PROPERTIES OF POLY LACTIC ACID/CELLULOSE NANOFIBER/GRAPHENE OXIDE/THYMOL NANOCOMPOSITE INSECTICIDE REPELLENT FILM

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ABSTRACT

Inefficient delivery of pesticides by conventional methods such as fumigation and direct application can cause adverse effects to the environment and organism. These issues can be avoided by polymer modification as a pesticide carrier with the ability to regulate the release of pesticides. Nanomaterials such as graphene oxide (GO) and cellulose nanofibre (CNF) have unique properties that can be incorporated into polylactic acid (PLA) based packaging to reinforce its mechanical and physical properties. A novel combination of both nanomaterials' functional properties can also be manipulated to regulate the release of pesticides so that the release of pesticides can be controlled as desired. GO and CNF from oil palm empty fruit bunch fibre was obtained via modified Hummer's method and hydrolysis method, respectively. The solution casting method was used in film preparation. The CNF, GO, and thymol loading in making hybrid nanocomposite was selected using response surface method. and conventional method. As a result, the loading of CNF and thymol was fixed to 0.5 phr and 5 phr respectively, whereas the GO loading was varied from 0-1.5 phr. The formed films were analysed based on their physical properties (tensile test and water vapour transmission rate), morphology (field emission scanning electron microscopy), and chemical properties (Fourier transform infrared (FTIR)). The release of active compound, thymol from the film was analysed for 9 days. In vivo study of insect repellency was done using rice as food simulant, and rice weevils (*Sitophilus oryzea*) as a test subject to determine the effectiveness of the nanocomposite film in protecting food and repelling insects. Results obtained show that the addition of both CNF and GO in a polymeric system synergistically improved the mechanical, physical, and release properties of the film. PLA incorporated with 5 phr of thymol, and 0.5 phr of CNF designated as PLA/5Thy/0.5CNF film showed the highest tensile strength up to 39.71 MPa after 1.00 phr of GO was added. The incorporation of 0.5 phr of GO in PLA/5Thy/0.5CNF film gave the highest elongation percentage of 40.8 %. Chemical characterisation by FTIR demonstrated that thymol interaction in the matrix was influenced by CNF and GO loading, which affects the thymol release behaviour. Cross-section morphology of nanocomposite film demonstrated a unique matrix arrangement with the addition of GO, affecting the mechanical properties and thymol release of the film. In vivo test on packaging towards rice weevils showed an increment in the repellency effect as well as the mortality rate of the rice weevils. Moreover, unsuccessful or no penetration of insects with minimal scratch was observed on the packaging incorporated with GO. In conclusion, the combination of CNF and GO enhanced the mechanical and physical properties of PLA based film. Interestingly, thymol release can also be modulated by varying the loading of CNF and GO. The formed synergy allows the insect repellent packaging to be specifically designed in order to suit the intended purposes.

ABSTRAK

Penyediaan racun perosak yang tidak cekap dengan kaedah konvensional seperti pengasapan dan aplikasi langsung boleh menyebabkan kesan buruk kepada alam sekitar dan organisma. Isu-isu ini boleh dihindari melalui pengubahsuaian polimer sebagai pembawa racun perosak dengan keupayaan mengawal pembebasan racun perosak. Nanobahan seperti grafin oksida (GO) dan gentian nano selulosa (CNF) mempunyai ciri-ciri unik yang boleh dimasukkan ke dalam filem pembungkus berasaskan poli asid laktik (PLA) untuk menguatkan sifat mekanikal dan fizikalnya. Gabungan novel kedua-dua sifat berfungsi nanobahan juga dapat dimanipulasi untuk mengatur pembebasan racun perosak supaya pembebasan racun perosak dapat dikawal seperti yang diingini. GO dan CNF dari gentian tandan buah kelapa sawit masing-masing diperoleh menerusi kaedah Hummer-diubahsuai dan kaedah hidrolisis. Kaedah penuangan larutan digunakan dalam penyediaan filem. Muatan CNF, GO dan timol dalam pembuatan komposit nano hibrid telah dipilih menggunakan kaedah sambutan permukaan dan kaedah konvensional. Hasilnya, muatan CNF dan timol masing-masing telah ditetapkan kepada 0.5 phr dan 5 phr, manakala muatan GO adalah antara 0-1.5 phr. Filem plastik yang terbentuk dianalisa berdasarkan sifat-sifat fizikal (ujian tegangan dan kadar penularan wap air), morfologi (mikroskopi imbasan elektron pemancaran medan), dan sifat-sifat kimia (spektroskopi jelmaan inframerah Fourier (FTIR)). Pelepasan bahan aktif iaitu timol dari filem dianalisa selama 9 hari. Dalam kajian secara *in vivo*, beras digunakan sebagai simulasi makanan, dan kutu beras (*Sitophilus oryzea*) sebagai subjek ujikaji untuk mengkaji keberkesanan filem komposit untuk melindungi makanan dan menghalau serangga. Hasil yang diperoleh menunjukkan bahawa penambahan kedua-dua CNF dan GO dalam sistem polimer secara sinerginya menambah baik sifat mekanikal, fizikal, dan sifat pelepasan timol daripada filem. PLA yang digabungkan dengan 5 phr timol dan 0.5 phr CNF yang dilabel sebagai sebagai filem PLA/5Thy/0.5CNF menunjukkan kekuatan tegangan tertinggi sehingga 39.71 MPa dengan penambahan 1.00 phr GO. Penambahan 0.5 phr GO dalam filem PLA/5Thy/0.5CNF memberikan peratusan pemanjangan tertinggi sebanyak 40.8 %. Pencirian kimia oleh FTIR menunjukkan bahawa interaksi timol dalam matriks dipengaruhi oleh muatan CNF dan GO yang juga berhubung kait dengan kelakuan pelepasan timol. Morfologi keratan rentas komposit menunjukkan susunan matriks yang unik dengan penambahan GO, dimana penambahan ini juga mempengaruhi sifat-sifat mekanik dan pelepasan timol. Ujian *in vivo* ke atas kutu beras menunjukkan peningkatan dalam kesan halangan terhadap serangga serta kadar kematian kutu beras. Kegagalan penembusan kutu beras dengan goresan minimum dilihat pada pembungkusan yang digabungkan dengan GO. Kesimpulannya, gabungan CNF dan GO meningkatkan sifat mekanikal dan fizikal filem berasaskan PLA. Menariknya, pelepasan bahan aktif (timol) juga boleh dikawal dengan mengubah muatan CNF dan GO. Sinergi ini membolehkan filem pembungkusan anti-serangga direka khusus untuk keperluan tertentu dihasilkan.

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LIST OF ABBREVIATIONS

AD	-	Anno Domini
AC	-	Active Compound
PLA	-	Polylactic Acid
CNF	-	Cellulose Nanofibre
GO	-	Graphene Oxide
GNP		Graphene Nanoplatelete
Thy	-	Thymol
Wt	-	Weight
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier-transform Infrared Spectroscopy
TEM	-	Transmission electron microscopy
AFM	-	Atomic Force Microscopy
DDT	-	Dichloro-diphenyl-trichloroethane
BHC	-	Benzene hexachloride
EO	-	Essential Oil
US	-	United States
CR	-	Controlled Release
PVP	-	Polyvinyl Pollidone
PHR	-	Per hundred parts
MAP	-	Monoammonium phosphate
WP	-	Wettable Powder
SP	-	Soluble Powder
SERS	-	Surface-enhanced Raman spectroscopy
PHA	-	Polyhydroxyalkanoates

PHB	-	Poly (hydroxybutyrate)
PHBV	-	Poly (hydroxybutyrate-valerate)
PLGA	-	Poly(lactic-co-glycolic acid)
PLLA	-	Poly(L-lactic acid)
PDLA	-	Poly(D-lactic acid)
PHEE	-	Poly(hydroxy ester ether)
PEG	-	Polyethylene-Glycol
AP	-	Active Packaging
TPS	-	Thermoplastic Starch
MFC	-	Microfibrillated Cellulose
DP	-	Degree of Polymerisation
OPEFB	-	Oil Palm Empty Fruit Bunch
EFB	-	Empty Fruit Bunch
DNA	-	Deoxyribonucleic Acid
AM	-	Anti Microbes
MW	-	Molecular Weight
USA	-	United States of America
EDX	-	Energy Dispersive X-ray
RPM	-	Revolution Per Minute
ANOVA	-	Analysis of Variance
ASTM	-	American Society for Testing and Materials
RH	-	Relative Humidity
HD	-	High Definition
SLR	-	Single Lense Reflex
AF	-	Auto Focus
CMOS	-	Complementary Metal-Oxide-Semiconductor
UV-Vis	-	Ultraviolet-Visible

UK	-	United Kingdom
HS	-	Head Space
SPME	-	Solid Phase Micro-Extraction
GC	-	Gas Chromatography
MS	-	Mass Spectrometry
PTFE	-	Polytetrafluoroethylene
OFAT	-	One Factor at a Time
RSM	-	Response Surface Methodology
WVTR	-	Water Vapor Transmission Rate
PEI	-	Polyethyleneimine
OLLA	-	Oligo-(L-lactic acid)
OH	-	Hydroxide
CABI	-	Centre of Agriculture and Biosciences International

LIST OF SYMBOLS

R^2	-	Coefficient of Determination
t	-	Time
J	-	Diffusion flux
D	-	Diffusion coefficient or diffusivity
C	-	Concentration of Active Compound
x	-	Distance
Q_0	-	Initial amount of drug in the solution
Q_t	-	Amount of drug dissolved at designated time, t
k_0	-	Zero-order release constant (concentration/time)
k	-	Rate constant
M_t	-	Amount of active agent diffused out of the film at a certain time
M_∞	-	Equilibrium amount of active agent released from the film
l	-	Thickness (film, or planar sheet)
K	-	Initial Slope
m_t	-	Amount of active agent released into the food simulant
m_p	-	Amount of active agent in the packaging material
v_0	-	Initial release rate (g/s)
ΔZ	-	Distance [nm]
%E	-	Elongation Percentage (%)
G/t	-	Slope of the straight line of weight increased vs time (g/hours)

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CHAPTER 1

INTRODUCTION

1.1 Background

A pesticide can be defined as a compound used to prevent, destroy, or repel pests. Its usage has continued to rise. As reported by the Food and Agriculture of United nation, pesticide trade value is projected to increase by 8.7% per year to 43.74 US Billion $ in 2020. Various types of pesticide and insecticide flooded the world since World War II. Statistically, one-third of the world's agricultural losses are caused by destructive organisms which 13.8% of it is due to insects and mites (Srivastava *et al.,* 2016). Crops and agricultural producers rely significantly on the use of pesticides because it is the only choice that they have to control the losses. That enormous economic loss resulting from diverse species of harmful insects, mites, and others have usurped humankind to develop and use various insecticides, pesticides, and acaricides to protect their crops.

In general, pests and insects can infest food produce during growing, pre-harvest, post-harvest, processing, packaging, and transportation. There are also possibilities that insects can enter vulnerable packaged goods during transportation, storage in the warehouse, or retail stores. Thus, it allows the pest to consume food commodities and contaminate the goods with cast skins, faeces, hairs, webbing dead bodies, and toxins. Manufacturers are affected as the consumer always blames them for any insect infestation, even if the cause of the problem is poor storage by a third party. Even though the use of pesticides contributes to positive growth in the agricultural economy, it will become hazardous when used irrationally and excessively. The use of any synthetic/biologically active compound are known can be accompanied by various degrees of toxic reactions or adverse effects.

For that reason, even reputed safe and biologically degradable pesticides may give hazard to the end-consumers: humans and animals. Another approach was also introduced, which were using natural pesticide such as thymol that mainly derived from aromatic plant extract. However, studies show that the usage of a high concentration of essential oil may cause skin irritation and may also be considered toxic (Buckle, 2003; Yuruktumen *et al.,* 2011). Thus, the application of regulated packaging that can retain the quality of food commodities while reducing the adverse effect of pesticides is fairly important. Previously, various method of pesticide delivery system has been applied. It includes a direct application, fumigation, pelleting, incorporation into a gel, and others. In grain storage, for example, the pesticide/additives were mixed directly into the grain package by fumigation/spraying to avoid insect infestation. A conventional method mentioned earlier has disadvantages where the spreading and release of pesticides are hard to control. It is almost impossible to maintain pesticide/repellent efficiency. This is because the pesticide delivery is not controlled and monitored. The introduction of an advanced pesticide delivery system allows the pesticide release to be controlled or regulated. Thus, protection from pests through each developmental stage, transport, and storage can be achieved.

Controlled release of pesticides using a biodegradable polymer matrix such as PLA is an emerging technology that can make sure that the pesticide is released in a controlled manner. Introduction of polymer composite or packaging in pesticide control has become more attractive due to its versatility, diverse function, and applications. In polymer packaging area itself, various modifications have been made to reach the "ideal" polymer packaging/composite. At the very beginning of the packaging and polymer technology, the fundamental purposes of polymer packaging are for containment and protection. However, advance in trend makes polymer packaging becomes more sophisticated. At this point, containment and protection of food or crops are not enough; the packaging needs to have added value. It includes the ability of the polymer to deliver active compounds such as pesticide or repellent. These, simultaneously able to reduce the adverse effect that comes from the overexposure of pesticides. Hence this is where both technologies, packaging technologies and controlled release can be integrated to serve the various field.

Trends in food packaging have been focusing on the development of new materials with enhanced properties to control polymer packaging and environment properties. Previous studies revealed the use of different active compounds in polymer and packaging that focused more on the antimicrobial and antioxidant agents, which become more communal. The introduction of pesticide and repellent in polymer packaging is rather new and available literature as scarce. Hence, more studies on packaging that are incorporated with insect repellent need to be revealed. It includes the understanding of the compatibility of polymer and pesticide, polymer modification for performance enhancement, and many more. Natural, non-toxic insect repellents to protect food-packaging materials are new and improved technology. Several types of encapsulated essential oil extract and/or oil fractions have both repellency and antifeedant effects on tested storage insects.

These provide a versatile system to be integrated compatibly into packaging materials to serve various purposes. In addition, if the packaging material itself is resistant to insect penetration, less insect repellent material is required to create an effective barrier against insect penetration into the packaged food. In other words, to prevent or repel such insect infestation, it would be preferable to render the packaging material impervious to insect penetration as treating the food directly with insect repellents causing it to be absorbed by the foods. Packaging represents a critical point in food quality preservation and the ultimate defence against pests. This effort should be paid towards the development of insect-proof packages. An active packaging, besides protecting the product, it can also interact with it (Vermeiren *et al.*, 1999). It means the packaging can respond based on product changes such as pH, moisture, temperature, and others. Some packaging can give information by changing its colour based on the pH of the packaged product (Balbinot-Alfaro *et al.,* 2019). In most cases, high pH usually indicates food spoilage. It gives extra benefits when compared to conventional packages. It is needed to be clear that insect-proof packaging is a derivation of active packaging. The application of polylactide acid (PLA) based active packaging is versatile that it can be used in perishable food and long term food storage such as grains.

The PLA-based active film is not just compostable, but an active compound incorporated in the film can provide a bacteriostatic and mechanism. PLA based packaging can be applied to the various stage in farming practice which includes preharvest, long term storage and perishable goods at the point of sale. Figure 1.1 shows that the typical food packaging systems that represent a package/food system or a package/headspace/food system. The main migration phenomena involved in the package/food system is the diffusion between the packaging material, food, and partitioning at the interface. Antimicrobial agents are initially incorporated into the packaging materials and might migrate into the food through diffusion and partitioning (Han, 2000). Foods packed in flexible packages, cups, and cartons, on the other hand, represent the package/headspace/food systems. The substance evaporation and distribution between headspace, packaging material, and/or food is considered as a part of the main migration mechanism. This migration mechanism can be controlled by the adaptation of controlled release technology.

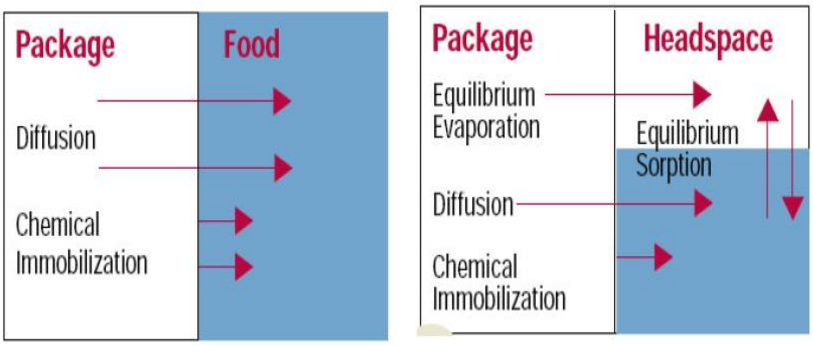

Figure 1.1 Package / food systems and Package / headspace / food systems

There are various ways to regulate the migration or release of active compound from the packaging. One of them is through the addition of nanomaterial/nanoparticles. This approach was widely used to control drug substance in a polymeric system for the pharmaceutical application (Rizvi and Saleh, 2018). It shows alterating the polymeric system with nanomaterial provides a customisable and safer pathway in delivering a drug or active compounds. Even though very limited publications reported on food packaging applications, this approach might still be the best in controlling an active compound release in the food packaging system.

Advancement such as nanoparticles was introduced into the system are not only to improve the polymer physically but to improve the pesticide. Nanotechnology is capable of assisting the agricultural revolution with a new mechanism for the rapid disease detection and treatments, improves nutrient absorption by the plant, precision farming by increasing the efficiency of pesticides and herbicide and more (Sekhon, 2014).

Most importantly, in packaging technology, nanomaterial has the ability to regulate the release of pesticides which can be an essential oil or chemical derived pesticide that intends to extend the food shelf life or repel pest from food. This study focused on the enhancement of PLA based packaging by incorporation of nanomaterials for the controlled delivery of pesticides that basically an important technology that has the potential to increase the efficiency of food production and decrease pollution.

1.2 Problem Statements

Pesticide is used to repel unwanted pests. However, it is hazardous when used excessively. For example, a fumigation procedure may use an excessive or too high concentration of pesticide, which likely to be absorbed by stored grain products. It is ineffective, as the pesticide residues can be hazardous when inhaled. It is known that in a conventional method, the spreading and release of pesticides is hard to control. A novel idea of pest repellent film could ensure the pesticide is released in a controlled manner. The pesticide or active compound can be embedded or be incorporated into the polymeric film to provide a more efficient pesticide delivery system. Hence it may reduce the amount of pesticide usage and any possible adverse effect. Polylactide acid (PLA), a type of biopolymer, can be utilised for that purpose. It can be incorporated with pesticide or active compounds and cast as a thin film. However, a PLA biopolymer is naturally brittle with poorer mechanical properties than the conventional non-biodegradable plastic films used in the food packaging industries (Abdul Khalil *et al.*, 2012). Food packaging is the last line of defence mechanism against insect infestation (Kim *et al.*, 2013). Insect in general, can attack packaged products by bore holes through packaging or enter packaged through existing holes. Food packaging especially derived from biomaterials, are prone to be invaded and penetrated. Thus the film should have high tensile and ductility. In terms of release property, the current issue that normally occurs in packaging film is the low capability for holding or retaining an active compound such as a pesticide or insect repellent. It eventually causes the release of pesticides to be rapidly reduced over time. This is because the conventional packaging system has no mechanism to regulate the release of the active compound to the outside environment. As the packaging system is unable to impregnate the active compound, thus active compounds will be released at a high dosage over a short period. The intention of having a controlled release mechanism is so that the pesticide can be released in a small effective dosage over an extended period of time. In PLA based film specifically, the mode and release behaviour of pesticide is one of the under-researched areas. The hybrid packaging system that uses both cellulose nanofiber and graphene oxide has not been explored yet. Thus, this exploration can contribute to the development of a biodegradable packaging system for pest control.

Some studies have been conducted on the improvement of biopolymer on physical, mechanical and release characteristics using various kinds of nanomaterials (Arjmandi *et al.*, 2015; Montes *et al.*, 2018; Ivanov *et al.*, 2019). The use of cellulose nanofiber and graphene oxide is novel and useful in developing a nanocomposite film. Its potential in pesticide delivery control especially in thymol release behaviour remains unexplored. With the better insight of both cellulose nanofiber and graphene oxide nanomaterials on their functional properties, chemical and physical properties, the PLA film can be modified to serve a specific purpose. As a result, the incorporation of both nanomaterials into the bioplastic may enhance the physical characteristics of the film and able to control the release of active agents (i.e., pesticide or repellent). Insect repellency in food packaging applications may solve or at least reduce numerous species of insects and mites attack on stored food that is known as one of the major reasons of dreadful economic loss.

The potential nanotechnology applications in the agriculture field such as material reinforcement, precision farming, smart delivery systems, food manufacturing, packaging, and food safety are acknowledged globally. Recent studies show that nano-sized filler was found to be impressively valuable in material reinforcement as it has significantly higher surface charges that promote excellent adhesion with matrix (Fleming *et al*., 2001). In food packaging applications, this finding could be potentially beneficial for further prospects in the active biodegradable packaging sector. In addition, the previous findings showed that the application of nanotechnology could control the release of the bioactive antimicrobial molecules (Cozzolino *et al*., 2013).

Cellulose nanofiber (CNF) has attracted massive attention because of its small nano-size that interacts better with the biodegradable polymer matrix and compatible to be blended into a flexible thin film. Cellulose nanofibre could give excellent mechanical properties to the biodegradable plastic with comparable strength to petroleum-based plastic. In its crystal region, CNF has high Young's modulus up to 140GPa (Deepa *et al.*, 2019). It shows a very low coefficient of thermal expansion along the longitudinal direction (Nishino *et al.*, 2004. This expounds that nano-size cellulose has a big potential in the development of new and enhanced biopolymers.

Graphene oxide (GO) is a newly emerged nanomaterial with unique dimensional structure (one to two atom sheet) that might provide this new functionality (controlled release of pesticide). Graphene sheet possesses numerous oxygen-containing groups on the surface, such as hydroxyls, epoxides, carbonyls, and carboxyl (Tramón, 2014). These available oxygen-containing groups can facilitate the interaction between polymer hosts and graphene oxide, also between graphene oxide and active compound (repellent) via covalent or non-covalent bonds (Liu *et al*., 2013). The effects of those interactions towards the release of pesticides in this case, thymol is still unreported. Intentionally, the addition of CNF and GO, which possessed different characteristics, can be merged into one polymeric system. Thus, the packaging function can be diversified and ultimately could be used to serve different purposes.

1.3 Objectives of Study

The objective of the study is to design, analyse, and optimise the properties of PLA/CNF/GO nanocomposite film for efficient controlled release of thymol as an insect repellent. This involved several specific objectives which are:

1. To develop and determine the optimum formulation of PLA based nanocomposite film incorporated with cellulose nanofibre, graphene oxide, and thymol so that a film with good tensile and ductility can be formed.
2. To investigate the effect of GO loading in hybrid nanocomposite film on physical, chemical, and mechanical properties. The intention is to improve the characteristic that perceived as good packaging films such as good barrier properties and other physical attributes.
3. To study the release of thymol from the PLA/CNF/GO nanocomposite film and determine its kinetic release model. Thus, the effect of nanomaterial addition on release behaviour can be determined. The release of pesticides can be controlled at an effective dosage for a longer time, so it can reduce the adverse effect and excessive usage of pesticides.
4. To observe the application of PLA/CNF/GO nanocomposite containing thymol as food packaging toward grain weevils using insect invasion and penetration test. Stronger packaging with additional features such as pesticide release mechanisms may prevent insect penetration and invasion in packaged food.

1.4 Scope of Study

This study covers several scopes. Nanomaterials cellulose nanofibre (CNF) and graphene oxide (GO) in nanocomposite film formulation were prepared using acid hydrolysis method and modified Hummer's method, respectively. A preliminary study was done to determine the lower and upper limit of nanomaterial and thymol incorporation loading (phr) in the formulation of nanocomposite film, which can significantly affect the mechanical properties. Response surface methodology (RSM), a mathematical approach was also used to optimise the nanocomposite formulation and systematically determine the factor that most influencing mechanical strength. The mathematical relationship between loading of a mixture (CNF, GO and thymol) with a response (tensile strength, percentage elongation at break, and Young's Modulus) was evaluated with design expert software as well as the adequacy of the derived model. The results from RSM and preliminary approach eventually reveal the most significant factor and least significant factor (nanomaterial and thymol loading) that would affect the mechanical strength of nanocomposite film.

Based on the evaluation of RSM on mechanical strength, a fixed loading either CNF or GO will be chosen as an initial composition for hybrid nanocomposite film. The addition of thymol in making hybrid nanocomposite, on the other hand, is obligatory, which loading was determined by RSM optimisation. The second nanomaterial evaluated by RSM for the nanocomposite to make it "hybrid" was determined by the least significant factor affecting mechanical strength. In hybrid nanocomposite, the second nanomaterial either CNF or GO was varied from 0.25 to 1.5 phr, and the mechanical strength, chemical properties, optical properties, water absorption, and water vapour transmission rate (WVTR) were evaluated. Those mechanical properties that include tensile strength, percentage elongation at break, and Young's modulus were evaluated referring to a method adapted from ASTM D 882-02. A texture analyser CT3 (Brookfield, USA) with a 10kg load cell and a TexturePro CT software was specifically used in this study.

The optical properties of the film were evaluated using UV-vis spectroscopy. The amount of water absorbed by nanocomposite film was recorded every day for 15 days in a controlled chamber at 30˚C or until the weight of the film remains unchanged. The water vapour transmission rate (WVTR) of the formed film, on the other hand, was determined gravimetrically in controlled humidity 90% RH, using Potassium Nitrate (KNO_3), at temperature 38˚C.

The release of thymol from the hybrid nanocomposite film was evaluated using headspace Solid Phase Micro-Extraction (SPME) followed by gas chromatography analysis (HS-SPME-GC-MS) periodically for 215 hours. The hybrid nanocomposite film with repellent was applied as grain packaging (biscuit as attractant and simulant) to study its ability to repel and withstand penetration of rice weevil from passing the film, mortal beetles and elapsed time for hole penetration periodically for 9 days, in controlled condition temperature 30˚C and relative humidity 85%.

1.4 Significance of Study

An infestation on packed food products occurs either by penetration or invasion by insects or pests. This study constructed a novel hybrid nanocomposite film that possesses high mechanical strength to withstand insect penetration and at the same time, can regulate the release of the active compound to keep insects away from the food. The packaging system also provides a distinct advantage that avoids treating the food itself directly with insect repellent that is likely to be absorbed by the food. This research also contributes to the progress of active packaging technology, especially in food application which utilising trending nanomaterials, i.e., CNF and GO. This study would help to understand the effect and function of both nanomaterials (CNF and GO) in a polymer system. Intentionally, combining both CNF and GO would create a hybrid nanocomposite system that provides a synergistic effect in terms of mechanical, physical and functionalities. The controlled release study delivers the conceptual framework and accurate concentration by which the active compound (in this case thymol) release can be manipulated at a desirable rate. Subsequently, this may help food manufacturers or industries to design smart repellent systems for future delivery applications, including agriculture, packaging, and processing, thus ensuring food safety to consumers.

substantially damage harvestable produce or stored food commodities. It is crucial to enhance agricultural productivity. However, the characteristics of pesticides in nature are hard to manage. Pesticide is a chemical substance used to kill or prevent the growth of pests that damage or interfere with the growth of crops and horticultural produce (Rathore, 2016).

The term pesticides cover a broad range of applications, namely insecticides, herbicides, fungicides, rodenticides, nematicides, plant growth regulators, and several others (Aktar *et al*., 2009). Pests, on the other hand, are not limited to insect but also includes rats and other pest, fungi, or microbes such as bacteria and viruses that cause damage to homes, crops, and human. In summary, pesticides can be classified as chemicals, biopesticides, and genetically modified organisms, also known as transgenic plant/organism. The subtopics below explained and summarised pesticide according to its class and group that commercially available in the market.

2.2.1 Chemical Pesticide

The discovery and usage of chemical pesticides by humankind are not new. Decades ago, during the 70 A.D, "Pliny the elder" anticipated the use of arsenic to kill insects. In the late sixteenth century, the Chinese empire used arsenic sulfide. Then, in early 1800, certain inorganic compounds were used as pesticides such as sodium fluorosilicate, Paris green (copper aceto-arsenite), and zinc phosphide. At that moment, people were unaware that pesticides could persevere in the ground for more than 40 years. The Revolution of organic-synthetic pesticides was initiated in 1940. Dichloro-diphenyl-trichloroethane (DDT) was originally synthesised in 1874 and rediscovered as a common and well-known insecticide in 1939. Years later benzene hexachloride (BHC) embarked. Then, numerous compounds were manufactured and applied in the farms ever since (Rathore, 2016). Classes of pesticides can be divided based on their chemical nature, as shown in Table 2.1.

In general, it can be classified according to their chemical functionalities (organochlorines, organophosphates, carbamates, and pyrethroids), their target organisms (insecticides, herbicides, fungicides, rodenticides, nematicides, and acaricides), and their mode of action (acetylcholinesterase inhibitors, calcium channel inhibitors) (Sifakis *et al*., 2011). There are many cases reported on the hazardous aftermath of pesticide usage. Thus, the agro-industry started to look for other alternatives bringing them into the field of biotechnology. The exploitation of transgenic crops is an outcome of the biotechnology. There is also development on microbiological pesticides, which uses bacteria to control pesticide, *Bacillus thuringiensis* (Bt) that releases Bt toxin to kill the pest. However, concerns arose among the customer on the safety of genetically modified produce (Hill and Johnstone, 1998).

Table 2.1 Classification of pesticides according to their chemical functionalities

Organochlorides	DDD, DDT, DDE, chlordane, kepone, dieldrin, endosulfan, heptachlor, lindane, mirex, Methoxychlor, Toxaphene
Organophosphorus	chlorpyrifos, glyphosate, diazinon, dimethoate, malathion, methamidophos, parathion, terbufos, tribufos, trichlorfon
Carbamates	aldicarb, carbaryl, carbofuran, fenoxycarb, propoxur
Pyrethroids	cypermethrin, fenvalerate, permethrin, pyrethrin, pyrethrum, resmethrin, tetramethrin
Anilides/anilines	metolachlor, pretilachlor, propachlor, trifluralin
Phenoxy	2,4-D, 2,4-DB, 2,4,5-T, MCPA, MCPB, fenoprop
Triazines	atrazine, cyanazine, hexazinone, prometryn, propazine, simazine, terbutryn
Quartenary	diquat, paraquat
Ureas	chlortoluron, DCMU, metsulfuron-methyl, monolinuron
Others	acetamiprid, amitraz, chlordimeform, cyromazine, diflubenzuron, nithiazine, sulfonamide, thiacloprid, xanthone

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Appendix O

List of Publications and Awards

Publications

1. **Salehudin, M. H.,** & Muhamad, I. I. (2018). Effect of Graphene Oxide and Cellulose Nanofiber Towards Mechanical Properties of Polylactic Acid Based Active Packaging Using Response Surface Methodology. Malaysian Journal of Analytical Sciences, 22(6), 984-998. doi:https://doi.org/10.17576/mjas-2018-2206-08 **(Q4, IF:0.18)**

2. Muhamad, I. I., **Salehudin, M. H.,** & Salleh, E. (2015). Cellulose Nanofiber for Eco-friendly Polymer Nanocomposites. In V. K. Thakur & M. K. Thakur (Eds.), Eco-friendly Polymer Nanocomposites: Processing and Properties (pp. 323-365). New Delhi: Springer India. **(Indexed by Scopus)**

3. Muhamad, I. I., Salleh, E., Khairudin, N., **Salehudin, M. H.,** & Karim, N. A. (2015). Active and Smart Packaging Film for Food and Postharvest Treatment. In M. W. Siddiqui (Ed.), Postharvest Biology and Technology of Horticultural Crops (pp. 217-242): Apple Academic Press. **(Indexed by Scopus)**

4. Muhamad, I. I., Salleh, E., Shaharuddin, S., Pa'e, N., Selvakumaran, S., & **Salehudin, M. H.** (2018). Incorporation of Filler/Additives in Polymer Gel for Advanced Application. In V. K. Thakur & M. K. Thakur (Eds.), Polymer Gels: Science and Fundamentals (pp. 445-492). Singapore: Springer Singapore. **(Indexed by Scopus)**

5. Muhamad, I. I., Selvakumaran, S., **Salehudin, M. H.,** & Razak, S. I. A. (2015). Eco-Friendly Polymer-Based Nanocomposites for Pharmaceutical Applications Handbook of Polymers for Pharmaceutical Technologies (pp. 341-371): John Wiley & Sons, Inc. **(Indexed by Scopus)**

6. Muhamad, I. I., Zahan, K. A., Pa'e, N., **Salehudin, M. H**., Khairuddin, N., Mohd Marsin, A., . . . Salleh, E. (2019). 8 - Accelerated testing methodology for long-term life prediction of cellulose-based polymeric composite materials. In M. Jawaid, M. Thariq, & N. Saba (Eds.), Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites (pp. 149-171): Woodhead Publishing. **(Indexed by Scopus)**

7. Pa’e, N., **Salehudin, M. H.,** Hassan, N. D., Marsin, A. M., & Muhamad, I. I. (2019). Thermal Behavior of Bacterial Cellulose-Based Hydrogels with Other Composites and Related Instrumental Analysis. In M. I. H. Mondal (Ed.), Cellulose-Based Superabsorbent Hydrogels (pp. 763-787). Cham: Springer International Publishing. **(Indexed by Scopus)**

Conference and Proceedings

1 **Mohd Harfiz Bin Salehudin,** Ida Idayu Muhamad; "Effect of Graphene Oxide and Cellulose Nanofiber Towards Mechanical Properties of Polylactic Acid Based Active Packaging Using Response Surface Methodology ', The 2nd International Conference of Separation Technologies (ICoST 2017) 15-16th April 2017, Johor, Malaysia. (ISBN 978-967-0194-85-1) -Oral Presentation/Conference Proceeding. **(Indexed by Scopus)**

2 **Mohd Harfiz Bin Salehudin**, Ida Idayu Muhamad; "Mechanical and Release Properties of Polylactic Acid Based Packaging Incorporated With Graphene and Cellulose Nanofiber', International Symposium of Food Security and Sustainable Development 2017 (ISSF2017), Industrial University of Ho Chi Minh City, Vietnam 22-24 November 2017. (ISBN-978-604-920-065-6) -Oral presentation/Conference proceeding **(Non-Indexed conference proceeding)**

Awards and Recognitions

1. (REPID) Insect Repellent Packaging with Microleak Indicator. International Invention Innovation Competition, Toronto International Society of Innovation and Advanced Skills (TISIAS), Toronto Canada, 27th August 2016 **(GOLD MEDAL)**

2. Meal to Heal Designed Food for Emergency Relief. Industrial Art and Technology Exhibition (INATEX), Dewan Sultan Iskandar (DSI) Universiti Teknologi Malaysia, Johor Bahru, Malaysia, 4th -6th October 2016 **(GOLD MEDAL)**

3. Microbial Feed for Growth (MiFGro)- High Thermotolerance Pelleted Probiotic. Invention, Innovation & Design Exposition 2015 (Iidex2015). Dewan Agong Tuanku Canselor (DATC), Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia, 27th-30th April 2015 **(SILVER MEDAL)**

Patents

1. A CONTROLLED RELEASED FILM COMPOSITION (PT/6230/UTM/17) **(Patent Filed)**

2. FoBEST - FoBERG Services and Technology. Trademark (IP/TM/2018/0153) **(Patent Filed)**

Consultations

1. Agensi Nuklear Malaysia - Uni-Technologies SDN BHD (UTSB) Universiti Teknologi Malaysia, Part 1: Outsourcing Antimicrobial and Antifungal Test of LDPE Based Active Packaging at Universiti teknologi Malaysia (October 2014-March 2015) **(1st Assistant Consultant)**

2. Agensi Nuklear Malaysia - Uni-Technologies SDN BHD (UTSB) Universiti Teknologi Malaysia , Part 2: Specific Migration and Toxicity Study of LDPE Based active packaging Responsibilities (May 2015-November 2015) **(2nd Assistant Consultant)**

Program and Activities

1. Inisiatif Kerjasama Universiti, Program Transformasi Luar Bandar (NBOS4) 2016. Fasa 1 : Pengenalan teknik penanaman serai wangi secara komersial, pengenalan kaedah pengekstrakan, (3 February 2016) **(Committee)**

2. Inisiatif Kerjasama Universiti, Program Transformasi Luar Bandar (NBOS4) 2016. Fasa 2 : Demonstrasi dan Amali Pengekstrakan Serai Wangi Dengan Alat Turbo Extractor, dan Pembangunan Produk berasaskan Serai wangi (6 August 2016) **(Committee)**

3. International Workshop on Sustainability of Food Resources and Supply Chain 2016, 20th November 2016 **(Committee)**

4. International Food Safety and SECURITY 2015 26th August 2015 **(Committee)**

5. International Conference on Probiotics and Food Sustainability 2018 (ICPFS2019) Malaysia, 23-24 September 2018 **(Committee)**