

Biobased Plastics With Insect-repellent Functionality

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Natural insecticides/repellents, such as pyrethrum (derived from chrysanthemum plants), and insect repellent *N,N*-Diethyl-meta-toluamide (DEET) were added to poly(lactic acid) (PLA) fibers through extrusion and spray coating on the PLA fabrics. Contact irritancy assay (CIA) showed that DEET-treated PLA fabrics caused the lowest relative escape response of mosquitoes with an escape frequency of $33.3\% \pm 3.3\%$, indicating that DEET was less effective compared with natural insecticides/repellents. This was followed by the extruded natural pyrethrum-treated PLA fabric with an escape frequency of $80\% \pm 6.3\%$. Finally, the PLA fabrics spray-coated with natural pyrethrum caused the highest escape frequency of $98.3\% \pm 1.7\%$. Thus, it was found that pyrethrum/PLA fabrics functioned as a mosquito repellent better than DEET/PLA fabrics. In addition, TGA and tensile testing results demonstrated that pyrethrum was sufficiently thermally stable to be extrusion compounded with PLA. GPC results showed that DEET promoted de-polymerization of PLA when co-extruded. The results demonstrated that pyrethrum can be a viable additive for PLA to produce fibers that function as mosquito repellent to produce temporary garments that are compostable. The potential use of the developed biobased fibers with natural insect repellents is for single use of personal protection equipment (PPE) garments. POLYM. ENG. SCI., 59:E460–E467, 2019. © 2019 Society of Plastics Engineers

INTRODUCTION

Climate change exerts effects on health issues on a global scale including shifts in insect pest emergence. Mosquitoes react directly to changes in the environment, and in particular temperature and moisture: they are able to reproduce rapidly, increase their breeding season and mobility in warmer temperatures and wetter climates [1]. This is compounded by the fact that warmer climates reduce the time for the development of microbes that they can spread as well as allowing the spread of these microbes further into mid-to-high latitudes compared with previously reported cases [2]. The mosquito *Aedes aegypti* is an example of the principal species that spreads yellow fever, dengue, chikungunya and, most recently, Zika. This species is highly resilient showing a high level of environmental adaptation, and thus

controlling their spread represents a significant challenge [3]. Malaria is another life-threatening disease caused by several species of *Anopheles* mosquitoes, the relevant species in the United States, such as *An. quadrimaculatus* (east), *An. freeborni* (west), and *An. pseudopunctipennis* (The United States and Mexico) [4].

This problem increases the need for protective garments for the world's population at risk to exposure of these mosquito-borne diseases. This is especially the case for public health and environmental safety providers. Because these products (personal protective equipment [PPE]) are typically either single-use or are designed to remain in the environment, there is a product performance benefit if these products were degradable and natural. One solution is the use of naturally derived insecticides/repellents to minimize the accumulation of synthetic insecticides in the environment. The use of natural insecticides, such as aromatic/essential oils, has been reported as far back as to antiquity, before the extensive use and production of current synthetic repellents [5]. The natural insecticides/repellents are a better choice compared with the synthetic based repellents, as they are less persistent in the environment and biodegradable.

Historically, the use of insect repellent has been reported in many areas, including soldiers who were supplied with creams containing citronella, camphor, and paraffin [6]. Other essential oil producing plants that have insect repellent capability are from the *Lamiaceae*, *Poaceae*, and *Myrtaceae* species. Despite the fact that numerous essential oils are available naturally, only a handful are effective in acting against the *Aedes aegypti* mosquito. These include *Pogostemon cablin* (Patchouli), *Cymbopogon nardus* (Citronella), *Zanthoxylum limonella*, and *Syzygium aromaticum* (Clove) that feature repellent activity up to 120 min [7]. Another study also showed that Neem oil (*Azadirachta indica*), when mixed with coconut oil, has the ability to repel mosquito for 12 h [8]. *N,N*-Diethyl-meta-toluamide (DEET) has been long used as an effective insect repellent. However, it is shown to degrade plastic eyeglass lenses and watch faces. Moreover, DEET is also shown to cause health problems to humans such as rashes, skin and mucus membrane irritation, dizziness, headaches, disorientation, and nausea [9]. Even with these considerations, DEET has shown to be mainly non-toxic to humans. However, EPA shows that it is slightly toxic to birds, fish, and aquatic animals [10].

On the contrary, pyrethrum, not only natural but also breaks down rapidly when in contact with light and does not accumulate or persist in the environment. It also possesses low mammalian toxicity and can be food-safe when applied in correct dosage. These characteristics makes pyrethrum a good choice to be used in sensitive environments where the long-term persistence is a

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concern. Other advantages of pyrethrum apart from its ability to repel insects include its broad spectrum activity against a wide spectrum of insect species, excellent flushing activity, and lack of recorded insect resistance [11]. Pyrethrum decomposes into a non-active, non-insecticidal product in the presence of oxygen, and ultraviolet light [12–14]. There have been several patents that preserve the insecticide treated fabrics by using coatings such as amylopectin or polyvinyl acetate to retain the insecticide while the fabric goes through wash cycles [12, 15, 16].

A possible biobased/compostable plastic as a base for fabric production of PPE garments is poly(lactic acid) (PLA). PLA is a thermoplastic polyester that is derived from renewable resources such as cornstarch, tapioca roots, or sugarcane. It is a widely used bio based and compostable polyester. PLA has relatively good mechanical properties, however, it is still relatively expensive compared with many conventional plastics.

The use of biobased plastic has several attractive attributes, including reducing the petrochemical-based polymer waste by 20% by volume per year, reduction of carbon dioxide emissions, the readily availability and inexpensive nature of natural resources and the biodegradability of the biobased plastic at the end of its life [17].

In this article, the natural insecticide, pyrethrum (derived from chrysanthemum plants), and insect repellent DEET were added to PLA fibers through extrusion and spray coating on the PLA fabrics. Contact irritancy assay (CIA) was used to evaluate the repellent efficacy. Thermal degradation of insecticides/repellents were investigated with both thermogravimetric analysis (TGA) and gas chromatography–mass spectrometry (GC–MS). The effect of incorporating insecticide on PLA was determined with gel permeation chromatography (GPC).

MATERIALS AND METHODS

Procurement

Two types of PLA resins were used, PLA 6100D and PLA 6202D (NatureWorks, Minnetonka, MN). Each resin had a density of 1.24 g/cm³. The melt indices (MI) for the resins were 2.4 and 2.2 dg/min (210°C), respectively. The melt density and thermal conductivity at about 230°C were 1.08 g/cm³ and 0.0016 W/(m °C), respectively, for each grade. PLA 6202D yarn was also obtained from NatureWorks and was used to make control groups for pyrethrum sprayed fabric. Synthetic repellent, *N,N*-diethyl-3-methylbenzamide (DEET, 97%) and natural insecticide, Pyrethrum extract (≥50% [sum of pyrethrins]) were purchased from Sigma-Aldrich (St. Louis, MO).

Thermogravimetric Analysis

To determine the degradation temperature of the insect repellents, the rate of weight change in both DEET, and pyrethrum as a function of increasing temperature were measured with a TA instrument Q50 V20.13 (New Castle, DE) thermal gravimetric analyzer (TGA) under nitrogen atmosphere. Each sample of 25 µL was placed in a ceramic pan and heated from 10°C to 200°C at a heating rate of 5°C/min, and the degradation profile was analyzed. These results were used to determine the thermal stability for the repellents during melt extrusion processing with PLA.

Extrusion

Prior to extruding, both grades of PLA were dried for 12 h at 65°C to reduce the possibility of hydrolysis of the PLA. About

1 kg of PLA 6100D was mixed with 50 g of DEET (5 wt%). Extruder temperatures were set at 160°C, 165°C, 160°C, and 150°C from the die to the hopper; the screw speed was 12 RPM. Extrusion was completed using a C.W. Brabender® single screw laboratory extruder (South Hackensack, NJ). The extruded PLA fiber was spun onto oscillating spool to traverse fiber evenly.

During extrusion, 100 g of PLA 6202D was mixed with 5 g of pyrethrum (5 wt%) and extruded at 155°C at the die, 150°C, 145°C, and 140°C near the hopper; the screw speed was 4 RPM. Only PLA 6202D was used because of its lower melt temperature compared with PLA 6100D to reduce thermal degradation of the pyrethrum. The fiber was then drawn using a DSM Xplore Fiber Spinning Unit & Conditioning Unit (Geleen, Netherlands). The drawing unit conditions were: Heater: 85°C; Start up speed: 500 cm/min; Speed: 6,000 cm/min; Factor: 4; Torque: 40, and Unwinding torque: 40.

The fibers compounded with DEET and pyrethrum were then woven into three 11.5 cm × 8 cm fabric mats. Another three samples of pyrethrum spray coated fabrics were made by weaving the PLA 6202D yarn procured from NatureWorks. The fabric was then weighed and 5% of the fabric weight was used as the amount of pyrethrum to be sprayed onto the fabric. To ensure that the same amount of pyrethrum was on each of the fabrics, the final weights were measured to determine the weight fraction of the insect repellents.

Tensile Tests

Prior to the tensile test the linear density of the PLA fibers was recorded for each sample. Linear density was measured by dividing the mass of the fiber to the length that was being tested. This was completed by measuring 5 cm of the fiber and recording its mass. The linear density was used to calculate the tenacity of the fibers. Tenacity, is a measurement of breaking force (mN) per linear density (tex), which is a more accurate and commonly used representation of the strength of the fiber for varying diameters. Tensile tests were performed using an Instron unit (Instron 5966, Boston, MA) at the rate of 5 mm/min. ASTM Standard Test Method for Tensile Properties of Single Textile Fibers (D3822/D3822M) was used for the tensile tests. A total of five tests were performed for each sample type.

Gel Permeation Chromatography Analysis

Five PLA samples were tested, PLA pellets, PLA fibers with 0, 2, 4 and 7% DEET, drawn once. The analysis was performed on samples prepared at approximately 10 mg/mL in 100% tetrahydrofuran (THF). Approximately 100 mg of sample was weighed into a tared scintillation vial and 10 mL of THF was added. The samples were heated on an incubator shaker at 45 °C for 3 h to assure dissolution. While the fibers were fully dissolved, the pellets had small amounts of un-dissolved residuals. Samples were filtered through a 0.45 µm syringe filters into Waters Alliance 2,695 HPLC system (Milford, MA) vials for analysis at a flow rate of 0.9 mL/min. Polystyrene standards from a molecular weight of 500 to 400 K were used as a calibration curve. Sample chromatograms were then analyzed and the peaks were compared against the polystyrene calibration curves.

Gas Chromatography–Mass Spectrometry (GC–MS) Analysis

Five samples were tested- PLA pellets, DEET, Pyrethrum, PLA fibers with 5% DEET and PLA fibers with 5% Pyrethrum.

250 mg of sample was weighed into 15 mL glass tubes with PTFE lined caps. About 10 mL of chloroform is added to make 25 mg/mL final volume and the sample was vortexed for 20 min. The sample was then sonicated for 10 min in water bath and vortexed again for a minute. 0.2 mL of the homogenized sample was diluted into 1.3 mL of hexane in microcentrifuge tubes. The sample was vortexed for 10 min and centrifuged for 7 min at max speed to separate any insoluble particles from the liquid fraction. 0.75 mL of upper hexane layer was transferred to GC vials. The hexane extracts were subjected to gas chromatography–mass spectrometry (GC–MS) on a 7890C gas chromatograph in tandem with a 5975C MSD. The GC oven program began with at 60 °C that was held to 0.5 min and was then ramped at 12.5 °C/min to 320 °C which was held for 3 min. The mass scan range was set at 40–800 m/z. The separation column was an HP5MSI (30 m long, 0.250 mm ID, 0.25 µm film thickness). The mass spectrometer operated under standard conditions with a 230 °C ion source. Analyte identification was conducted using Agilent ChemStation and AMDIS software using GC–MS NIST17 and Wiley 11 GC–MS spectral libraries. Pyrethrum identifications were also supported by previous results [18].

Mosquitoes

Yellow fever mosquitoes (*Aedes aegypti*) were obtained from an established colony in the Medical Entomology Laboratory in the Department of Entomology at Iowa State University, Ames, Iowa. Mosquito rearing was performed by established protocols that are maintained by the Medical Entomology Laboratory. In short, mosquitoes were maintained in colony cages at 27 °C, 80% relative humidity, and on a 16:8 h light: dark photoperiod environment (ideal for rearing). Mosquitoes were blood fed once every week and eggs were collected. These eggs were hatched into larval pans and TetraMin Flakes Fish Food (Tetra Blacksburg, VA) were provided as necessary to maintain larvae. After approximately 7–10 days, pupae were collected and separated by sex, based on the large size dimorphism between male and female pupae (female pupae are larger). The female pupae used for this bioassays were collected and separated into groups of 50 and placed into 1-pint soup cups.

Repellency bioassays were performed with adult female mosquitoes that were 5–7 days post-emergent. After emergence and prior to testing, adult mosquitoes were supplied with a piece of cotton that was soaked in a 10% sucrose solution *ad libitum* as their food; the mosquitoes tested did not receive a blood meal. Prior to testing, the mosquitoes, were held at 27 °C, 80% relative humidity, and on a 16:8 h light: dark photoperiod.

Contact Irritancy Assay

A slightly modified contact irritancy assay protocol outlined by Grieco et al. (as shown in Fig. 1) was used for assessing repellency of the various DEET, Pyrethrum-treated and control untreated fabrics [19]. Natural pyrethrum-treated fabric mats and one DEET-treated fabric (11.5 cm × 8 cm) were cut to coat the inside of the contact irritancy chamber (Fig. 2). Three types of fabrics were draped around the interior of the exposure chamber for the 5% pyrethrum (sprayed) PLA fabric (control) and the 5% pyrethrum (extruded) PLA. This allowed the evaluation of the irritancy of the treated fabric toward adult, female mosquitoes. For fabrics that cause a higher level of contact irritancy, more mosquitoes migrate

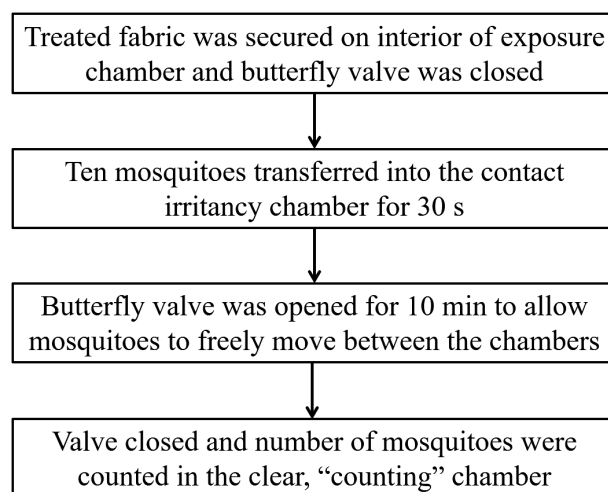


FIG. 1. Modified contact irritancy assay (CIA) protocol.

into the untreated, clear, “counting” chamber. The number of mosquitoes knocked down (defined as any mosquito that (i) cannot stand, (ii) cannot fly in a coordinated manner, (iii) lies on its back, moving but unable to take off (iv) can stand and take off briefly but falls down immediately [20]) in both the exposure chamber and the clear counting chamber were also recorded as a metric of repellency and insecticidal efficacy. Six replicates were completed for each treatment. Control treatments of untreated fabrics were tested in parallel with each treated types of fabric. Figure 2 is a schematic representing the experimental device used to evaluate the efficacy of these compounds to illicit contact irritancy.

RESULTS

TGA Analysis

The thermal stability results are shown in Figs. 3 and 4 represented as weight loss curves as functions of temperature for

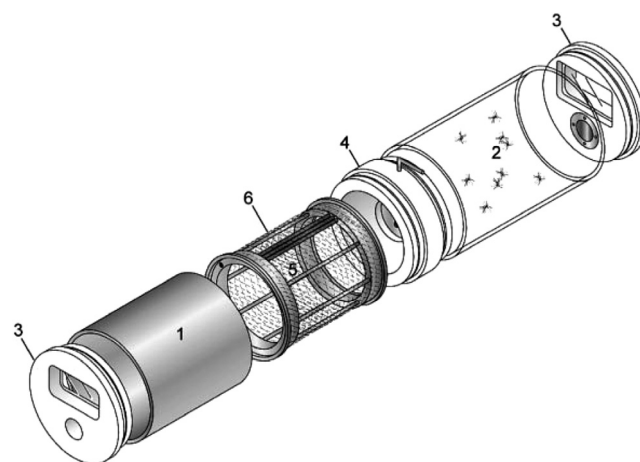


FIG. 2. Experimental set-up for the contact irritancy chamber as described by Grieco et al. [19]. This device is separated into two primary regions, an exposure chamber and a viewing chamber. Sections of the device are labeled as follows: 1: Outer metal housing for the exposure chamber, 2: Clear viewing chamber, 3: Outer viewing window, 4: Butterfly valve, 5: Interior of exposure chamber (where treated fabric is draped), 6: Interior metal housing for the exposure chamber.

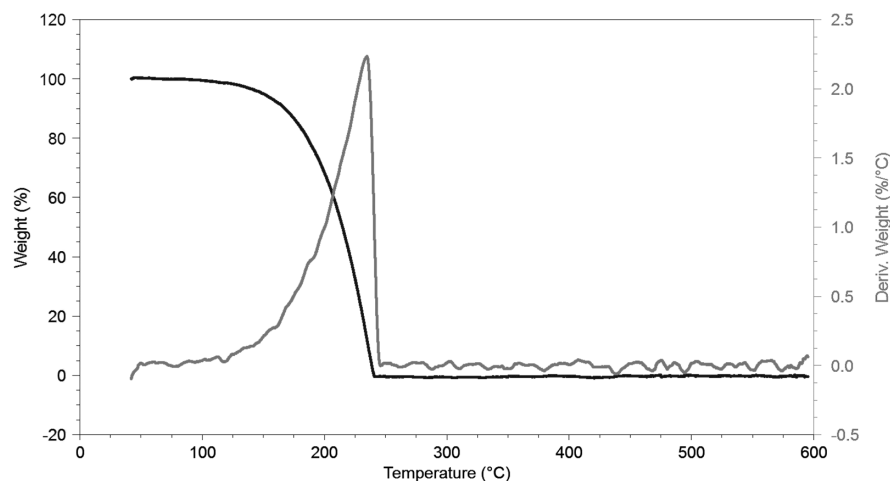


FIG. 3. TGA and weight derivative curves of DEET.

DEET (Fig. 3) and pyrethrum (Fig. 4). As can be seen in the figure, the pyrethrum extract started to lose 10% of its weight at 120 °C, while DEET started to lose 10% of its weight at 180 °C. While DEET has relatively thermal stability, it is seen that pyrethrum is sufficiently thermally stable to be melt mixed with PLA that can be extruded at 150 °C.

Tensile Tests

As seen in Fig. 5, the tenacities of the samples were generally proportional to the number of drawings (#D) for all samples tested except for the 7% DEET concentrations. In more detail, no significant difference in tenacity are seen between 1-drawing and 2-drawing fiber at 7% DEET. When comparing the tenacities of the extruded DEET at various concentrations (0, 2, 4, 7%), all of the tenacities are higher compared with the NatureWorks (NW) control samples. The fiber with the highest tenacity 852 (mN/tex) is the sample extruded with 2% DEET and two drawings while the samples of NW, has the lowest tenacity of 27 (mN/tex).

As seen in Fig. 6, the stress strain curves for the 2nd drawn samples showed that higher concentrations of DEET in the PLA fibers decreases extension (%). Additionally, low amounts of

DEET concentrations (2%) have minimal effect on the tensile properties of PLA fibers while high concentrations of DEET (4 and 7%) reduced both the extension and the maximum tensile stress. It is believed that because of the plasticity and strength both decreased with higher levels of DEET, the DEET depolymerized PLA and did not simply act as a plasticizer (solvent).

Gel Permeation Chromatography Analysis

Because there have been antidotal reports the DEET can either act as a solvent or even depolymerize polyesters, such as PLA, gel permeation chromatography (GPC) analysis was conducted to characterize the molecular weight distribution of the polymer samples when extruded with DEET samples [21]. The GPC analysis of the five different PLA samples measured the number average of the molecular weight (M_n) and the weight average of the molecular weight (M_w) and the polydispersity (PDI). Table 1, GPC analysis against 500–400 k M_w polystyrene standards, details that both the M_w and the M_n is inversely proportional to the amount of DEET, which is in agreement with the observation of strength that DEET promotes depolymerization. The PLA fiber with 7% DEET concentration, it is seen that the M_w and M_n is

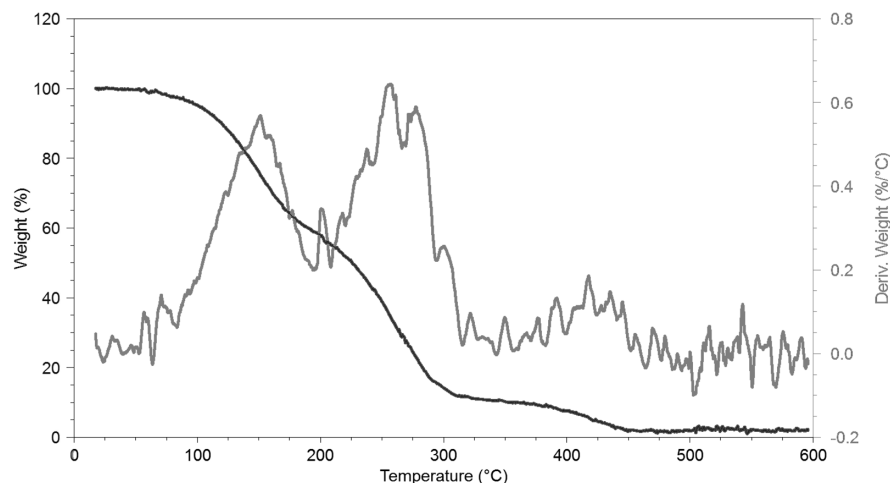


FIG. 4. TGA and weight derivative curves of pyrethrum.

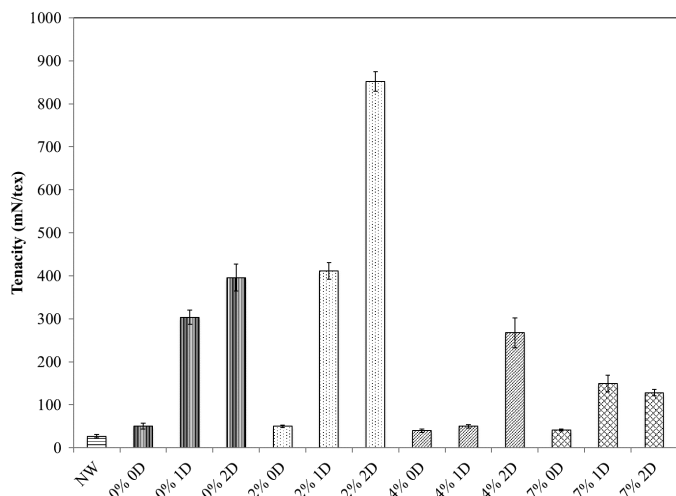


FIG. 5. Tenacities (mN/tex) compared with sample type. Percent values represent concentration of DEET in sample; D values correspond to the number of drawings preformed.

decreased by a factor of 2 compared with the PLA pellets with no DEET.

The effect of depolymerization of PLA because of the increase in the DEET concentration can also be seen in the GPC graph in Fig. 7 below. The M_w is determined based on length of retention time and is independent of overall height of peak. Height of peak is a function of the amount of polymer dissolved. The shift of peaks to the right indicates reduction in molecular weight. Figure 7 shows that the peaks move to the right as the DEET concentration increases. The PLA fiber compounded with 7% DEET has the peak at the furthest right, indicating the molecules are lower compared with the balance of the samples.

Gas Chromatography–Mass Spectrometry Analysis

Gas chromatography–mass spectrometry (GC–MS) analysis of the extract from pyrethrum extract (positive control), neat PLA pellets (negative control) and PLA extruded with pyrethrum indicates the generation of a variety of peaks from pyrethrum is

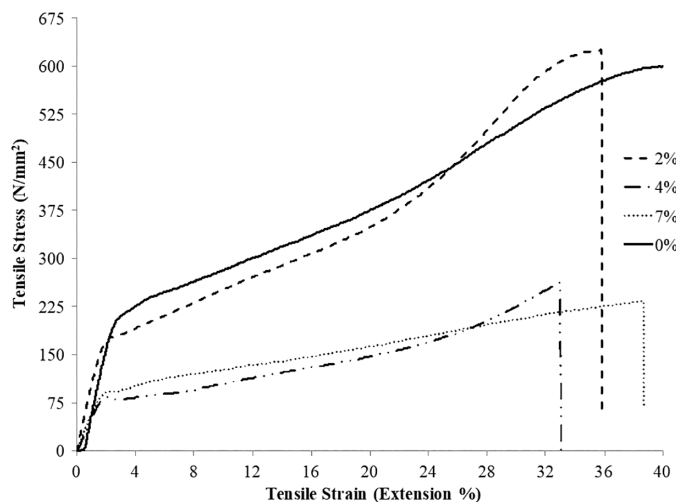


FIG. 6. Samples of graphs of tensile stress against tensile strain for extruded samples after 2nd draw.

TABLE 1. GPC analysis against 500–400 k M_w polystyrene standards.

Samples	M_w	M_n	Polydispersity
Pellet	160,667	100,950	1.59
0% DEET	104,200	60,522	1.72
2% DEET	99,167	57,808	1.72
4% DEET	95,876	54,899	1.75
7% DEET	79,850	46,608	1.71

shown in Fig. 8. Each peak represents an individual compound that was separated from a sample mixture. The six main chemical constituents and their retention times were showed in the following Table 2. In Fig. 9, the peaks from GC–MS analysis of the extract from DEET (positive control), neat PLA pellets (negative control) and PLA extruded with DEET is reported. The major peak for DEET compound appears at 10.5 min for both DEET and PLA extruded with DEET samples reinforcing the thermal stabilization of DEET for extrusion as found in the TGA analysis.

10-Minute Exposure Interval Testing

Mosquitoes responded well in each of the experimental intervals and escape frequencies for each type of fabric tested were normally distributed and were consistent. As seen in Fig. 10, the untreated PLA fabric produced a relatively low escape rate compared with the other treated fabrics. No outliers in mosquito response were observed and the standard deviation for the escape rate were relatively low ($\pm$ error bars in Fig. 10). The treatment effects (i.e., type of fabric screened) were statistically significant in the one-way ANOVA model used to assess statistical significance, with a F value of 62.1 with 3° of freedom ($p < 0.001$). This allowed for further comparisons between treatments using a post-hoc Bonferroni-corrected t -test. After a 10-min exposure in the control, untreated PLA fabric, 10% $\pm$ 3.6% of mosquitoes migrated (escaped) into the clear viewing chamber (Fig. 10). In addition, no knockdown (immobilized mosquitoes) in the viewing or exposure chambers was observed with exposure to the untreated fabric. Among the treated PLA fabrics, mosquito escape frequency into the clear viewing chamber were significantly higher compared with the untreated controls of each fabric. The escape frequencies for each of the treated fabrics ranged from 33.3% $\pm$ 7.14% to 98.3% $\pm$ 1.7%. The 5% DEET-treated PLA fabric promoted the lowest escape response with an escape frequency of 33.3% $\pm$ 7.1%. The extruded natural pyrethrum-treated PLA fabric exhibited an escape frequency of 80% $\pm$ 6.3%. In addition, the spray coated pyrethrum PLA fabric caused an escape frequency of 98.3% $\pm$ 1.7%. All treated fabrics caused repellency that were significant compared with the control. The DEET-treated fabric was statistically less repellent compared with both pyrethrum treated fabrics which were statistically equivalent in their ability to promote relative escape.

Significant knockdown was observed in mosquitoes exposed to sprayed natural pyrethrum-treated fabric (Table 3). These effects were statistically significant and reduced the escape frequency during the 10-min exposure time interval as the mosquitoes were demobilized and not able to escape. The sprayed natural pyrethrum-treated fabric produced higher knockdown rates in the viewing chamber compared with the control untreated fabric or any of the other treated fabrics (Bonferroni post-hoc t -test, $\alpha = 0.05$). The relative amount of the knockdown in the viewing chamber was 98.3% $\pm$ 1.3%. This indicates that the sprayed

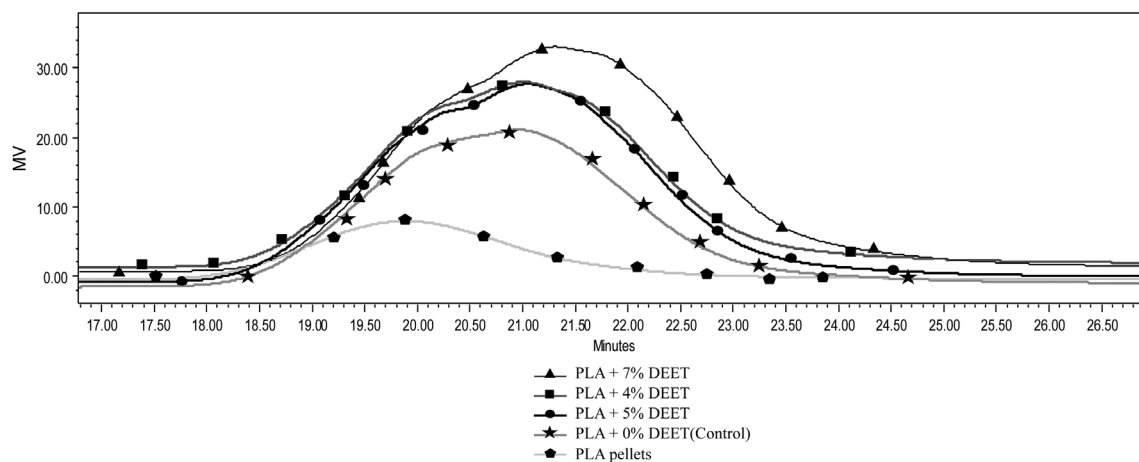


FIG. 7. Typical GPC chromatograms of PLA samples with various DEET concentration.

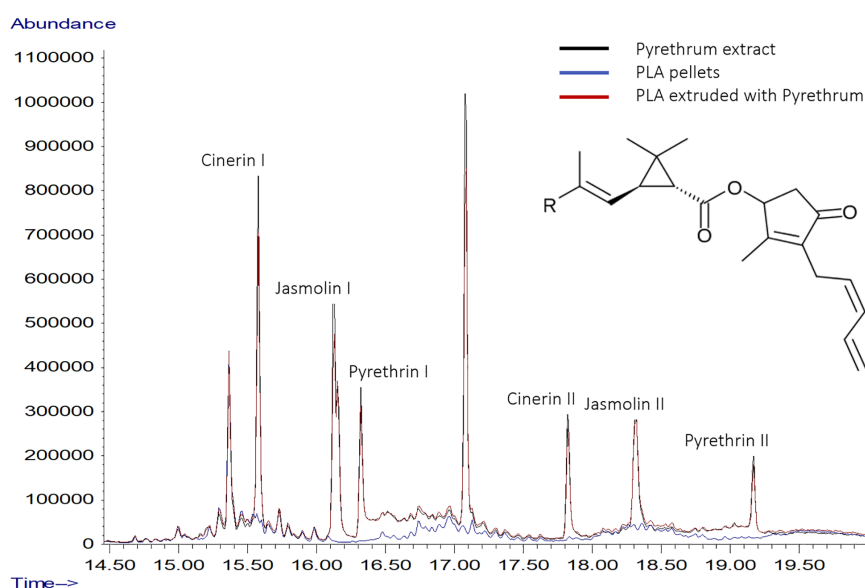


FIG. 8. Identification of pyrethrum extract with GC-MS.

natural pyrethrum-treated fabric was significantly more repellent compared with the other treated fabrics.

DISCUSSION

The study on the effect of compounding DEET with PLA showed that DEET, in increasing concentration causes higher depolymerization of PLA. This depolymerization was seen in a reduction of both the number average molecular weight (M_n) and the weight average molecular weight (M_w). Both the M_n and M_w

TABLE 2. Retention time of constituents in pyrethrum extract.

Chemical compounds	Retention time (min)
Cinerin I	15.6
Jasmolin I	16.1
Pyrethrin I	16.3
Cinerin II	17.8
Jasmolin II	18.3
Pyrethrin II	19.2

are critical for promoting tensile strength, impact strength, hardness, and reduction of brittleness of PLA and it was seen that with the reduced molecular weight there was a correlating loss of mechanical properties in the PLA.

All six pesticidal active compounds of pyrethrins are all present in the GC-MS in accordance with the study done by Cai et al. who investigated the main chemical compounds in pyrethrum extract by supercritical fluid extraction [22]. It is also important to note that the peaks from pure pyrethrum extract (positive control) matched perfectly with the peaks from PLA extruded with pyrethrum. This result suggests that no obvious degradation occurs to the pyrethrum during the extrusion process and pyrethrum is thermally stable to be compounded with PLA at 160°C even though the TGA results show that pyrethrum, on its own starts degrading at 120°C. In this case, the thermal stabilization of pyrethrum could be result of the polymer shielding the chemical compounds.

The goal of this study was to characterize the overall repellency of PLA fabrics when different insect repellents/insecticides were incorporated into them. All treated fabrics (extruded and spray coated), were repellent and caused higher escape frequencies compared with

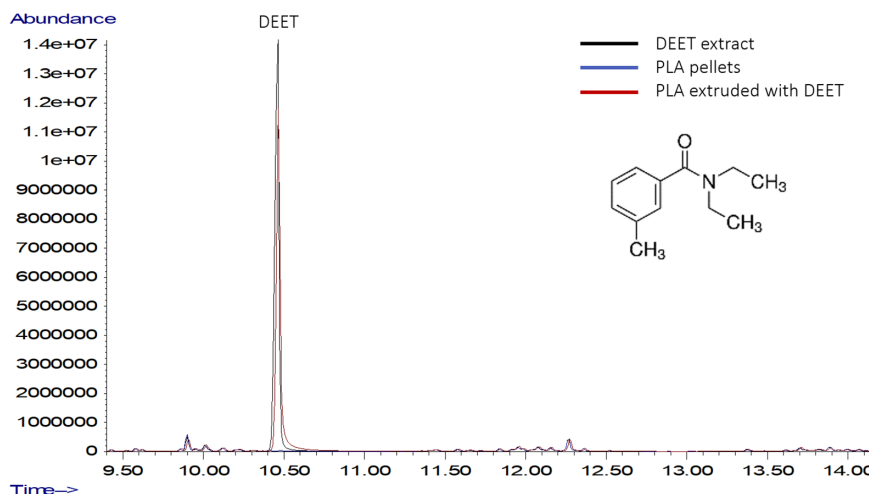


FIG. 9. Identification of DEET with GC-MS.

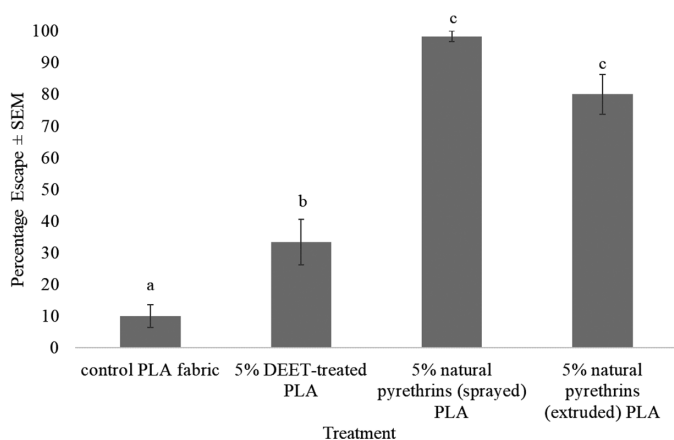


FIG. 10. Contact irritancy of various untreated and repellent/insecticide-treated fabrics for adult female *Aedes aegypti* after a 10-min exposure interval.

TABLE 3. Knockdown caused by various untreated and treated fabrics after a 10-min exposure interval.

Treated fabric	Knockdown in viewing chamber	Knockdown in exposure chamber
Control PLA	0 ± 0 ^a	1.7 ± 1.7 ^a
5% DEET PLA	0 ± 0 ^a	1.7 ± 1.7 ^a
5% pyrethrum (sprayed) PLA	98.3 ± 1.7 ^b	1.7 ± 1.7 ^a
5% pyrethrum (extruded) PLA	0 ± 0 ^a	1.7 ± 1.7 ^a

Significant knockdown may indicate that mosquitoes may not be able to freely move between chambers. This may confound percentage escape. The 5% natural pyrethrum (sprayed) PLA caused significant knockdown in the viewing chamber.

^{a,b}Means with the same letter within a chamber do not significantly differ.

the control untreated fabric. This effect was significant for each of the corresponding insecticide-treated/repellent-treated fabric compared with the control untreated fabric pairings. In the 10-min mosquito exposure interval assay, significant knockdown was observed for one of the treated fabrics; the PLA with pyrethrum. Significant knockdown was observed in the sprayed natural pyrethrum-treated fabric, with approximately 100% of mosquitoes experiencing immobilization after escaping into the viewing chamber. The primary signs of

exposure toxicity included knockdown in the viewing chamber with very little knockdown observed in the exposure chamber. Knockdown in the viewing chamber can be indicative of latent toxicity of the repellent after the mosquito has escaped from the exposure chamber into the repellency chamber (viewing chamber). This is common for repellents/insecticides that produce a rapid excitatory response in the mosquitoes after coming in contact with the treated-surface, followed by a toxic effect after the mosquito is no longer exposed to the repellent (such as in the viewing chamber). Pyrethroids and natural pyrethrins are known excito-repellents, at sufficiently repellent levels, and this behavior is documented in the bioassay system used in this study [23]. Although the frequency of escape in the 10-min exposure interval assay were statistically equivalent for the natural pyrethrum-treated fabrics, significant knockdown in the sprayed natural pyrethrum-treated fabric was noted.

It was also indicated that there was no significant thermal degradation of insecticide during extrusion as it remained a relatively active replant after extrusion. However, it is possible that the sprayed natural pyrethrum-treated fabric was more repellent compared with the extruded natural pyrethrum-treated fabric because of limited denaturing/degradation during thermal extrusion.

CONCLUSION

In conclusion, addition of DEET in making PLA fibers causes depolymerization and corresponding reduction in M_w and M_n and mechanical properties. All treated fabrics were significantly repellent compared with the corresponding untreated control PLA fabric. While significant escape frequency was observed in the 10-min exposure interval assay, the relatively high knockdown in the sprayed natural pyrethrum was seen, however co-blended pyrethrum and PLA had similar performance in terms of mosquito repellency. Overall, all treated fabrics were significantly more repellent than the untreated control PLA fabric but natural pyrethrum-treated fabrics (both sprayed and extruded) exhibited higher efficacy than DEET (synthetic) in repelling mosquitoes.

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