as major crop pests. In scientific studies considering ILs as a new ecological alternative substance for use in agrochemistry, ILs have been mainly used as bactericides, fungicides, herbicides, and insect antifeedants for the food industry.⁸⁵ Indeed, ILs have been used to develop an environmentally friendly pesticide with dual functions: as an herbicide on the white mustard weed *Sinapis alba* L. and as a fungicide against the gray mold agent *Botrytis cinerea* Pers.⁸⁶ Different ILs with various structures turned out to be feeding deterrents against numerous stored grain insects. A monoterpene-based IL impregnated on a filter paper disk in a Petri dish showed a repellent activity on the red flour beetle *Tribolium castaneum* (Herbst.) and the drugstore beetle *Stegobium paniceum* (L.) with a RI of 56.5 and 56.3%, respectively.⁸⁷ Wheat wafer disks dipped in a 1% solution of IL with a didecyldimethylammonium cation demonstrated a strong deterrent activity against the granary weevil *Sitophilus granarius* (L.) and the confused flour beetle *Tribolium confusum* with a respective RI of 92.3 and 87.6%.⁴⁹ Finally, a series of recent studies using the same bioassay with dicationic, glycine betaine-, and amino acid-based ILs recorded a very good total deterrence coefficient (150–200) on adults of the

granary weevil and the confused flour beetle, as well as larvae of the khapra beetle *Trogoderma granarium* Everts.^{88–90}

These different reactions can be explained by the chemical nature of ILs. Indeed, it appears that the biological activity of ILs could be dependent on the length of the alkyl chain, the presence of an ester group in the cation, the properties of the anion (hydrophobicity and stability) and the cation (lipophilicity), as well as the concentration used.^{49,85,90–92} Based on these characteristics, ILs will exhibit distinct mechanisms of interaction with cells (membrane binding, insertion, and disruption). Thus, unlike diepoxidized IL which have no ester groups, tri- and tetra-epoxidized ILs show an increase in the number of ester groups from one to two, respectively, which could be the cause of their repellent activity against the pea aphid *A. pisum*. It is worth noting that the increase in ester groups with short alkyl moieties within the cations of tri- and tetra-epoxidized ILs leads to an increase in their repellent activity, as documented in previous research.⁹⁰

4. CONCLUSIONS

This study describes for the first time the development of PLA electrospun mats using di-, tri-, and tetra-epoxidized imidazolium ILs as insect-repellent active agents. Electrospinning is shown to be a suitable process for producing nonwoven mats with submicrometric fibers, high porosity, and flexibility. The incorporation of ILs provides new functionality to the mats, allowing them to exhibit a good compromise between stiffness (50–140 MPa) and ability to sustain large deformations (strain at break), ranging from 50 to 90%, combined with hydrophobic behavior and insect-repellent activity. Indeed, PLA electrospun mats with epoxidized ILs had an effect on the pea aphid *A. pisum* starting from a concentration at 5 wt %. Diepoxidized IL showed an attractive effect while tri- and tetra-epoxidized ILs were repellent and even potentially toxic at 10 wt %. The repellency of tri- and tetra-epoxidized ILs may be related to the presence of ester groups, which may affect insect taste organs differently, making them more effective against insects. In this context, it is possible to conclude that electrospun mats of PLA with tri- and tetra-epoxidized ILs have insect-repellent activity, which can be valuable in the preventive control of crop pests. Moreover, due to the presence of the cleavable ester groups on the tri- and tetra-epoxidized ILs, we can conclude that the ILs (mainly the cations) are only partially biodegradable despite the non-biodegradable fluorinated counteranion (TFSI). For future work, and due to the repellent effect of these ILs, more thermostable and environmentally safe anions will be considered.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c06753>.

Thermal stability of the di-, tri-, and tetra-epoxidized ILs, DSC curves of the tri- and tetra-epoxidized showing the homopolymerization reaction, and molecular weight of PLA and PLA/ILs after extrusion (PDF)

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Notes

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