



Article

# Investigating the Effectiveness of Novel Repellent Labels Produced from Invasive Plant Species

Klemen Možina \* , Zala Mavrič and Urška Vrabič-Brodnjak 

Department of Textiles, Graphic Arts and Design, Faculty of Natural Sciences and Engineering, University of Ljubljana, Snežniška 5, 1000 Ljubljana, Slovenia; zala.mavric@gmail.com (Z.M.); urska.vrabic@ntf.uni-lj.si (U.V.-B.)

\* Correspondence: klemen.mozina@ntf.uni-lj.si; Tel.: +386-1-200-32-99

**Abstract:** Although N,N-diethyl-3-methylbenzamide (DEET) remains the most effective repellent against mosquitoes and ticks, concerns about skin irritation, rashes, and neurological problems in children have driven the search for natural alternatives. The aim of this research was to develop, manufacture, and test prototype stickers derived from invasive plant species in Europe. These labels contained a coating with encapsulated repellents made from essential oils to protect against mosquito bites and similar blood-sucking insects. Six samples of invasive plant species in Europe such as Japanese knotweed (*Fallopia japonica*), goldenrod (*Solidago gigantea*), and black locust (*Robinia pseudoacacia*) were coated with two essential oil mixtures (of geranium, lavender, and eucalyptus) and were encapsulated on solid carriers for prolonged evaporation. Analysis of the structural properties (weight, thickness, density, and specific volume) were carried out on the coated label samples. Analysis of surface properties (roughness and porosity), capillary absorption, and a comparison of time and evaporation of essential oils were also carried out. Scanning electron microscopy was performed on the samples and the solid carrier with different mixtures of essential oils. The Japanese knotweed sample, coated with a blend of geranium, lavender, and eucalyptus essential oils, showed the highest efficacy and stability.

**Keywords:** essential oils; encapsulation; invasive plant species; label materials; natural insecticides



**Citation:** Možina, K.; Mavrič, Z.; Vrabič-Brodnjak, U. Investigating the Effectiveness of Novel Repellent Labels Produced from Invasive Plant Species. *Coatings* **2024**, *14*, 642. <https://doi.org/10.3390/coatings14050642>

Academic Editor: Alina Vladescu

Received: 30 April 2024

Revised: 15 May 2024

Accepted: 17 May 2024

Published: 19 May 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Label stickers in which the essential oils of various fragrances are bound to porous carriers in the coating layer improve conventional label stickers and add a new function to them, while, at the same time, representing a new product. Such label stickers would be used for functional or protective purposes, such as preventing unwanted odours in food, as product odour samples on sales packaging, as repellents, and to provide antimicrobial or fire protection. Repellent labels become effective when they are affected by physical forces from the outside or when a coating is applied to them that contains porous carriers with a repellent substance that repels mosquitoes.

In the fight against mosquitoes, there are many repellent products that come from graphic materials and application methods, including wristbands, tattoos, and stickers. Today's mosquito repellent labels are made from rubber, ammonium benzoate, zinc oxide, and synthetic adhesive [1–4]. The paper industry has started to use invasive alien plants to produce alternative forms of labels, as they are a growing environmental problem and have a significant impact on human health, directly threatening and affecting habitat structure, soil abiotic properties, and geomorphological processes, thereby significantly altering the chemical composition of the soil. Researchers working on alternative sources of cellulose fibres have found that invasive alien plants can be useful for the production of paper and labels [5–10].

The impact of invasive, non-native plants is the most conspicuous of all, as they form dense stands that radically change the appearance of the landscape in a short time [11].

Other plants cannot thrive due to the lack of light, as the dense growth causes shading of the lower layers. The habitat of native species shrinks, as some invasive non-native plants even secrete chemical substances into the soil. The dense growth of invasive plants can be found in open areas, forest clearings, along roads or railway lines and along watercourses [11,12]. They make it difficult to rejuvenate the tree species and, thus, forest regeneration, so that the seeds of the tree species cannot thrive in the shade of the non-native plants. In the coming decades, invasive alien species will have an even greater impact on the appearance of our forests. Due to global and local impacts, there is an increasing need for action, early detection, awareness, and rapid response, which is crucial to prevent the further spread of invasive alien species [13,14].

In recent years, plant-based insecticides have become increasingly popular as an alternative to synthetic chemical pesticides, as they are said to pose a lower risk to the environment and human health. N,N-diethyl-3-methylbenzamide (DEET) is the most commonly available repellent, especially against mosquitoes and ticks [15,16]. However, research has reported cases of skin irritation, rashes, and some cases of neurological problems in children, following the use of DEET. For this reason, consumer interest in natural, alternative repellents is growing [17]. Chemical pesticides help to repel insects by confusing their sense of smell. The mosquito is first attracted to the carbon dioxide we exhale, and then, sensing the lactic acid on our skin, it targets a specific spot. If these odours are masked by another odour, it misses its target and moves on [18]. Normally, insect repellents work by forming a vapour barrier that prevents arthropods from coming into contact with the skin [19]. Botanical repellents contain essential oils (EOs), which are complex mixtures of volatile compounds isolated from a variety of plants. These properties repel a variety of insects, with certain compounds being the basis for commercial repellents [20]. Most plants contain compounds that they use in defence against attacks by herbivorous insects [21]. These chemicals can be divided into several categories, including repellents, toxins, and growth regulators. These examples can be categorised into five main chemical categories [22], as follows:

- Nitrogen compounds (mainly alkaloids),
- Terpenoids,
- Phenols,
- Proteinase inhibitors, and
- Growth regulators.

The primary function of these compounds is defence against herbivorous insects, but many are also effective against mosquitoes and other blood-sucking insects [23,24]. Studies [22,23] have even shown that linalool has the same effect on mosquitoes as DEET. According to the study of Mishra et al., linalool, a monoterpene compound, is often used as the main component of the essential oils of various aromatic species [23]. In fact, linalool is often used as an active ingredient in common insect repellents [24]. In a study from Ogilvie-Battersby et al., geraniol, the active component of geranium essential oil, was found to be even more effective than other repellents [25]. Longer-lasting retention was achieved through the encapsulation of geraniol compared to similar systems, allowing its use as an insect-repellent coating or its incorporation into various carrier solutions for application as area treatments.

Some monoterpenes such as alpha-pinene, eucalyptol, eugenol, limonene, terpinolene, citronellol, citronellal, camphor, and thymol are common components of many essential oils that have a mosquito-repellent effect [26]. EOs are a natural alternative to conventional insect repellents. Each oil consists of different active ingredients, so it is not possible to use all oils to repel the same pests. Combinations of two or three EOs are the most effective [20,26–29]. Despite their effectiveness, EOs are only effective against mosquitoes during their evaporation period, which is relatively short. To ensure a longer release, the essential oil can be embedded in porous carriers that slow down the evaporation of the repellent and, thus, prolong the repellent effect [6,17,30,31]. From the study by Chattopadhyay et al., polymer patches based on essential oils were found to be an environmentally friendly,

acceptable, and safe alternative to synthetic mosquito repellents and offered comparable protection against *Ae. (S) albopictus* mosquitoes [32].

This research aimed to pioneer the development of labels derived from invasive plant species in Europe, with coatings of essential oils firmly bound to porous carriers to protect them from mosquitoes and other blood-sucking insects. This study was the first time that paper from invasive plant species was used as a base material for repellent labels. In addition, the research focussed on identifying the most effective combination of repellent labels with paper from invasive plant species and specific essential oils. Comprehensive evaluations were conducted to assess the release and repellent effect of each combination of essential oils and to investigate the compatibility of the coating with different invasive plant species substrates.

## 2. Materials and Methods

### 2.1. Materials

For the production of labels, different materials have been used. Labels were produced from base paper from invasive plant species (Japanese knotweed (*Fallopia japonica*), goldenrod (*Solidago gigantea*), and black locust (*Robinia pseudoacacia*). Coating solutions were made from essential oil, transparent base material—carrier for a prolonged release of essential oils—and base coating solution.

#### (a) Paper from invasive plant species

For the production of repellent labels, three different types of paper from invasive plant species that differ in their raw material composition were used. Three paper samples from different invasive alien plants with a grammage of 90 g/m<sup>2</sup> and a thickness of 0.5 mm were tested, namely Japanese knotweed (*Fallopia japonica*), goldenrod (*Solidago gigantea*), and black locust (*Robinia pseudoacacia*) (Pulp and Paper Institute, Ljubljana, Slovenia).

#### (b) Essential oils

Six different essential oils that are the most effective in the fight against mosquitoes were used (Table 1). Two combinations of essential oils (EOs), containing three different oils that complement each other, were included. The two blends were created based on different levels of each essential oil in [%]. The manufacturer of all six essential oils is Favn, d.o.o., Grosuplje, Slovenia.

**Table 1.** Used essential oils and their main components.

Type of EO	Main Components					
BIO Citronella	32.2% citronellal	19.5% geraniol	8.5% geranyl acetate	8.2% citronellol	5.3% citronellyl acetate	Other < 5%
Lemongrass	41.8% geranial	31.8% neral	5.5% geraniol		Other < 5%	
Peppermint	36.9% menthol	26% menthone	6.8% cineole	5% menthyl acetate		Other < 5%
Geranium	32.3% citronellol	13.4% geraniol	7.09% citronellyl formate	6.36% isomenthone		Other < 5%
Lavender	42.7% linalool	36.9% linayl acetate			Other < 5%	
Eucalyptus	83.2% eucalyptol			Other < 5%		

The EO mixture was prepared as follows. The first mixture (hereafter, M1) contained essential oils of citronella, lemongrass, and peppermint, while the second mixture (M2)

contained essential oils of geranium, lavender, and eucalyptus. Table 2 shows the content of each essential oil in each blend.

**Table 2.** EO mixtures and the proportions of each EO.

EO Mixture	Proportion [%]					
	Citronella	Lemongrass	Peppermint	Geranium	Lavender	Eucalyptus
M1	60	30	10	/	/	/
M2	/	/	/	45	45	10

(c) Transparent carriers for EOs

Transparent carriers were used for the prolonged release of essential oils from the labels. The following porous material was used due to its ability to absorb and vaporise liquids over a longer period: SYLOID<sup>®</sup>XDP 3100 (W. R. Grace & Co.-Conn., Columbia, MD, USA).

(d) Coatings

The invasive plant species paper samples were coated with a coating containing 15% transparent carriers, mixed with an 80% mixture of essential oils. A special coating on top of the EO and porous carrier was used from Papirnica Vevče (Ljubljana, Slovenia), which is shown in Table 3.

**Table 3.** Basic properties of the coating.

Coating Properties	
Brand name	Niklaselect
Pre-coating	Filmpress [6 g/m <sup>2</sup> ]
Coating	Blade coater [12 g/m <sup>2</sup> ]
Dry matter	Filmpress 61% in Blade Coater 68%
Viscosity (b100)	PP 350 mPa.s in TP 900–1000 mPa.s
Purpose of the coating	Label paper

## 2.2. Methods

The preparation of the EO mixture was initiated and the first blend (M1) consisted of the essential oils of citronella, lemongrass, and peppermint, whereas the second blend (M2) comprised essential oils of geranium, lavender, and eucalyptus.

The dispersion of the porous carrier and essential oils was subsequently prepared. Porous carriers (SYLOID<sup>®</sup> XDP 3100) were mixed with mixture M1 and M2. Filled porous carriers, constituting 80%, were prepared in the following manner:

- a total of 6 g of the porous carrier, SYLOID<sup>®</sup> XDP 3100, was added to the beaker,
- M1 and M2 essential oils were prepared and 4.8 g of the essential oil mixture was added to the beaker with the porous carrier,
- the contents of the beaker were mixed.

The mixed contents were added to the industrially prepared coating mixture of Papirnica Vevče d.d. (Slovenia), incorporating the added porous carriers M1 and M2, comprising 15% of the mass of the coating mixture.

### 2.2.1. Coating Procedure

Coating was carried out at a temperature of 23 °C and a relative humidity of 48%. The samples were manually coated using the K Hand Coater, brand RKPrint (RK PrintCoat Instruments Ltd., Royston, UK). The paper samples of invasive plant species in A4 format were coated with the coating mixture in a single pass using a number 1 coating stick, resulting in a coating thickness of 6 µm.

The coated samples were subsequently dried at room temperature (23 °C) and in air for 5 h and were then utilised for further analysis. Table 4 presents the coated samples, the paper base, the type of transparent carrier, and the mixture of essential oils used for each sample.

**Table 4.** Coated samples, type of the base material, and used blend of EOs.

Sample	Type of Paper	Type of Transparent Carrier	EO Blend
S1	Black locust	SYLOID <sup>®</sup> XDP 3100	M1
S2	Japanese knotweed	SYLOID <sup>®</sup> XDP 3100	M1
S3	Goldenrod	SYLOID <sup>®</sup> XDP 3100	M1
S4	Black locust	SYLOID <sup>®</sup> XDP 3100	M2
S5	Japanese knotweed	SYLOID <sup>®</sup> XDP 3100	M2
S6	Goldenrod	SYLOID <sup>®</sup> XDP 3100	M2

### 2.2.2. Thermogravimetric Analysis (TGA)

The weight loss of a transparent carrier sample with 80% pore filling with essential oils was measured using TGA. A sample heating program was employed, with heating from 30 to 95 °C at a rate of 20 °K/min, followed by an isothermal phase of 30 min and reheating from 95 to 250 °C at 20 °K/min. The measurement was conducted in a nitrogen atmosphere with a flow rate of 50 mL/min. The test was replicated for the completed labels and a comparison of the time and evaporation rate was made for the individual mixtures.

### 2.2.3. Analysis of the Release of the Repellent at 0% Humidity

A portion of the prepared mixture of essential oils and transparent carriers was placed in a desiccator with 0% moisture content. The samples were subjected to drying for 24 h and the mass was monitored at specified time intervals (15 and 30 min and 1, 3, 6, and 24 h). At the designated times, the sample was taken out of the desiccator and its mass was ascertained. In this manner, the profile of essential oil evaporation from the carriers was determined.

### 2.2.4. Analysis of the Material Properties

The material properties such as grammage (according to standard ISO 536:2019), thickness (according to standard ISO 534:2011, <https://www.iso.org/standard/53060.html>, 15 May 2024), density (according to standard ISO 534:2011, <https://www.iso.org/standard/53060.html>, 15 May 2024), specific volume (according to standard ISO 534:2011, <https://www.iso.org/standard/53060.html>, 15 May 2024), roughness and porosity—Bendtsen method (according to standard ISO 8791-2:2013, <https://www.iso.org/standard/51265.html>, 15 May 2024), Klemm capillary rise method (according to standard ISO 8787, <https://www.iso.org/standard/16211.html>, 15 May 2024), and surface characterisation, using a scanning electron microscope (SEM) Jeol JSM 5610 (JEOL, Tokyo, Japan) were analysed.

## 3. Results and Discussion

Table 5 shows the raw material composition of the tested samples. The values for the cellulose fibre content of non-indigenous plants, eucalyptus, and unbleached conifers are shown. The composition of the individual paper samples influenced the further tests and, consequently, the selection of the best combination in terms of mosquito defence.

**Table 5.** Composition of used papers from invasive plant species.

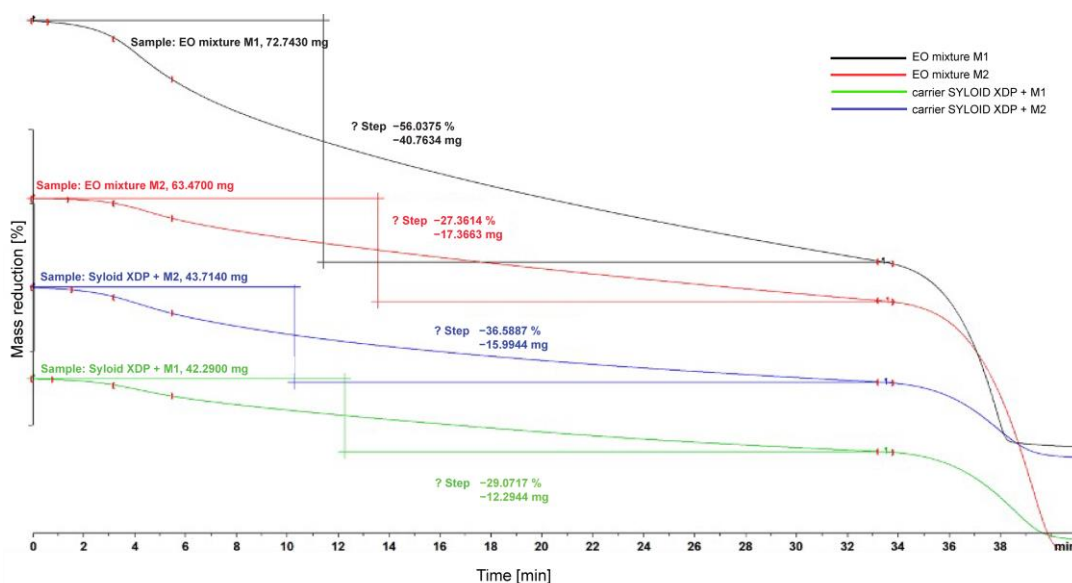
Sample	Composition [%]		
	Fibres of Invasive Plant Species	Eucalyptus	Unbleached Conifers
Japanese knotweed	35–40	36–38	26–28
Black locust	45	30	25
Goldenrod	52	24	24

Based on the measurements and calculations of the properties, the test methods have been divided into the following two groups:

- Release of essential oils bound to porous carriers
- Basic, surface, and structural properties of used materials.

*3.1. Release of Essential Oils Bound to Porous Carriers and Release of the Repellent at 0% Humidity*

The evaporation rate of the combinations of essential oils with TGA was measured and compared with the evaporation rate of essential oils on an 80% filled carrier—SYLOID® XDP 3100—under certain conditions. The difference between the tested samples is presented in Figure 1.



**Figure 1.** The sample mass reduction according to analysis time.

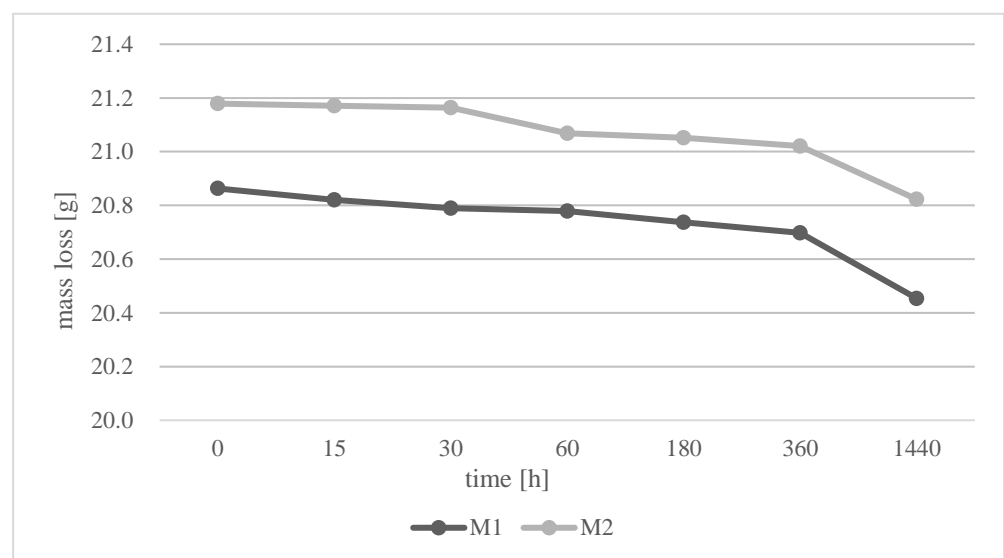
The greatest proportion of mass reduction was observed in mixture M2 (Figure 1), where a 56.04% decrease in the initial mass was noted throughout the test, while the decrease in mass was less pronounced in mixture M1, with only 27.36% of the initial mass evaporating. It can be concluded from the tests that, under the same conditions, certain essential oils (geranium, lavender, or eucalyptus) evaporate faster in M2 than in M1. Sample M1, composed of citronella, lemongrass, and peppermint essential oils, experienced an evaporation of 17.313 mg of the initial mass (63.470 mg) during the test, while M2 evaporated 40.801 mg of the initial mass (72.743 mg), signifying a 27% higher evaporation compared to M1. When testing the samples on an 80% filled SYLOID® XDP 3100 carrier, a decrease in the mass fraction of essential oils was observed. The mass fraction of M1 decreased by less than 1.75%, whereas the mass fraction of M2 decreased by 19.24%. These results lead to the conclusion that the M1 blend exhibits greater durability under

specific conditions. Additionally, the results indicate that utilising a solid carrier allows for a reduction in the evaporation rate by nearly 20%.

The release of the repellent mixture at 0% humidity over a period of 24 h is shown in Table 6. In the absence of humidity (0%), the repellent mixture was released more slowly than at the specified temperature tested using TGA. The release of the repellent increases with time (Figure 2).

**Table 6.** Results of the repellent release at 0% humidity from 0 to 1440 min (24 h).

EO Mixture/Time	Release of the Repellent at 0% Humidity [g]						
	0'	15'	30'	60'	180'	360'	1440'
M1	20.863	20.821	20.790	20.779	20.737	20.698	20.454
M2	21.179	21.171	21.164	21.069	21.052	21.012	20.823



**Figure 2.** Time course of mass loss during the release of the repellent in 24 h.

Over a period of 24 h, 2.0% of the repellent was released by M1, while 1.7% of the repellent was released by M2. It is inferred that the impact of the absence of moisture in the air on M1 is greater than that of M2, suggesting that M2 incorporates essential oils with a slower release rate than M1 in the absence of humidity. In contrast to the TGA tests, where temperature exerted a more pronounced influence on the repellent release in M2, the opposite effect is observed here.

### 3.2. Results of Material Analysis

The results of the grammage, thickness, specific volume, and density of the samples are presented in Table 7. The standards for the production of the analysed papers on the pilot paper machine of the Institute for Pulp and Paper (ICP) in Ljubljana, Slovenia were adhered to, in terms of the basis weight for all examined label sticker samples. The highest weight variations were observed in samples S2 and S4, exhibiting a coefficient of variation ranging between 4.8 and 5.5%. Following coating, the primary fibre samples of acacia paper S1 and S4 demonstrated the highest basis weight, ranging from 159 to 164 g/m<sup>2</sup>, with a coefficient of variation between 3.2 and 4.8%. Conversely, paper samples derived from the primary acacia fibre exhibited the lowest weight, ranging between 112 and 115 g/m<sup>2</sup>. The basis weight experienced an increase with coating, considering the base basis weight of the uncoated papers was 90 g/m<sup>2</sup>. This fulfils the fundamental objective of coating the paper, promoting greater uniformity, and consequently facilitating the easier evaporation of essential oils. The variation in thickness is increased with each of the refinement processes.

The greatest thickness was measured for samples S1 and S4, where the average thickness ranged between 0.315 and 0.318 mm, with a coefficient of variation of 2.6% for S1 and 4.3% for S4. The thinnest sample, S2, exhibited an average thickness of 0.161 mm, accompanied by a coefficient of variation of 5.6%. The thickness is primarily influenced by the base of the coated paper, with similarities observed in the values of the same base for S1 and S4, S2 and S5, as well as S3 and S6.

**Table 7.** Basic properties of paper samples (average values— $\bar{x}$ , standard deviation— $S_x$ , and coefficient of variation—CV).

Sample	Statistics	Grammage [g/m <sup>2</sup> ]	Thickness [mm]	Specific Volume [cm <sup>3</sup> /g]	Density [kg/m <sup>3</sup> ]
S1	$\bar{x}$	159.1	0.3	1.9	501
	$S_x$	5.0	7.5	0.1	17.0
	CV	3.18	2.68	3.40	3.48
S2	$\bar{x}$	112.5	0.2	1.4	700
	$S_x$	6.2	0.1	0.1	64.0
	CV	5.51	5.58	9.10	9.24
S3	$\bar{x}$	123.8	0.2	1.5	669
	$S_x$	2.8	0.1	0.1	226.0
	CV	2.33	3.48	4.76	33.74
S4	$\bar{x}$	164.9	0.3	1.9	525
	$S_x$	8.0	0.0	0.1	37.0
	CV	4.87	4.31	6.91	7.12
S5	$\bar{x}$	115.7	0.2	1.4	705
	$S_x$	2.3	0.1	0.1	16.0
	CV	2.06	1.50	2.35	2.37
S6	$\bar{x}$	125.9	0.2	1.5	671
	$S_x$	2.2	0.1	0.1	12.0
	CV	1.76	1.72	1.81	1.81

The value of the specific volume is decreased by coated papers in comparison to uncoated papers, as the reduction in the free volume in the material is influenced by them. The highest deviation of the specific volume is observed for sample S2, with 9.1%; for sample S4, the coefficient of variation is 6.9%; as well as sample S3, with 4.7%. An increased degree of inhomogeneity is indicated by these deviations, given that the coefficient of variation for the other samples (S1, S5, and S6) ranges between 1.8 and 3.4%. The effect of increasing the density of papers is achieved through finishing processes. Higher values for the density of the analysed samples are also anticipated, due to the refinement. The highest average value, 705 kg/m<sup>3</sup>, is observed in S5, while the lowest is found in S1, with a value of 500 kg/m<sup>3</sup>, which also possesses the highest average thickness of 0.318 mm. The most calculated constant density values are exhibited by samples S1, S5, and S6, with their coefficient of variation ranging between 1.82% and 3.48%. The highest deviation is observed in Sample S3, with a coefficient of variation of 33.75%.

The highest roughness values for coated and uncoated samples are samples S1 and S4 (on the A side), at 1101 and 1065 mL/min for coated samples and 2646 mL/min for the uncoated sample, as shown in Table 8. Samples S1 and S4 are based on black locust paper, with the highest basis weight values. The uneven basis weight distribution affects the roughness. The average roughness values for coated samples (S2, S3, S5, and S6 on the A side) are between 362 and 462 mL/min, while the values for uncoated samples vary between 1100 and 1096 mL/min. Based on these results, it can be concluded that the coating process enabled us to reduce the roughness of all samples analysed by more than 50%. Like the roughness, the air flow through the paper (porosity) was also reduced in the coated samples. The average values of the coated samples are between 41 mL/min (S2

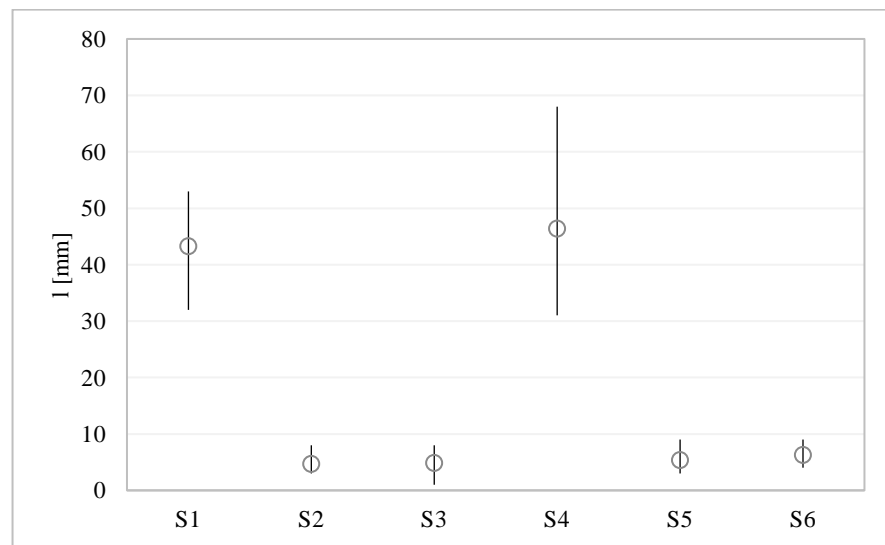


on the B side) and 262 mL/min (S1 on side A), while the values for uncoated samples are between 350 (S2 on side B) and 2350 mL/min (S1 on side A). As a result of the elaborate processes used to finish the paper, the air permeability through the material decreased to 94.6%, which means that, by reducing the porosity, we increased the release time of the essential oils from the coating itself.

**Table 8.** Results of roughness and porosity—Bendtsen method for coated and uncoated samples (average values— $\bar{x}$ , standard deviation— $S_x$ , and coefficient of variation—CV).

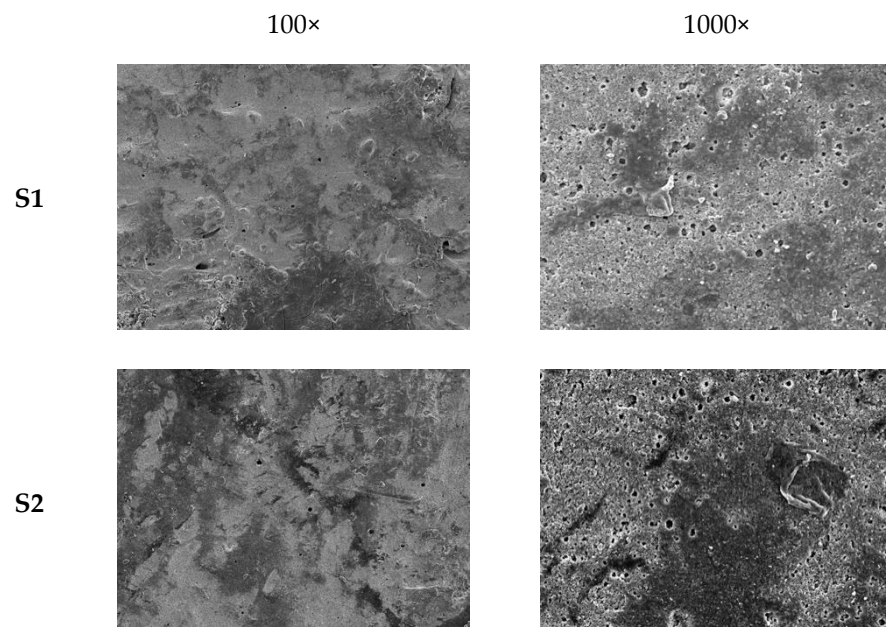
Coated Samples						Uncoated Samples					
		Roughness [mL/min]		Porosity [mL/min]				Roughness [mL/min]		Porosity [mL/min]	
		A Side	B Side	A Side	B Side			A Side	B Side	A Side	B Side
S1	$\bar{x}$	1102	2627	262	240	Japanese knotweed	$\bar{x}$	2646	2593	2350	2420
	$S_x$	107	183	50	63		$S_x$	124	221	235	271
	CV	9.73	6.98	19.19	26.35		CV	4.68	8.51	10.01	11.19
S2	$\bar{x}$	419	1137	47	41	Black locust	$\bar{x}$	1196	1297	318	318
	$S_x$	26	104	9	12		$S_x$	96	149	26	22
	CV	6.11	9.15	18.60	30.31		CV	8.05	11.46	8.10	6.92
S3	$\bar{x}$	362	808	84.4	80	Goldenrod	$\bar{x}$	940	997	1505.2	1480
	$S_x$	72	129	15	12		$S_x$	86	186	96	50
	CV	19.95	16.01	18.19	14.43		CV	9.18	18.66	6.41	3.36
S4	$\bar{x}$	1065	2559	225	242						
	$S_x$	107	207	30	27						
	CV	10.07	8.08	13.13	11.19						
S5	$\bar{x}$	459	983	53	48						
	$S_x$	45	125	6	10						
	CV	9.87	12.70	11.73	20.37						
S6	$\bar{x}$	463	729	86	80						
	$S_x$	68	125	19	11						
	CV	14.58	17.10	21.74	13.54						

The structural properties also included analysing the capillary absorption capacity, which was used to determine the amount of water absorbed in the samples based on the capillary forces in the samples. The differences between the samples are shown in Figure 3. The maximum capillary absorptivity was achieved by sample S4, namely 46 mm, with a coefficient of variation of 21.8%, while the largest coefficient of variation was for sample S3, namely 42.9%. The lowest capillary absorption was achieved for sample S2, with 5 mm. A lower capillary absorption is the result of the surface finishing of the coated paper.

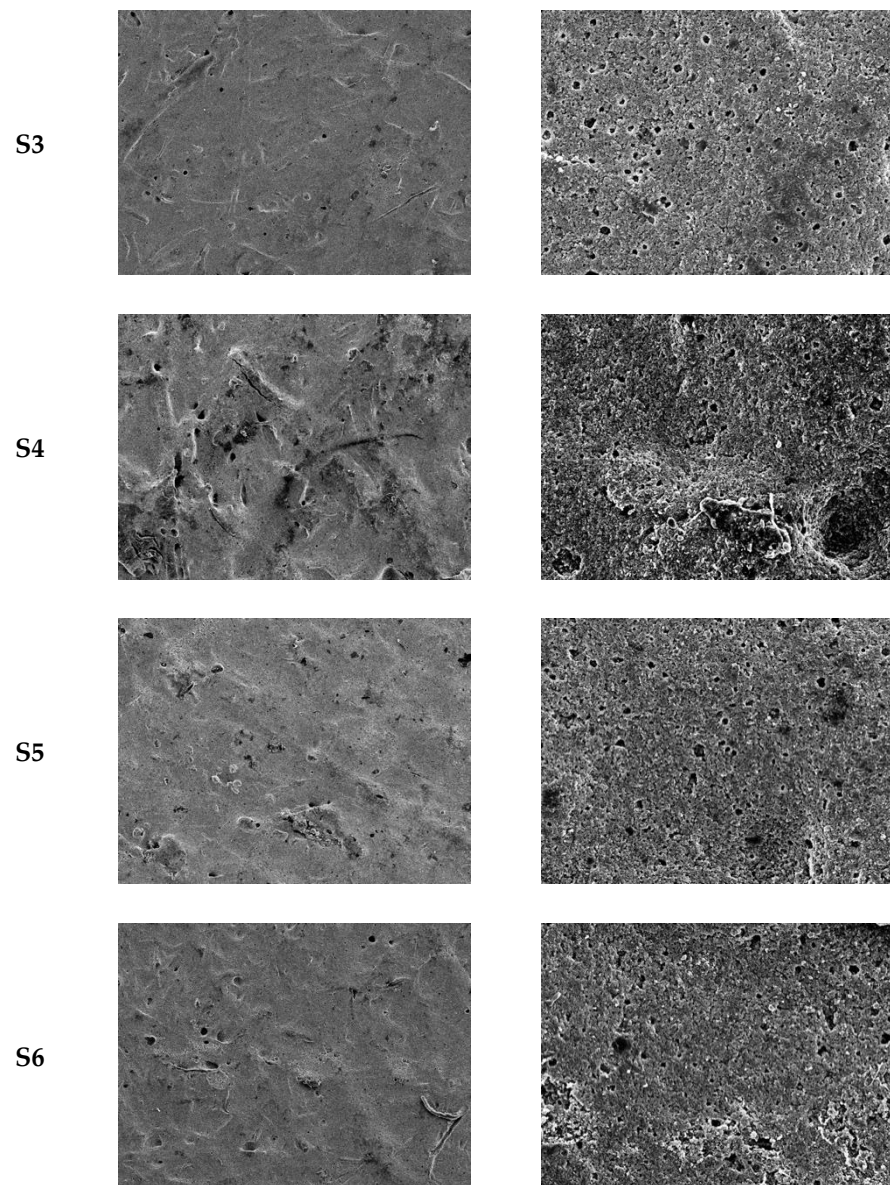


**Figure 3.** Capillary absorption capacity of labels according to Klemm method on coated samples.

The structural properties that were analysed with a scanning electron microscope (SEM) showed that the samples are quite different, especially with regard to the unevenness of the surface and the proportion of air bubbles. The SEM images of the samples at  $100\times$  magnification (Figure 4) show that samples S1 and S2 have a more uneven surface, i.e., greater roughness, which can be confirmed using Bendtsen roughness measurements (Table 7). When magnified from  $1000\times$ , it can be seen that the coating contained a considerable amount of air bubbles, which left open spaces during drying and thus increased the number of pores, which results in a greater permeability to the air flow. This agrees with the results of the porosity measurements according to Bendtsen (Table 8).

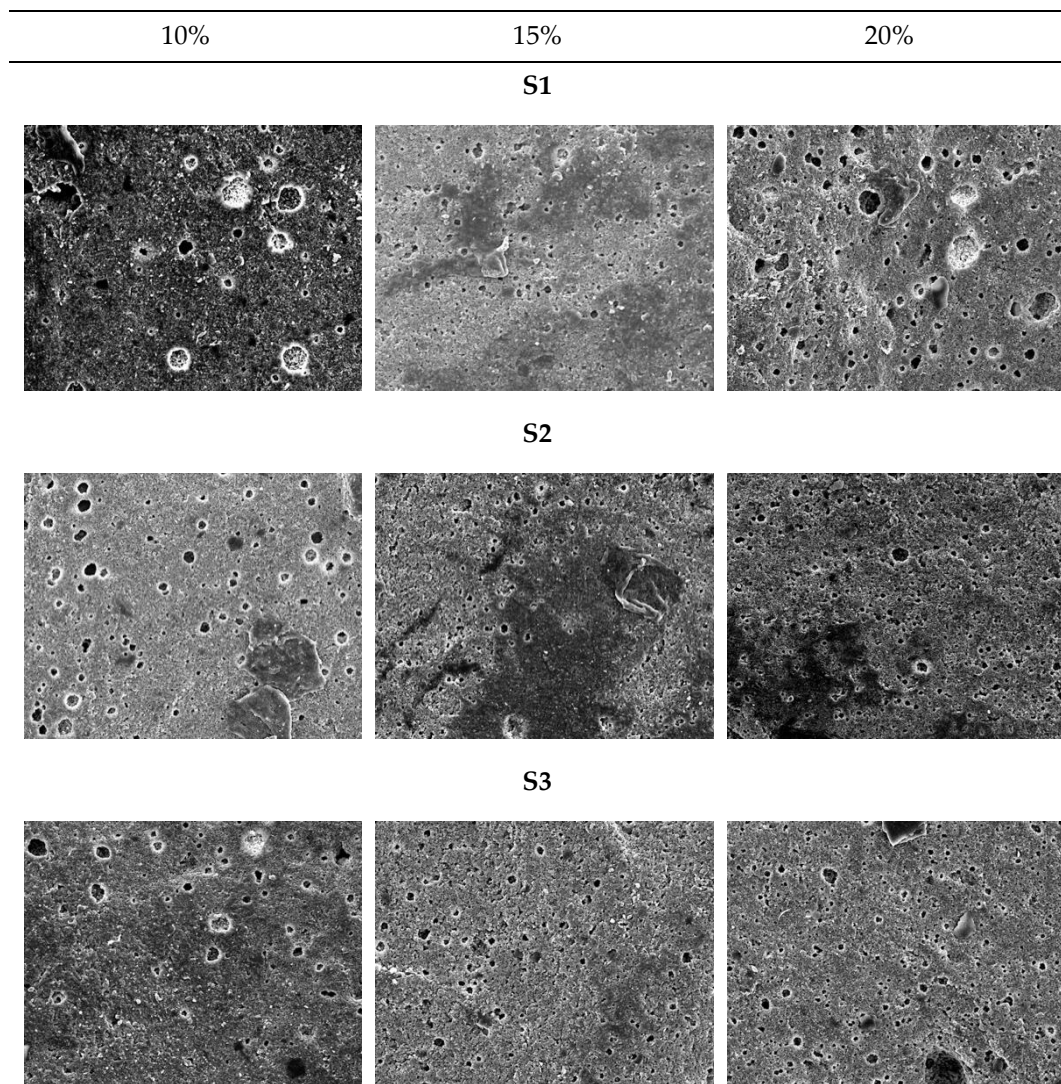


**Figure 4.** *Cont.*

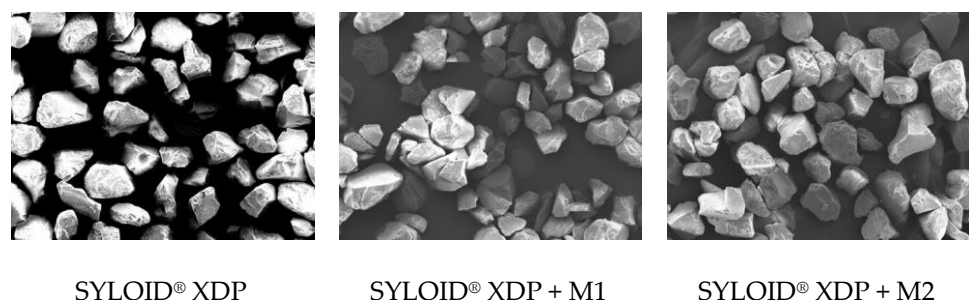


**Figure 4.** SEM micrographs of the surfaces of the investigated papers (S1–S6) at 100× and 1000× magnification.

Figure 5 shows SEM images at 1000× magnification of samples with different saturation (10, 15, and 20%) of the solid support with the M1 mixture. We can see the differences (the number of white “dots”) between each saturation, which represent the percentage of solid carrier content (Figure 6). The differences in the number of air bubbles can also be seen. The SEM images also show that the coating covers the solid carriers and these are not particularly noticeable, which also allows for a longer release of the essential oils.



**Figure 5.** SEM micrographs of the surfaces of the investigated papers (S1–S3), with solid carrier contents of 10, 15, and 20%, at 1000× magnification.



**Figure 6.** SEM micrographs of the surfaces of the SYLOID® XDP 3100 support, without EOs and with M1 and M1, at 1000× magnification.

#### 4. Conclusions

The increasing interest in mosquito repellent products with biologically active ingredients, particularly those based on essential oils, has led to a growing market for alternative options. This study aimed to contribute to sustainable product development by addressing the issues of harmful waste and invasive alien plants. The coated samples, utilising two different essential oil blends (M1 and M2), demonstrated distinctive features, with M2

exhibiting a notable 19.2% prolongation in evaporation when using the porous carrier SYLOID<sup>®</sup> XDP. Thermogravimetric analysis confirmed that the evaporation rate could be slowed down, particularly for M2. The release of repellent at varying humidity levels indicated the potential for long-lasting efficacy under certain conditions. However, no conditions achieved a 50% reduction in evaporation. The properties of the final labels, influenced by substrate characteristics, revealed that the Japanese knotweed base yielded the best results. Increasing the concentration of solid carriers enhanced surface filling and extended effectiveness, although it presented challenges in the coating process due to the binding of the liquid part to solid carriers and the presence of dry pigments. This study provided a viable example suitable for the market, aligning with consumer preferences for alternative mosquito repellent options. The use of repellent labels derived from invasive plant species not only addresses environmental concerns related to invasive species, but also offers a sustainable product to the market.

**Author Contributions:** Conceptualisation, K.M. and U.V.-B.; methodology, K.M.; validation, K.M., Z.M., and U.V.-B.; formal analysis, Z.M.; investigation, Z.M. and K.M.; resources, K.M., Z.M., and U.V.-B.; data curation, Z.M. and K.M.; writing—original draft preparation, K.M., Z.M., and U.V.-B.; writing—review and editing, K.M. and U.V.-B. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors acknowledge financial support from the Slovenian Research Agency (research core funding No. P2-0450).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

**Acknowledgments:** The authors would like to thank Blaž Grilc for their help with sample preparations (essential oils and coating solutions).

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Revay, E.E.; Junnila, A.; Xue, R.D.; Kline, D.L.; Bernier, U.R.; Kravchenko, V.D.; Qualls, W.A.; Ghattas, N.; Müller, G.C. Evaluation of commercial products for personal protection against mosquitoes. *Acta Trop.* **2013**, *125*, 226–230. [[CrossRef](#)] [[PubMed](#)]
2. Kang, S.M.; An, J.H. Robust and Transparent Lossless Directional Omniphobic Ultra-Thin Sticker-Type Film with Re-entrant Micro-Stripe Arrays. *ACS Appl. Mater. Interfaces* **2022**, *14*, 39646–39653. [[CrossRef](#)] [[PubMed](#)]
3. Marsin, A.M.; Muhamad, I.I.; Anis, S.N.S.; Lazim, N.A.M.; Ching, L.W.; Dolhaji, N.H. Essential oils as insect repellent agents in food packaging: A review. *Eur. Food Res. Technol.* **2020**, *246*, 1519–1532. [[CrossRef](#)]
4. Baharudin, A.; Jani, N.A.; Azreen, A.; Assyura, A.A.; Pornomo, H.; Mehat, M.H. Potential of citronella oil as natural mosquito repellent agent in formulated fabric softener finishes. *Borneo Akademika* **2020**, *4*, 1–12.
5. Basak, S.; Saxena, S.; Raja, A.S.M.; Patil, P.G.; Krishnaprasad, G.; Narkar, R.; Kambli, N. Development of cotton fibre based fragrance pack and its characterization. *Cellulose* **2021**, *28*, 7185–7200. [[CrossRef](#)]
6. Vrabič Brodnjak, U.; Tihole, K. Chitosan solution containing zein and essential oil as bio based coating on packaging paper. *Coatings* **2020**, *10*, 497. [[CrossRef](#)]
7. Vasilev, S.; Vodyashkin, A.; Vasileva, D.; Zelenovskiy, P.; Chezganov, D.; Yuzhakov, V.; Shur, V.; O'Reilly, E.; Vinogradov, A. An investigative study on the effect of pre-coating polymer solutions on the fabrication of low cost anti-adhesive release paper. *Nanomaterials* **2020**, *10*, 1436. [[CrossRef](#)] [[PubMed](#)]
8. Stejskal, V.; Vendl, T.; Aulicky, R.; Athanassiou, C. Synthetic and natural insecticides: Gas, liquid, gel and solid formulations for stored-product and food-industry pest control. *Insects* **2021**, *12*, 590. [[CrossRef](#)] [[PubMed](#)]
9. El Bourakadi, K.; Qaiss, A.E.K.; Bouhfid, R. *Essential Oils Used in Packaging: Perspectives and Limitations*; Wiley: Hoboken, NJ, USA, 2023.
10. Kessler, S.; Romero, A.; Cooksey, K. Advancements in Post-packaging Technologies. In *Food Safety Engineering*; Springer: Berlin/Heidelberg, Germany, 2020; pp. 719–744.
11. Vrabič-Brodnjak, U.; Možina, K. Invasive alien plant species for use in paper and packaging materials. *Fibers* **2022**, *10*, 94. [[CrossRef](#)]
12. Tataridas, A.; Jabran, K.; Kanatas, P.; Oliveira, R.S.; Freitas, H.; Travlos, I. Early detection, herbicide resistance screening, and integrated management of invasive plant species: A review. *Pest Manag. Sci.* **2022**, *78*, 3957–3972. [[CrossRef](#)]

13. Papp, L.; Van Leeuwen, B.; Szilassi, P.; Tobak, Z.; Szatmári, J.; Árvai, M.; Mészáros, J.; Pásztor, L. Monitoring invasive plant species using hyperspectral remote sensing data. *Land* **2021**, *10*, 29. [[CrossRef](#)]
14. Weidlich, E.W.; Flórido, F.G.; Sorriani, T.B.; Brancalion, P.H. Controlling invasive plant species in ecological restoration: A global review. *J. Appl. Ecol.* **2020**, *57*, 1806–1817. [[CrossRef](#)]
15. Vilar, W.T.S.; Barbosa, M.F.; Pinto, L.; de Araújo, M.C.U.; Pontes, M.J.C. Determination of N,N-diethyl-3-methylbenzamide and ethyl-butyl-acetylaminopropionate in insect repellent using near infrared spectroscopy and multivariate calibration. *Microchem. J.* **2020**, *152*, 104285. [[CrossRef](#)]
16. Yener, H.E.; Hillrichs, G.; Androsch, R. Phase behavior of solvent-rich compositions of the polymer/drug system poly (butylene succinate) and N, N-diethyl-3-methylbenzamide (DEET). *Colloid Polym. Sci.* **2021**, *299*, 873–881. [[CrossRef](#)]
17. da Silva, M.R.M.; Ricci-Júnior, E. An approach to natural insect repellent formulations: From basic research to technological development. *Acta Trop.* **2020**, *212*, 105419. [[CrossRef](#)] [[PubMed](#)]
18. Grison, C.; Carrasco, D.; Pelissier, F.; Moderc, A. Reflexion on bio-sourced mosquito repellents: Nature, activity, and preparation. *Front. Ecol. Evol.* **2020**, *8*, 8. [[CrossRef](#)]
19. Debboun, M.; Goodyer, L.I. Arthropod repellents in public health. In *Advances in Arthropod Repellents*; Academic Press: Cambridge, MA, USA, 2022; pp. 1–18.
20. de Oliveira, L.H.; Trigueiro, P.; Souza, J.S.N.; de Carvalho, M.S.; Osajima, J.A.; da Silva-Filho, E.C.; Fonseca, M.G. Montmorillonite with essential oils as antimicrobial agents, packaging, repellents, and insecticides: An overview. *Colloids Surf. B Biointerfaces* **2022**, *209*, 112186.
21. Sukrutha, S.K.; Ramachandra, R.; Anand, S. Insect repellent plants: A recent update. In *Natural Products in Vector-Borne Disease Management*; Academic Press: Cambridge, MA, USA, 2023; pp. 517–532.
22. Abubakar, Y.; Tijjani, H.; Egbuna, C.; Adetunji, C.O.; Kala, S.; Kryeziu, T.L.; Ifemeje, J.C.; Patrick-Iwuanyanwu, K.C. Pesticides, history, and classification. In *Natural Remedies for Pest, Disease and Weed Control*; Academic Press: Cambridge, MA, USA, 2020; pp. 29–42.
23. Mishra, P.; Kumar, J.; Verma, A.; Prabakar, A.E.; Verma, A.K. Linalool Based Herbal Mosquito Repellent. *Int. J. Mosq. Res.* **2023**, *10*, 15–23. [[CrossRef](#)]
24. Al-Sarar, A.S.; Hussein, H.I.; Abobakr, Y.; Al-Zabib, A.A.; Bazeyad, A.Y. Mosquitocidal and repellent activities of essential oils against *Culex pipiens* L. *Entomol. Res.* **2020**, *50*, 182–188. [[CrossRef](#)]
25. Ogilvie-Battersby, J.D.; Nagarajan, R.; Mosurkal, R.; Orbey, N. Microencapsulation and controlled release of insect repellent geraniol in gelatin/gum arabic microcapsules. *Coll. Surf.* **2022**, *640*, 128494. [[CrossRef](#)]
26. Jugreet, B.S.; Suroowan, S.; Rengasamy, R.K.; Mahomoodally, M.F. Chemistry, bioactivities, mode of action and industrial applications of essential oils. *Trends Food Sci. Technol.* **2020**, *101*, 89–105. [[CrossRef](#)]
27. Zhang, X.; Ismail, B.B.; Cheng, H.; Jin, T.Z.; Qian, M.; Arabi, S.A.; Liu, D.; Guo, M. Emerging chitosan-essential oil films and coatings for food preservation—A review of advances and applications. *Carbohydr. Polym.* **2021**, *273*, 118616. [[CrossRef](#)] [[PubMed](#)]
28. Chen, X.; Chen, W.; Lu, X.; Mao, Y.; Luo, X.; Liu, G.; Zhu, L.; Zhang, Y. Effect of chitosan coating incorporated with oregano or cinnamon essential oil on the bacterial diversity and shelf life of roast duck in modified atmosphere packaging. *Food Res. Int.* **2021**, *147*, 110491. [[CrossRef](#)] [[PubMed](#)]
29. Carpena, M.; Nuñez-Estevéz, B.; Soria-Lopez, A.; Garcia-Oliveira, P.; Prieto, M.A. Essential oils and their application on active packaging systems: A review. *Resources* **2021**, *10*, 7. [[CrossRef](#)]
30. Chinthaka, S.D.M.; Delpagodage, C.J.; Perera, A.G.W.U. A review on the comparative analysis of synthetic insect repellents and essential oil based sustained-release insect repellent formulations. *Vidyodaya J. Sci.* **2023**, *147*, 47–53.
31. Sousa, V.I.; Parente, J.F.; Marques, J.F.; Forte, M.A.; Tavares, C.J. Microencapsulation of essential oils: A review. *Polymers* **2022**, *14*, 1730.
32. Chattopadhyay, P.; Dhiman, S.; Borah, S.; Rabha, B.; Chaurasia, A.; Veer, V. Essential oil based polymeric patch development and evaluating its repellent activity against mosquitoes. *Acta Trop.* **2015**, *147*, 45–53. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.