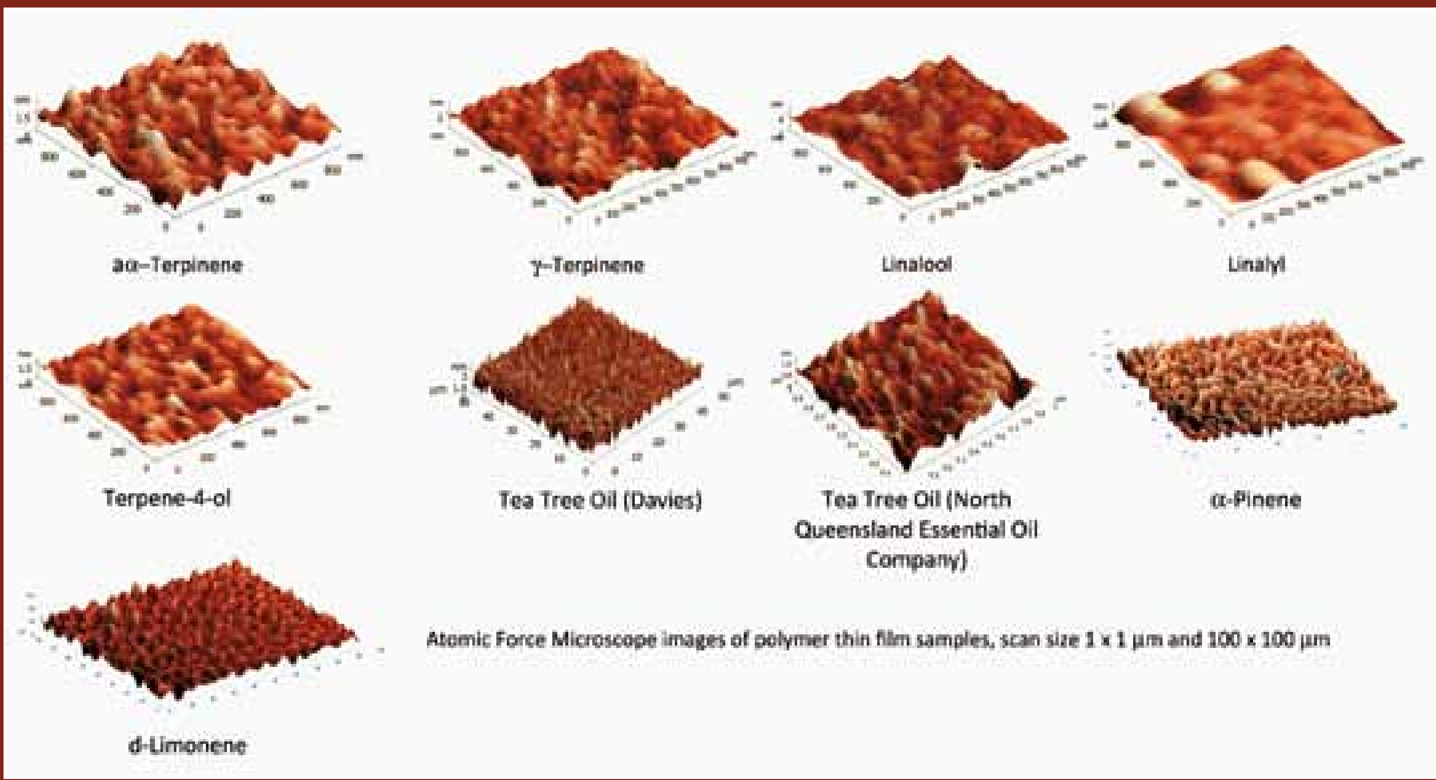
Australian Government

Rural Industries Research and Development Corporation

Fabrication of Electronic Materials from Australian Essential Oils



Atomic Force Microscope images of polymer thin film samples, scan size 1 x 1 μm and 100 x 100 μm

RIRDC New ideas for rural Australia

Australian Government

Rural Industries Research and Development Corporation

Fabrication of Electronic Materials from the Australian Essential Oils

by Mohan Jacob and Kateryna Bazaka

October 2010

RIRDC Publication No 10/193
RIRDC Project No PRJ-000795

ISBN 978-1-74254-160-0
ISSN 1440-6845

Fabrication of Electronic Materials from the Australian Essential Oils
Publication No. 10/193
Project No. PRJ-000795

.

Researcher Contact Details

Dr Mohan V Jacob Electronic Material Research Group, School of Engineering, James Cook University Townsville QLD 4811 Phone: 0747814379 Fax: 0747815177 Email: Mohan.Jacob@jcu.edu.au	

In submitting this report, the researcher has agreed to RIRDC publishing this material in its edited form.

RIRDC Contact Details

Rural Industries Research and Development Corporation
Level 2, 15 National Circuit
BARTON   ACT   2600

PO Box 4776
KINGSTON   ACT   2604

Phone: 02 6271 4100
Fax: 02 6271 4199
Email: rirdc@rirdc.gov.au.
Web: http://www.rirdc.gov.au

Electronically published by RIRDC in October 2010
Print-on-demand by Union Offset Printing, Canberra at www.rirdc.gov.au
or phone 1300 634 313

Foreword

Essential oils are utilised widely as flavouring, fragrances, components in pharmaceuticals, antiseptics and aromatherapy products and as insect repellants.

The domestic Australian market for essential oils represents only 1-2% of the world market with most producers competing on the world market[1]. Australia exported $26.8 million of essential oils in 2003-04 and imported $22.7 million[2]. To be competitive industry must look at growing the market for Australian product and improving industry and research capacity. To this end RIRDC sponsored research carried out by James Cook University over a 2 year period to investigate the *Fabrication of Electronic Materials from Australian Essential Oils*.

The aim of the project was to find a new non-pharmaceutical industrial application for essential oils and to increase the demand for Australian product. More specifically, this project investigated the fabrication of polymer material from essential oils for use in protective coatings, electronics and bio-medical materials. Bio-based polymers are environmentally friendly and inexpensive to fabricate representing an opportunity for the essential oils industry.

This report discusses a process for production of polymers from essential oils and their applications across such industries as optics, electronics, protective coatings, and bio-material industries.

Importantly this project determined that it is possible to use an environmentally friendly, inexpensive process of polymerisation to fabricate materials from essential oils in a reproducible manner with properties required by the above industries.

The scope of this research area is very high and a multitude of applications can be developed if dedicated funding for further enhancements and commercialisation is available. Therefore it is important that further funding is directed to research and development of essential oil based polymers for specific devices, for example flexible electronic devices and implementation as a biomedical coating. This will enable the product to be proven and developed in novel end products increasing the demand for Australian essential oils.

This report was funded from RIRDC Core Funds provided by the Australian Government.

This report, an addition to RIRDC's diverse range of over 2,000 research publications, forms part of our Essential Oils and Plant Extracts R&D sub-program which aims to support the growth of a profitable and sustainable essential oils and natural plant extracts industry in Australia.

Most of RIRDC's publications are available for viewing, downloading or purchasing online at www.rirdc.gov.au. Purchases can also be made by phoning 1300 634 313.

Craig Burns
Managing Director
Rural Industries Research and Development Corporation

About the Author

A/Prof. Mohan Jacob, James Cook University, was the principal investigator of this project. He was a James Cook University Principal Research Fellow and ARC Australian Research Fellow at the time of this project.

Ms. Kateryna Bazaka was the research assistant for this project and a PhD student.

Acknowledgments

We are grateful to RIRDC for funding this research work. We acknowledge the support provided by G R Davies, North Queensland Essential Oils and Australian Botanical Products. We are very thankful to Dr. Roslyn Prinsley for assistance.

Contents

Tables

Figures

Executive Summary

What the report is about

This document reports the findings and recommendations of the RIRDC funded study, "Fabrication of Electronic Materials from Australian Essential Oils". This project was undertaken to facilitate an expansion of the Australian Essential Oils Industry through the development of novel applications in the Electronic and Bio-Materials Industries.

Who is the report targeted at?

The findings presented in this report will provide value broadly across the Australian Essential Oils Industry, and more particularly to the growers involved in the production of tea tree, lavender and other essential oils.

Background

The essential oil industry in Australia is characterised by a low producer base and a highly competitive global market. Many essential oils currently traded are produced in developing, low cost countries and are thus traded at prices which are below the cost at which they can be produced in Australia[1]. In order for Australian producers to be competitive, the industry must continue to look to value adding or production/cost efficiencies. Through this particular project, we focus on value adding by fabrication of polymer thin films from essential oils and their applications across industries.

Traditionally polymers were thought of as insulators however the discovery that certain modified plastics can transmit electricity has opened up a myriad of opportunities. New technologies could soon see organic polymers replacing silicon (the foundation for semiconductors) in applications such as transistors, TV display screens and solar cells. Future opportunities for organic polymers are varied, from flexible computer and TV displays which can be rolled up like a newspaper to cheaper and flexible solar cells.

The advantages of organic polymers are that they are cheap, easily processed, light and flexible. There is a need to move on from inorganic and expensive semiconductors such as silicon to these cheaper, safer and environmentally friendly polymer materials in the electronics and biomedical industries.

Importantly, research is required into suitable materials for use as polymers and devices for advancement of this exciting area.

This project focuses on the suitability of essential oils to produce polymers as an initial scoping study. This innovative research will have positive outcomes for the Australian essential oil industry through potential value adding of the product and novel application in the electronics and bio-materials industries.

Aims/objectives

The main objective of this project was to find a new industrial application for essential oils and hence increase the demand for Australian produced essential oils.

The project aims were to:

- Fabricate high quality Plasma Polymerised thin films from Australian essential oils (tea tree, lavender and eucalyptus) as compared to d-limonene and alpha-pinene.

- Study the electrical and optical properties of the polymer thin films and find suitable applications for the films
- Test the polymer thin films as a protective/anticorrosive layer in devices.

Methods used

The polymerisation of the essential oils was carried out by the RF plasma polymerisation. A number of characterisation tools were used to identify the material properties. These included Atomic Force Microscope, Ellipsometer, FTIR Spectrometer, UV-Vis Spectrometer, Electrometer etc.

Results/key findings

Several essential oils, namely tea tree oil, sandalwood oil, eucalyptus oil, alpha-pinene, d-limonene, lavender oil (a separate PhD project) and five major components of tea tree oil were tested. With the exception of sandalwood oil, all oils investigated were successfully polymerised.

Importantly, this project determined that it is possible to use an environmentally friendly, inexpensive process of polymerisation to fabricate materials from essential oils in a reproducible manner with properties required by the optics, electronics, protective coatings, and bio-material industries.

This project delivered the following specific findings:

- Thin films of a wide range of thickness (from 200nm to 2000nm) can be fabricated indicating suitability to various optical and electrical applications - from thin robust plastic electronic displays to lightweight plastic solar cells.

- All the fabricated thin films were transparent to the optical wavelengths indicating their suitability for use as transparent protective coatings and encapsulating technologies to significantly prolong the lifetime of organic electronic devices.

- Across all samples, the refractive index indicated the material could be used in optics in many lens applications, including high refractive index lenses (the refractive index varied from 1.53 to 1.7 in the wavelength range 200 nm to 1000nm). As the organic polymer is flexible, can conduct electricity and does not impair vision it could be used in novel technology such as smart contact lenses with built-in pressures sensors to monitor conditions like glaucoma.

- The fabricated polymer thin films were very smooth (roughness below 1nm), uniform and defect free, an important characteristic for use in microelectronics. In terms of surface properties and smoothness, the materials fabricated from tea tree oil and its components were found to be superior to that of alpha-pinene and d-limonene.

- The hardness of the material varied across materials tested, with Terpenine-4-ol exhibiting the highest hardness value. Furthermore, the hardness of the material could be varied by changing the input RF power. Materials fabricated at low RF power were very soft and at high RF power were hard. Therefore, it is possible to fabricate materials of different hardness from essential oils to suit the environment the polymer is destined for.

- The chemical properties of the monomer and polymer were studied to understand the stability of the material, particularly in terms of the variation of the contents between different sources. The properties were not affected by the slight variations in the base material properties that are likely to occur. This is important given that each oil contains a multitude of components that can vary depending on the region where the oil is harvested, method of harvesting, season etc. The ability to achieve films with consistent properties irrespective of base material origin or time of harvest is essential for successful integration into the manufacturing process. The properties of the material were also not altered with time and hence could be used in many protective layer coating applications.

- The electrical properties were studied by looking at the energy gap of the material. All the materials investigated exhibited energy gap in the range of 2.6 to 3.1 eV putting the materials in the semiconducting range.

- Additionally, this study indicated that Polymer thin films fabricated from tea tree oil are biocompatible in mice. These results, albeit in mice, are very interesting and indicate the potential for essential oil polymers to be used in bio-medical devices such as organ implants.

Implications for the stakeholders

The implication for stakeholders, in particular agricultural producers, the electronics industry and the biomaterials industry, are as exciting as they are varied.

The study identified a new non-pharmaceutical market for the Australian Essential Oils Industry that has potential to increase demand for the produce and be of economic benefit to growers.

The novel organic polymer materials discussed in this study are likely to find applications across multiple industries such as:

- protective coatings (i.e. encapsulating technologies, anti-reflective coatings, barrier layers, etc);

- electronics (organic light-emitting diodes, organic field effect transistors, organic RF tags, etc), and

- bio-medical materials (coatings for organ implants, drug delivery vessels, etc).

Further research is currently being conducted by undergraduate and postgraduate students in this area at James Cook University aiming to:

- optimise the manufacturing process;

- study the properties and likely applications of individual oil components, and

- incorporate the materials into electronic devices.

The next stage is advancing very well and we are expecting to develop a prototype flexible electronic device by 2010 using the polymers we developed. The exponential growth and advancement of the flexible electronic circuit manufacturing industry demands more environmentally friendly materials and therefore it is important to invest in research and development of essential oil based polymers for specific devices. This will enable the product to be proven and developed in novel end products increasing the demand for Australian essential oils.

Recommendations

It is our recommendation that since the scope of this study is very broad; a more detailed study be carried out to understand the polymerisation process and the feasibility of utilising these organic polymers in biomedical devices. For application in industry, it is essential to investigate the polymerisation of individual components and their physical, chemical, mechanical, biomedical properties.

Another area of research which has to be thoroughly investigated is engineering of materials which can retain the antimicrobial property of the original oil.

In order to support future development in the Fabrication of Electronic Materials from Australian Essential Oils, James Cook University has established the basic facilities and infrastructure to pursue advanced and systematic research in this area. Industry support is critical in advancing this area of research. Only through such collaborations can novel applications for essential oils truly be investigated and applied. Further funding would enable such research to continue and effectively contribute to industry.

Introduction

The essential oil industry in Australia is characterised by a low producer base and a highly competitive global market. Australian producers, although recognised for their high quality oil are faced with higher labour costs than overseas competitors[3]. In order for Australian producers to be competitive the industry must continue to look to value adding for a high end product or production/cost efficiencies. Through this particular project we focus on value adding by fabrication of polymer thin films from essential oils and their applications across such industries as optics, electronics, protective coatings, and bio-material industries.

The total polymer industry around the world is worth billions of dollars and employs millions of people. The polymer materials are used in a myriad of applications, ranging from normal domestic applications to the state of the art technologies.

Most of the disciplines of science and technology have applications for polymer materials, including electronics and biomedical industries. Most of the commercially available polymers are chemically derived and are not biodegradable. Furthermore, synthetic polymers are hazardous to the environment and are thought to contain carcinogenic materials. Bio-based polymers, on the other hand, lead towards a sustainable and environmentally friendly future.

Traditionally polymers were thought of as insulators however the discovery that certain modified plastics can transmit electricity has opened up a myriad of opportunities. New technologies could soon see organic polymers replacing silicon (the foundation for semiconductors) in applications such as transistors, TV display screens and solar cells.

Future opportunities for organic polymers include flexible computer and TV displays which can be rolled up like a newspaper, cheaper and flexible solar cells and polymer based lighting with potential to be more efficient than fluorescent lights.

The advantages of organic polymers are that they are cheap, easily processed, light and flexible and a wide range of substrates can be utilised. There is a need to move on from inorganic and expensive semiconductors such as silicon to these cheaper, safer and environmentally friendly plastic materials in the electronics and biomedical industries.

This project focused on the fabrication of polymer thin films from essential oils and their applications across such industries as optics, electronics, protective coatings, and bio-material industries.

The RF/AC/DC polymerisation technology utilised in this project is an effective tool to fabricate thin films and offers a high degree of control over the physical and chemical properties of the resultant polymer thin films. The advantages of this approach are that:

- No special safety requirements are needed within the production environment.
- The films produced by this technique have the advantage of having a smooth surface and being pinhole free, properties that essential in electronics applications

This innovative research will have positive outcomes for the Australian essential oil industry through potential value adding and novel application in the electronics and bio-materials industries. The findings presented in this report will be of particular benefit to growers involved in the production of tea tree, lavender and eucalyptus oils.

Objectives

The main objective of this project was to find a non-medical application for essential oils and hence encourage Australian farmers to increase the production of essential oils. The project aimed to:

Fabricate high quality Plasma Polymerised thin films from Australian essential oils (d-limonene, alpha-pinene, tea tree, lavender and eucalyptus oils);

Study the electrical and optical properties of the polymer thin films and find suitable applications for those, and

Test the polymer thin films as a protective/anticorrosive layer in devices.

Methodology

The polymerisation of the essential oil was carried out by the RF plasma polymerisation. A number of characterisation tools were used to identify the material properties.

These included Atomic Force Microscope, Ellipsometer, FTIR Spectrometer, UV-Vis Spectrometer, and Electrometer.

Plasma polymerisation takes place in a low pressure and low temperature plasma that is produced by a glow discharge through an organic gas or vapour. Plasma polymerisation depends on monomer flow rate, system pressure and discharge power among other variable parameters such as the geometry of the system, the reactivity of the starting monomer, the frequency of the excitation signal and the temperature of the substrate. Various plasma polymer deposition methods such as DC, AF-magnetron and RF are discussed by prominent scientists like Yasuda and Biderman. The overall power input in plasma polymerisation is used for two things: for creating the plasma and for the fragmentation of the monomer. Plasma is a direct consequence of the ionization of the gases present in the reactor and fragmentation leading to polymerization is a secondary process. As increasing voltage is applied between two parallel plate electrodes, an abrupt increase in current implies the breakdown of the gases in between the electrodes. High-energy electrons collide with hydrocarbon molecules to produce positive ions, C+, CH+, CH2+ etc., excited molecular or atomic fragments, radicals, new compounds etc. Positive ions are accelerated towards a cathode and produce secondary electrons in the process. Excited atoms emit photons and create glow. Since remaining positive ions also flow towards the cathode, the most intense glow in the reactor is at the cathode.

The positive column (space spread between the cathode and anode) containing electrons, ions and radicals, is electrically neutral. This is plasma but it is also referred to as a glow discharge. The major polymer deposition occurs onto the substrate surface that makes contact with the glow. Not all glow discharges yield polymer deposition though. The plasmas of Ar, Ne, O2, N2 are non-polymer forming and as such can be used to maintain the glow in the vacuum chamber while the monomer vapour is used efficiently for polymer conversion. A comprehensive review on glow discharge polymerisation was written by Yasuda.

Although plasma polymerisation occurs predominantly in the glow region, the volume of glow is not always the same as the volume of the reactor. Both the volume of the glow discharge and the intensity of the glow also depend on the mode of discharge, the discharge power and the pressure of the system. Under plasma conditions, the monomer molecules undergo fragmentation and are deposited as polymer molecules, and a non-polymer forming by-product like hydrogen gas is evolved. The plasma polymer does not contain regularly repeating units; the chains are branched and are randomly terminated with a high degree of cross-linking. The chains adhere well to solid surfaces. Pyrolysis results of plasma-polymerised organosilicones suggest a cationic oligomerization from the electron bombardment of the monomer followed by UV initiated cross-linking in solid phase to give the final product. Chemical reactions that occur under plasma conditions are generally very complex and nonspecific in nature. Glow discharge polymerisation of organic compounds seems to proceed by the free radical mechanism and the extent of ionization is small. The combination and recombination of these radicals form high molecular weight compounds called polymers. The free radicals are trapped in these films which continue to react and change the polymer network over time. Since radicals are formed by fragmentation of monomer, some elements and groups of the original monomer may be absent from the resulting polymer. The degree of fragmentation depends on the electron density or input power and monomer flow rate. Cross-linking reactions occur on the surface or in the bulk of the newly forming plasma polymer between oligomers. The film may also change over time due to reactions with oxygen and water vapours in atmosphere.

Although the polymer deposition rate is linearly dependent on the current density, the minimum wattage necessary for the plasma polymerisation of a given monomer differs significantly from that of another monomer. This is because discharge power needed to initiate glow discharge varies from one monomer to another. The cross-linking in plasma polymer increases with the intensity and energy of bombarding ions. If the inter-electrode distance is too large, then, at a given applied potential, the local electric field in the plasma will be too low to deliver sufficient energy to the electrons. The atoms in a vacuum travel in straight lines. If there is residual gas in the chamber, the atoms will collide with the gas and would go in all directions losing some of their energy as heat. At higher pressures, the collisions will cause atoms to condense in air before reaching the substrate surface giving rise to powder deposits. A magnetically enhanced audio frequency discharge is reported to have some advantages for plasma polymerization. Magnetron, as this is called, is a properly shaped, intense magnetic field which traps electrons in an electric field and cause them to move in spirals instead of straight lines. This increases the frequency of collision between electrons and gas molecules, causing more fragmentation, higher deposition rates and denser polymer deposits at lower pressures.

Experiments

A custom-manufactured glass deposition chamber was used to fabricate the RF polymer thin films of different essential oil based monomers. Copper electrodes are capacitive coupled to the reactor so that RF energy is delivered into the deposition chamber. The distance between the electrodes was adjusted to 10 cm in order to achieve optimal deposition conditions. The RF generator used operated within the 13.56 MHz (an ISM frequency band). We have employed different substrate materials such as glass, quartz, silicon, Teflon etc. The substrates were washed in a solution of Extran and distilled water. The substrates were subjected to a further 30 minute ultrasonic clean in distilled water heated to 50° C followed by a Propan-2-ol rinse and air-dry. The deposition chamber and the substrates were flushed with argon for 1 minute to remove oxygen. The chamber was then evacuated to achieve a pressure of 300 mTorr. The RF energy was applied across the electrodes such that a glow discharge could be maintained within the electrodes. The monomer was released gradually into the chamber – the glow was maintained by controlling the monomer flow by means of a vacuum stop cock. Deposition was performed at room temperature, pressure of 300 mTorr and at different RF powers to achieve the polymerisation. During the polymerization, the energy of most electrons is enough to break virtually any chemical linkage pertinent to organic molecules and organic structures containing main group elements, with higher energies needed to dissociate unsaturated bonds. A result of the plasma state processes, the high molecular weight networks generated from collisions and subsequent recombination of the charged and neutral species with each other and the surfaces that constrain the discharge, possess structural attributes that significantly differ from the ones of the original monomer. Such structures are not built from repeating monomer units and are likely to possess unsaturated, branched and cross-linked architecture.

Results

The main objective was to understand the feasibility of polymerising the essential oils under investigation and to study the physical and chemical properties of the resultant polymer materials. The typical properties investigated for this research area are:

- *Thickness:* Various applications call for films of specific thickness.
- *Transparency*: Transparency is important to determine whether the material could be used in transparent protective coatings and encapsulating technologies that can significantly prolong the lifetime of organic electronics devices.
- *Refractive index:* The refractive index indicates whether the material could be used in optics or lens applications.
- *Energy Gap:* The energy gap measures the ability of the organic material to conduct electricity.
- *Surface Profile:* Smooth and defect free surfaces are essential if thin films are to be used in microelectronic devices.
- *Hardness:* How material is affected by its environment will be decisive of where the material is applied – if material is likely to disappear as a result of its environment it can be applied as a sacrificial layer in the electronic devices; if, on the other hand, it is robust such material can be used as a protective coating or a buffer layer.
- *FTIR:* The ability to achieve films with consistent properties irrespective of base material origin or time of harvest is essential for successful integration into the manufacturing process.

Summary of Results

Several essential oils, such as tea tree oil, sandalwood oil, eucalyptus oil, alpha-pinene, d-limonene, lavender Oil (a separate PhD project) and five different major components of two essential oils were tested. **With the exception of sandalwood oil, all oils investigated were successfully polymerised. The investigations showed the properties of the fabricated polymer thin films could be tailored to suit different optical and electrical applications.** We have repeated all the tests mentioned in this report at least 20 times for each monomer.

Thickness: Thin films of a wide range of thickness were fabricated, ranging from 200nm to 2000nm. The film thickness could be varied by changing the deposition conditions to meet the requirements for a given application. Therefore, films derived from essential oils can be used in a range of applications from thin robust plastic electronic displays to lightweight plastic solar cells. In addition, flexible ultrathin organic films will allow for further miniaturization of the electronic devices.

Transparency: All the fabricated thin films were transparent to the optical wavelengths and the film thickness varied from 200nm to 2000nm. Essential oil based polymers can therefore be used in applications where visual transparency is essential. This includes transparent protective coatings and encapsulating technologies that can significantly prolong the lifetime of organic electronic devices.

Refractive Index: Across all samples, the refractive index varied from 1.53 to 1.7 in the wavelength range 200 nm to 1000nm. The refractive index is above that of the glass surface and results show that the material could be used in glasses and lenses. As the organic polymer is flexible, can conduct electricity and doesn't impair vision it could be used in novel technology such as smart contact lenses with built-in pressures sensors to monitor conditions like glaucoma. Organic polymers are traditionally used to make contact lenses however in recent times new technology has seen the modification of organic polymers so that they can conduct electricity. This enables sensors to be incorporated into the organic polymer. These type of sensors could obviate the need for constant visits to the physician to test eye pressure. Results also indicate that it is feasible to achieve consistent material properties even if there is a variation in constituents of the essential oil across the sources. The properties were not affected by the slight variations in the base material properties.

Energy Gap: The electrical properties were studied by looking at the energy gap. All the materials investigated exhibited energy gap in the range 2.6 to 3.1eV putting the materials in the semiconducting range.

Surface Profile: The surface profile showed that the fabricated polymer thin films were very smooth (roughness around 1 nm or smaller), uniform and defect free. The materials fabricated from tea tree oil and its components were superior to that of alpha-pinene and d-Limonene. Smooth and defect free surfaces are essential if thin films are to be used in microelectronic devices.

Hardness: The hardness of the material varied across materials tested, with Terpenine-4-ol exhibiting the highest hardness value. The hardness of the material varied from 0.11 to 0.65 for the samples fabricated under the normal deposition conditions. Furthermore, the hardness of the material could be varied by changing the input RF power. Materials fabricated at low RF power were very soft whilst the ones manufactured at high RF power were hard. Therefore, materials of different hardness could be fabricated from the essential oil to meet the demands of a particular application.

FTIR: The chemical properties of the monomer and polymer were studied. The polymer thin films show very consistent and stable material properties. There was no inconsistency observed in terms of chemical, optical or electrical properties between the samples fabricated based on monomers from different sources. This is important given that each oil contains a multitude of components that can vary depending on the region where the oil is harvested, method of harvesting, season etc. The properties of the material were also not altered with time and hence could be used in many protective layer coating applications.

Biocompatibility: Additionally this study indicated that Polymer thin films fabricated from tea tree oil are biocompatible in mice. Biocompatibility refers to the body's response to a bio device (i.e. from biodegradable sutures to cochlear implants) as well as the device's response to the physiological conditions when implanted into tissue. These results, albeit in mice, are very interesting and indicate the potential for essential oil polymers to be used in bio-medical devices such as organ implants.

Optical Transparency

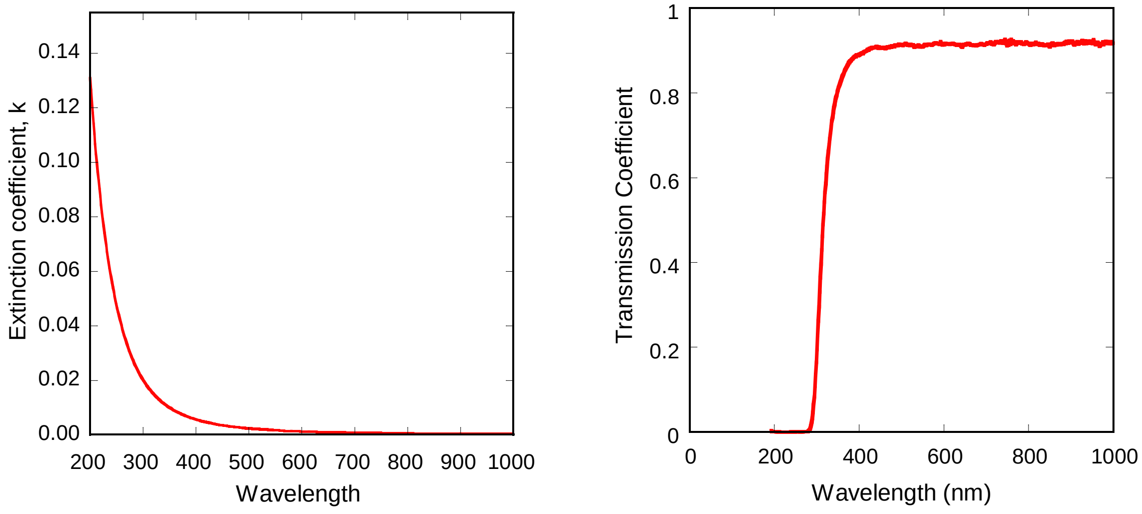


Fig. 1 Extinction coefficient and optical transparency of the fabricated polymer thin film based on Tea Tree Oil

All the samples fabricated from different essential oils or their components were tested to determine the optical transparency of the fabricated material. The graphs in Fig.1 clearly show that the polymer sample derived from essential oil is indeed transparent over the visible range. As all of the investigated samples showed similar properties, **the materials fabricated from essential oils are promising materials for optical coatings.**

Refractive Index

The refractive index of a medium is a measure for how much the speed of light is reduced inside the medium. The optical properties of materials, transparent materials in particular are directly related to their refractive index. As an example, light reflects partially from surfaces that have a refractive index different from that of their surroundings; light rays change direction when they cross the interface from air to the material, an effect that is used in lenses and glasses. We have investigated the optical properties of the material using ellipsometry.

The refractive indices of all the materials fabricated were studied and highest and lowest values as a function of wavelength are reported in Fig. 2. In terms of the refractive index, the discrepancy between the samples obtained from different components of the essential oil (or the base monomer) is very small. The maximum difference between the highest and lowest refractive index material is only 0.05 (or 3%). **This shows that it is feasible to achieve consistent material properties even if there is a variation in constituents of the essential oil across the sources.**

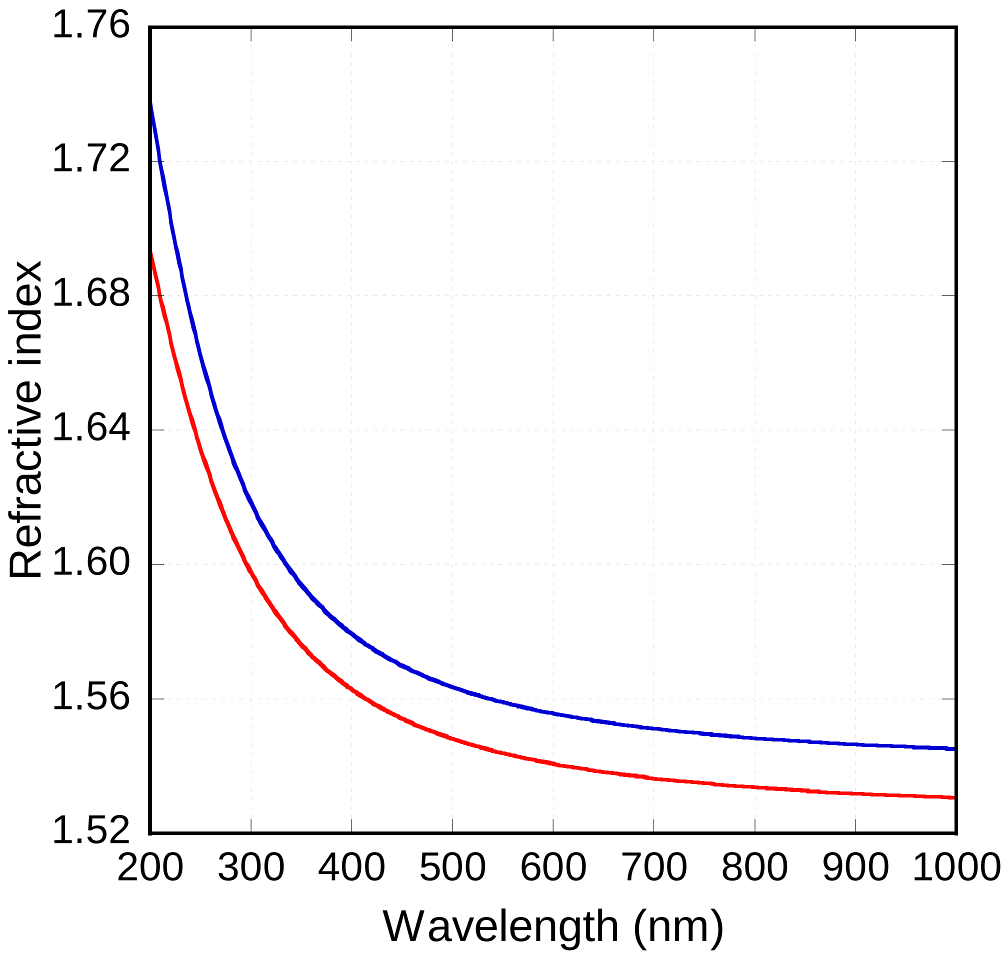


Fig. 2 Refractive indices of fabricated Tea Tree Oil polymer thin film samples (with individual values falling within the indentified range).

Energy Gap

The energy gap of the material can be estimated using the optical absorption coefficient data obtained from spectroscopic analysis or by applying a Tauc-Lorentz relation to ellipsometric data. Method of a deriving the energy gap from spectroscopic data is illustrated in Fig. 3. Both spectroscopic and ellipsometric techniques we used for the estimation of the optical energy gap of the polymer films. Table 1 contains the examples of the energy gap values obtained for the tested samples. It is clear there **is a potential for these materials in the organic semiconducting applications.**

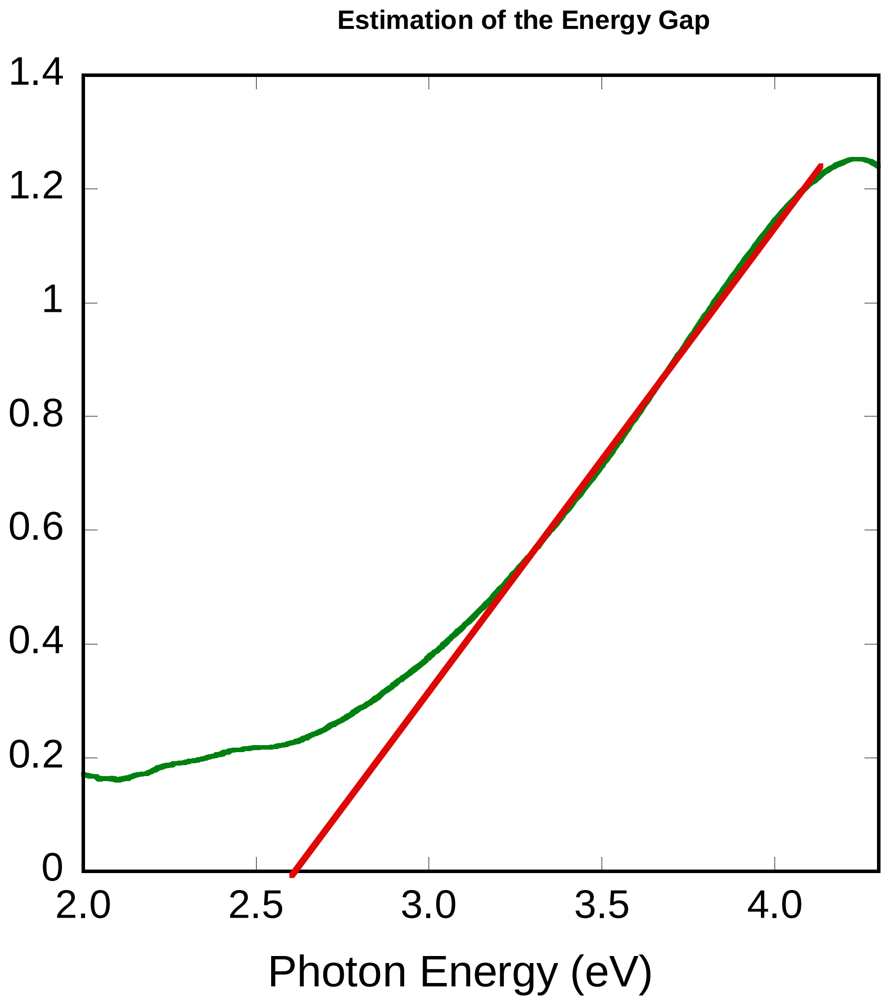


Fig. 3 Classification of the material's conductivity group through estimation of energy gap from the absorption spectrum

Table 1: Electrical Conductivity Study: The Energy Gap (eV) for different oil components

Linalool	2.92
Linalyl	2.78
Terpene-4-ol	2.66
α-Terpinene	2.94
γ-Terpinene	3.03
Tea Tree Oil (Davies)	2.85
Tea Tree Oil (North Queensland Essential Oil Company)	2.82

Hardness Evaluation using nano-indentation

The hardness of the material can be estimated by using nano-indentation. This involves applying a certain load to the surface of the sample and measuring the indent size. The hardness is calculated as a function of load force and contact area, where the contact area is not directly measured but inferred from the contact depth using a 6th-order tip area function. Several indents were performed at different loading forces. An example of a series of indentations resulting from the application of different forces is presented in Fig. 4.

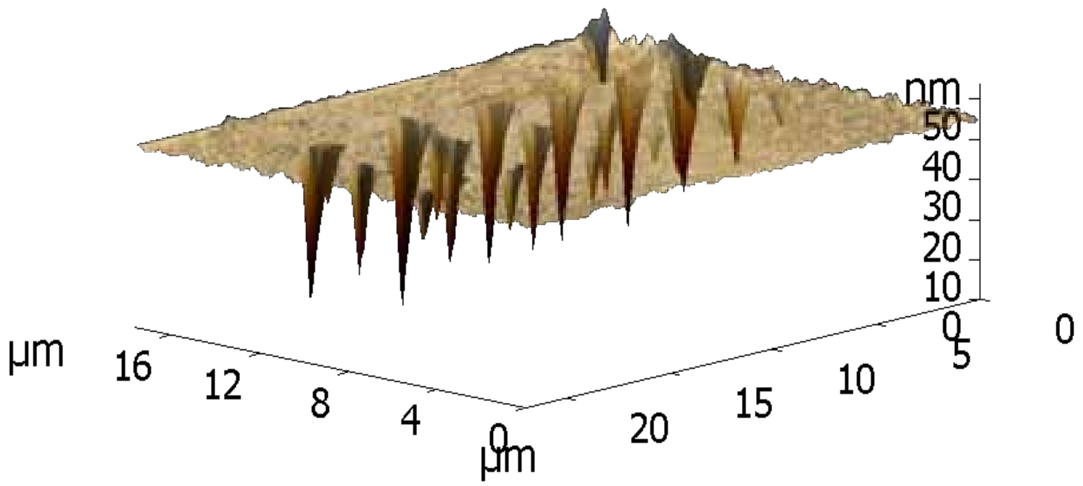


Fig. 4 AFM image of a series of nanoindentations performed on the thin polymer film sample

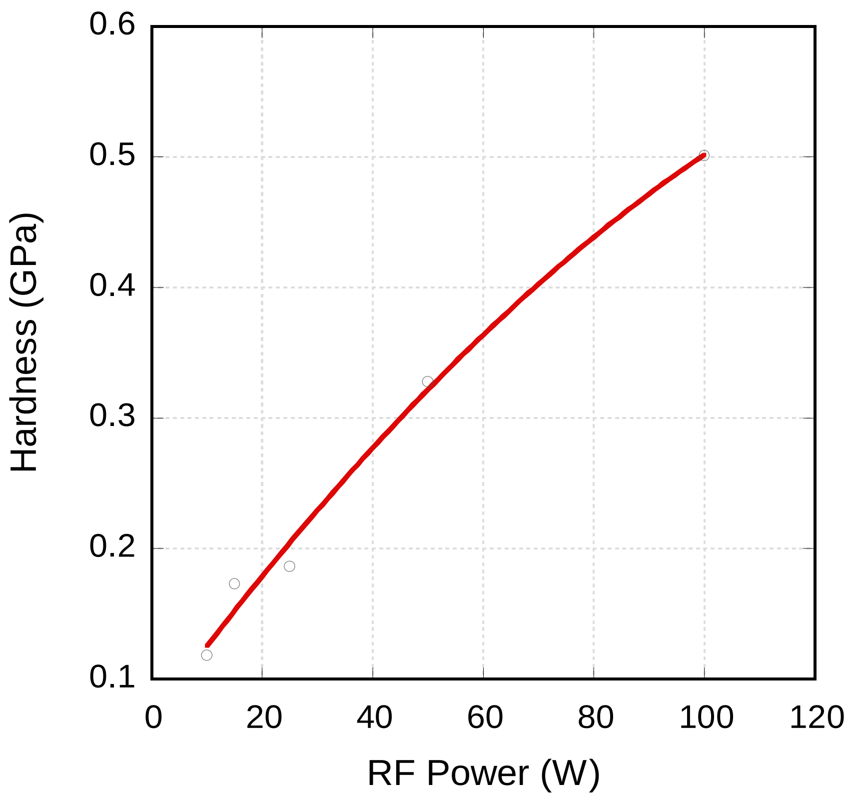


Fig. 5 Typical hardness profile of the tea tree oil polymer thin films (thickness lower than 20nm)

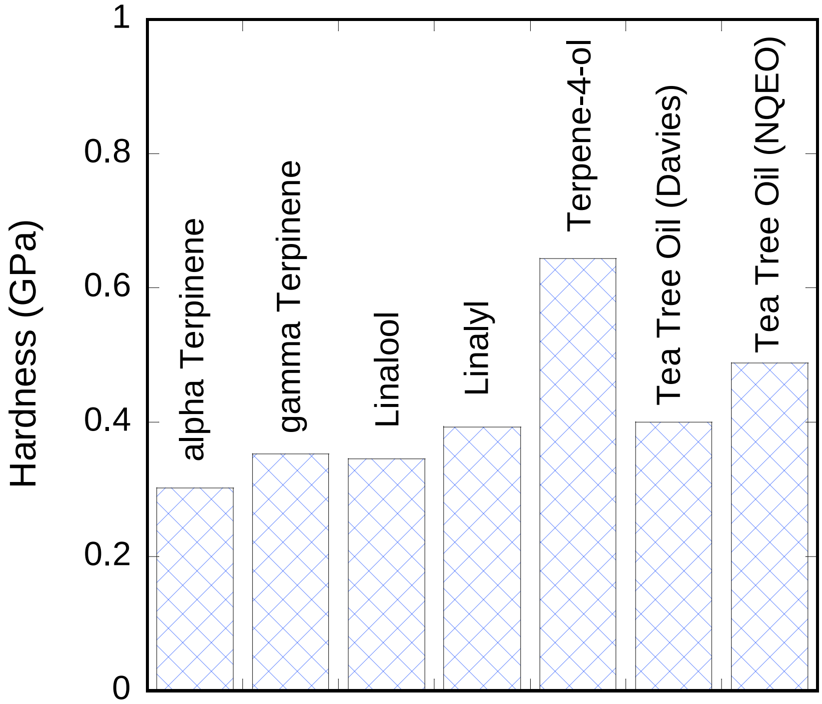
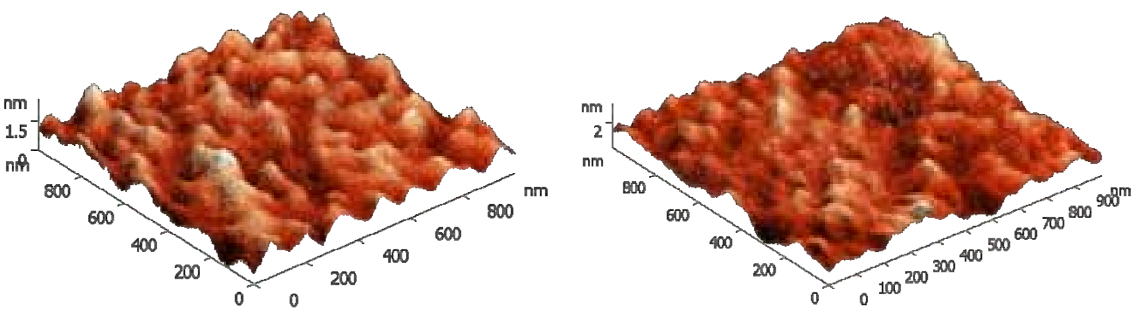


Fig. 6 Hardness of the polymer thin film materials derived from different components of the essential oil

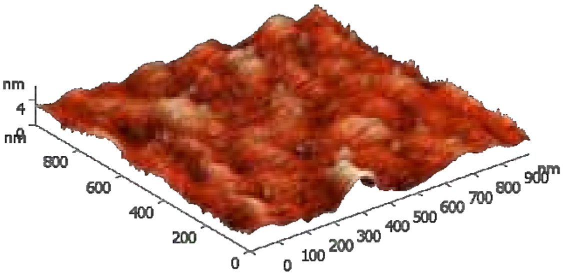
Surface profile of different polymer samples

The surfaces of samples were imaged using the NT-MDT NTEGRA Prima Atomic Force Microscope (AFM) in semi-contact mode. The scan area was either 100 x 100 μm or 1 μm x 1 μm. The surface profile varied from sample to sample.

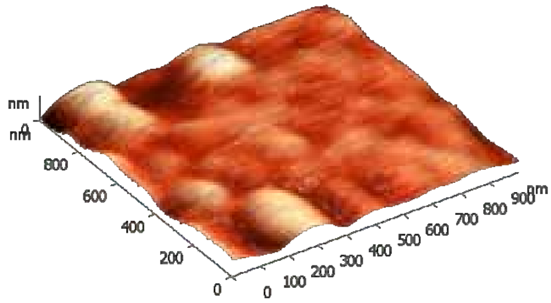
Surface profile of different polymer samples fabricated from essential oil and its components are shown in Fig. 7. The roughness of most of the thin film surfaces is less than 1 nm substantiating the feasibility of very smooth, uniform and pin hole free thin films. The two exceptions are alpha-pinene and d-limonene, for which the surface roughness was very high (around 200nm).



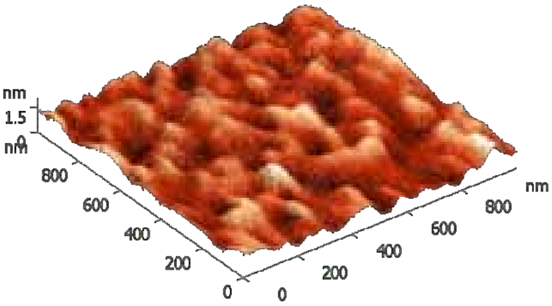
aα–Terpinene γ–Terpinene



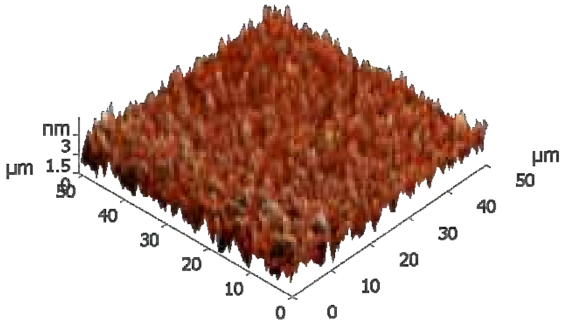
Linalool



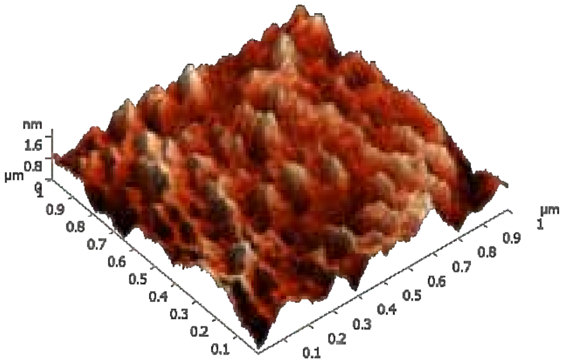
Linalyl



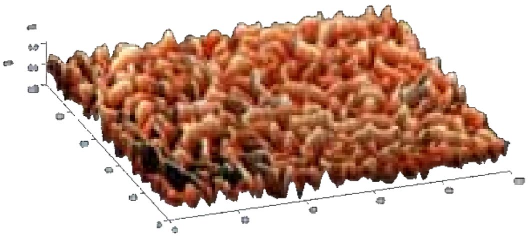
Terpene-4-ol



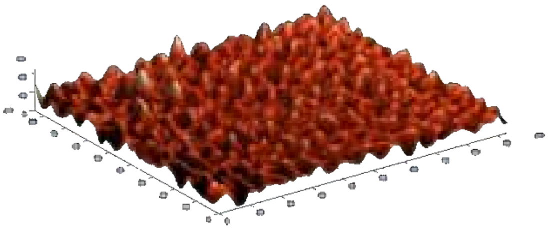
Tea Tree Oil (Davies)



Tea Tree Oil (North Queensland Essential Oil Company)



α-Pinene

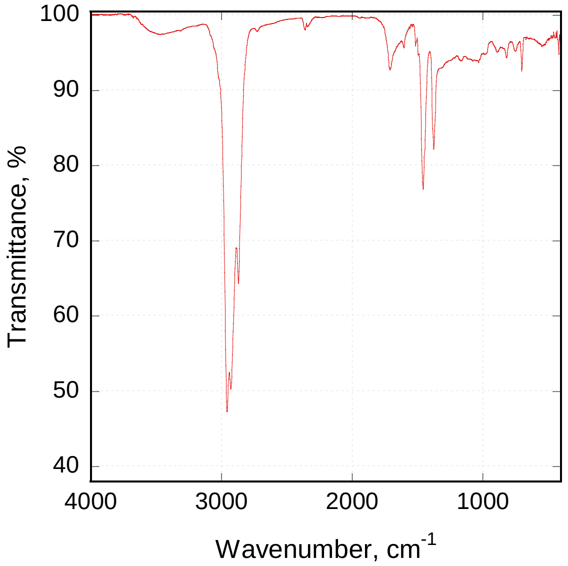


d-Limonene

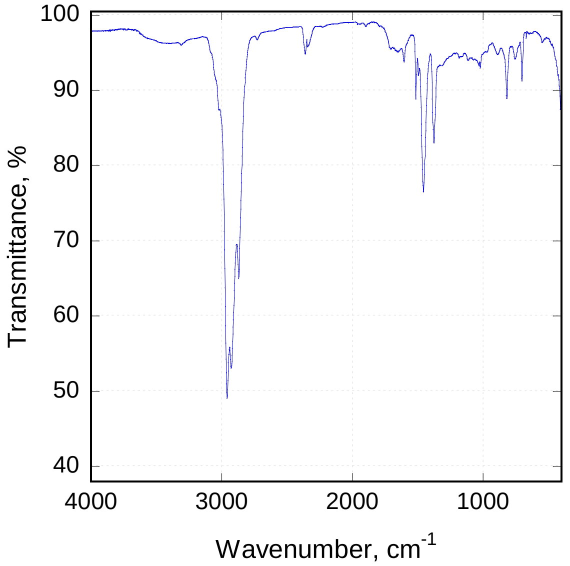
Fig. 7 AFM images of polymer thin film samples, scan size 1 x 1 µm and 100 x 100 µm

Chemical Characterization using FTIR

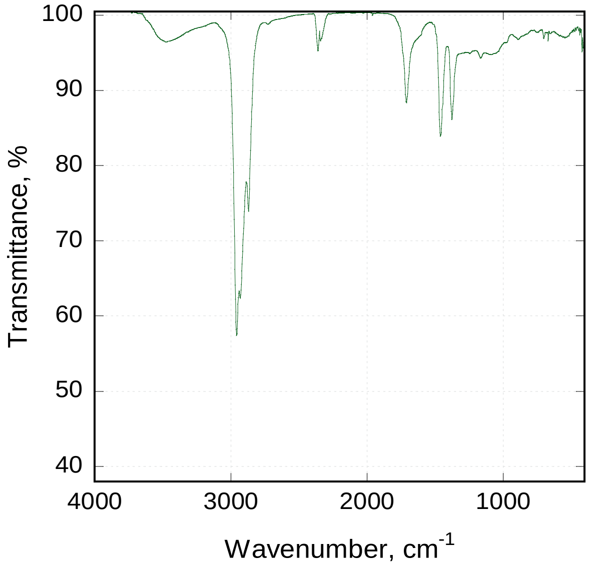
The chemical characterization is an important tool to identify the types of bonds and the feasibility of obtaining consistent polymer samples from the various precursors. The FTIR spectra clearly illustrate the polymerisation of the monomer. Several samples were studied and the absorption peaks substantiate that **the chemical structure was not significantly different between polymer samples**. Furthermore, it is possible to control the oxygen content in the sample by changing the fabrication conditions.



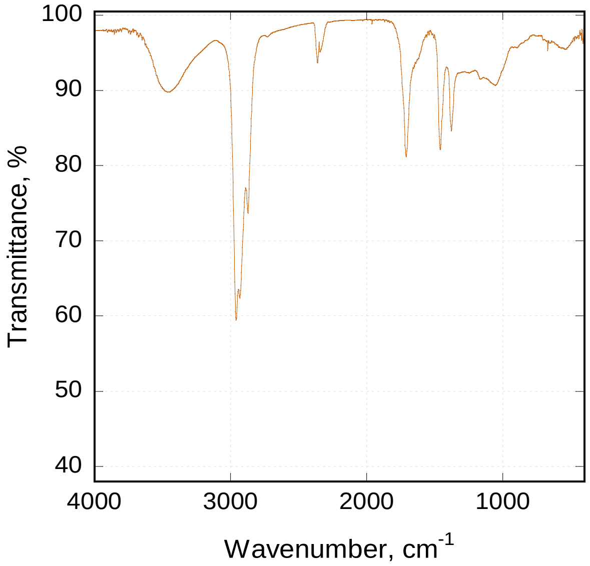
α-Terpinene



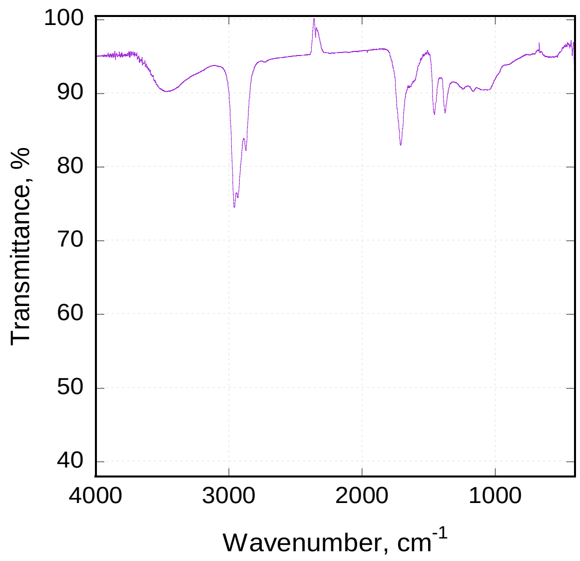
γ-Terpinene



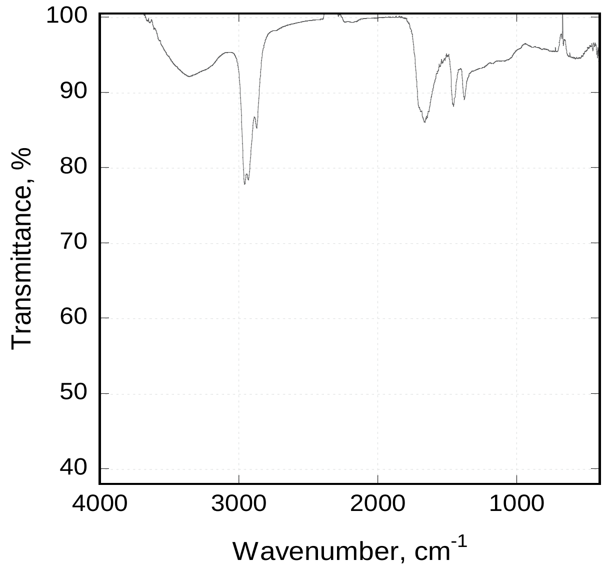
Linalool



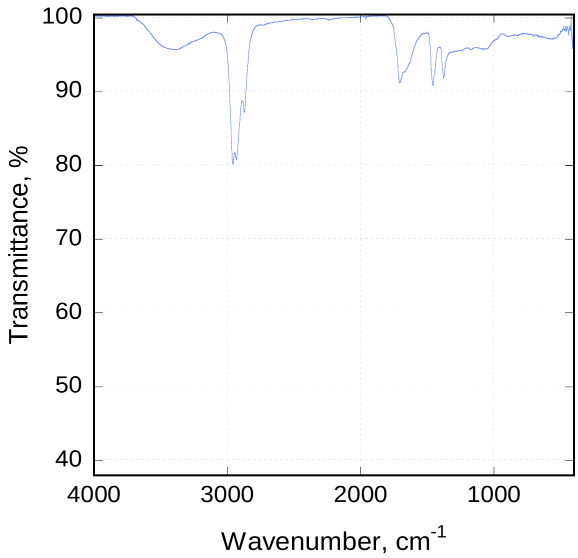
Terpene-4-ol



Linalyl



Tea Tree Oil (Davies)



Tea Tree Oil (NQEO)

Fig. 8 FTIR spectra of polymer thin films fabricated from different components of the oil

Bio-compatibility

Bio-compatibility encompasses the host responses to medical devices as well as the material responses to physiological conditions. The problems encountered when exposing medical devices to the human body include deposition of proteins, cells and tissue growth leading to failure, toxic responses, abnormal cell/tissue responses, and device degradation leading to failure.

This study investigated the Biocompatibility of the essential oil polymer fabricated materials. 90 samples were used for the experiments (30 samples each deposited at 25, 50 and 75 W RF power). These samples (90) and control (30) were implanted in 120 mice. Out of every batch, 10 mice were examined after 3 days, 14 days and 28 days respectively.

Table 2: Mice numbers as assigned to thin polymer films deposited at 25, 50 and 75W

Time (days)	**Plasma Polymer Variant (Inserted into MOUSE)**				
	25W	**50W**	**75W**	**Control**	**Total**
3	10	10	10	10	**40**
14	10	10	10	10	**40**
28	10	10	10	10	**40**
Total	**30**	**30**	**30**	**30**	**120 MICE**

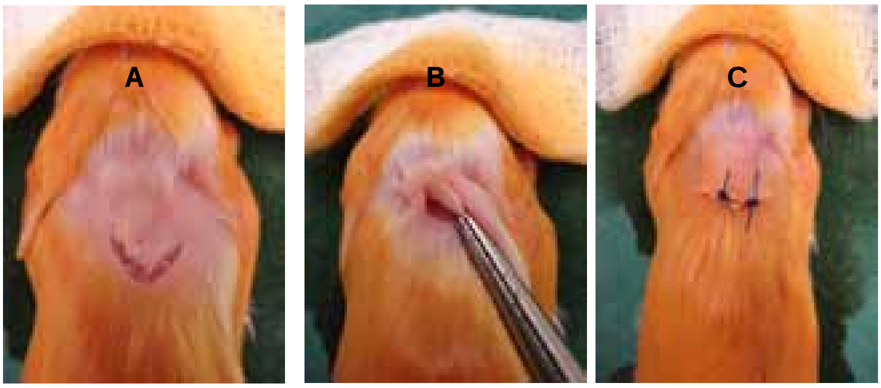


Fig. 9 Sample insertion process

The results of this study confirm that the fabricated polymer is a biocompatible material i.e. it did not produce an unwanted host or material response. In a few mice sinus formation was observed (Table 3) even though it was not critical.

Table 3: Sinus formation in mice as a result of the sample insertion

Sinus Formation/ Sample				
25W	**50W**	**75W**	**Control**	**Total**
0/10	0/10	0/10	0/10	**0/40**
1/10	5/10	2/10	0/10	**8/40**
1/10	0/10	1/10	0/10	**2/40**
2/30	**5/30**	**3/30**	**0/30**	**10/120 MICE**

As presented in Table 3, 2 mice showed sinus in the 25W polymer film group, 5 mice showed sinus in the 50W polymer film group and 3 mice showed sinus in the 75W polymer film group. The sinus formed in the 50W healed after 28 days by itself.

A detailed study on a larger number of mice is necessary in the future to prove the potential of using the tea tree oil based polymer as a biocompatible material for animal implants.

Further Outcomes

In addition to the scientific results presented above this project has:

- Helped foster a new collaboration between James Cook University, Royal Melbourne Institute of Technology, Swinburne University and the Australian Nuclear Science and Technology Organisation.
- Helped train our next generation with three PhD, one Masters and three undergraduate students working on the project. Two undergraduate students also completed their Honours theses as a part of the project.
- Helped develop a new Radio Frequency Polymerisation facility at James Cook University. At this stage, the facility is fully functional and is available for polymer thin film fabrication and optical characterisation.
- Led to the following accepted/submitted publications, conference presentations:

1) Easton, Jacob and Krupka, “Non-destructive complex permittivity measurement of low permittivity thin film materials”, Measurement Science and Technology, vol. 18 pp. 2869–2877 (2007).
2) M.V. Jacob, C.D. Easton, G.S. Woods, C.C. Berndt, Fabrication of a novel organic polymer thin film, Thin Solid Films, doi:10.1016/j.tsf.2007.07.151
3) C. D. Easton and M. V. Jacob, “Evaluation of the different methods used for determining the energy gap and optical band gap of amorphous polymer thin films”, IUMRS-ICAM: 10th International Conference on Advanced Materials October 8-13, 2007.
4) M. V. Jacob, C. D. Easton, G. S. Woods, and C. C. Berndt, "Fabrication of a novel organic polymer thin film," Thin Solid Films, vol. 516, pp. 3884-3887, 2008.
5) C. D. Easton, M. V. Jacob, and J. Krupka, "Non-destructive complex permittivity measurement of low permittivity thin film materials," Measurement Science & Technology, vol. 18, pp. 2869-2877, 2007.
6) C. D. Easton, M. V. Jacob, R. A. Shanks, and B. F. Bowden, "Surface and chemical characterisation of polyLA thin films fabricated using plasma polymerisation," Chemical Vapor Deposition, In press.
7) C. D. Easton and M. V. Jacob, "Optical Characterisation of RF Plasma Polymerised Lavandula Angustifolia Essential Oil Thin Films," Thin Solid Films, In press.
8) C. D. Easton and M. V. Jacob, "Ageing and thermal degradation of plasma polymerised thin films derived from Lavandula angustifolia essential oil," Polymer Degradation and Stability, In Press.
9) C. D. Easton, M. V. Jacob, and R. A. Shanks, “Plasma polymerisation of the constituents of Lavandula angustifolia essential oil,” Polymer Engineering and Science (under submission).

10) C. D. Easton, M. V. Jacob, and R. A. Shanks, “Fabrication and characterisation of polymer thin-films derived from cineole using radio frequency plasma polymerisation,” Polymer, In press.

11) C. D. Easton and M. V. Jacob, “Adhesion and solubility characteristics of plasma polymerised thin films derived from Lavandula angustifolia essential oil,” Journal of Applied Polymer Science, Under review.

12) K. Bazaka, M.V. Jacob, Radio Frequency Plasma polymerization of non-synthetic Terpinen-4-ol, Materials Letters, in Press.

PhD Thesis: Christopher David EASTON Development of Lavender oil Based Polymer Films for Emerging Technologies, Submitted to James Cook University, April 2009.

Conclusions

Overall conclusion of the project is that essential oil based polymers and the polymers derived from the individual components of the essential oils have excellent properties which could be tailored for material in electronic and biomedical applications. The fabricated materials have not exhibited any noticeable degradation and materials coated on different surfaces were not affected by any environmental variations. The fabricated materials have potential applications in organic electronics, bio-medical applications and protective coatings.

Table 4: Price Comparison (Essential Oil prices are based on Sydney Essential Oil Company or Australian Botanical Products Pvt Ltd and Chemicals are based on Sigma Aldrich Website).

Chemical/ Essential Oil	Price ($)/Litre
Tea Tree Oil	88
Lavender Oil	66
Eucalyptus Oil	31
d-Lemonene	20
α-Pinene	20
Terpene-4-ol	120
α-Terpene	130
γ-Terpene	130
Linalool	100
Linalyl	100
Aniline (Chemical)	239
Thiophene (Chemical)	1000
Pyrrole (Chemical)	490

Table 4 shows the price of Essential Oil and 3 popular Chemicals used in laboratories for similar research. Essential Oil based monomers for the fabrication of ‘*organic polymers*' could assist the production of cheaper polymers and also reduce the environmental impacts. A market prediction for these chemicals cannot be provided at this stage since only very few ‘*organic polymer*’ devices are available in the market at this stage. Currently the Organic Electronics industry market worth $700M but by 2015, the market is predicted to grow to $400Billion. By 2015 there will be big need for Organic Polymer Electronics and therefore we should expect a high demand for organic polymers.

Implications

The study indentified a new non-pharmaceutical market for the Australian Essential Oils Industry. This market has the potential to increase demand for the produce and be of economic benefit to growers.

Novel materials discussed in this study are likely to find applications across multiple industries as protective coatings, encapsulating technologies, electronics and bio-medical materials to name but a few. Electronics applications include organic field effect transistors (the basic building blocks of all electronic devices), light emitting diodes, higher efficiency solar cells, etc. In terms of biomedical applications, these materials have a potential to be used as bio-compatible coatings for organ implants and in drug delivery systems.

This study showed it is possible to use an environmentally friendly, inexpensive process of polymerisation to fabricate materials from essential oils in a reproducible manner with properties required by the above mentioned applications.

Typically the diversity of the essential oils industries has meant there is relatively little potential for generic R&D[2]. However this research demonstrates valued technologies for a number of essential oils thereby spreading the cost of R&D. The polymers developed from a range of sources showed no inconsistency in terms of chemical, optical or electrical properties.

Further research is currently being conducted by undergraduate and postgraduate students in this area at James Cook University aiming to:

- optimise the manufacturing process;
- study the properties and likely applications of individual oil components,;
- incorporate the materials into electronic devices such as organic field effect transistors and RF identification tags

The next stage of this project is advancing with a prototype flexible electronic device expected to be produced by 2010 utilising essential oil polymers. Further research support is needed to progress in this research area. More postgraduate Scholarships, research grants to maintain the experimental system and supply of essential oil will definitely enhance the development of the environmentally friendly non-synthetic polymer thin films from essential oils, and thereby finding novel applications.

New products generally face a long development period, including considerable testing for safety and effectiveness. Similarly markets take time to develop unless the product is a response to a clear need[2]. The market potential for essential oil polymers would appear positive given the shift from silicon based electronic materials to more sustainable environmentally friendly materials. Based on further biocompatibility tests there may also be an excellent market for essential oil polymers as bio materials. In order to progress these research findings it is essential that industry, researchers and funding organisations work collaboratively towards developing this exciting product. Ultimately the essential oils industry will benefit from a high end value added product with the potential to grow the market for Australian product.

Recommendations

A detailed preliminary study was carried out as part of this RIRDC project. It is our recommendation that since the scope of this study is very broad; a more detailed study is carried out to understand the polymerisation process and the feasibility of utilising these organic polymers in practical applications, in particular in biomedical devices.

For application in industry, it is essential to investigate the polymerisation of individual components and their physical, chemical, mechanical, biomedical properties. Another area of research which has to be thoroughly investigated is engineering of materials which can retain the antimicrobial property of the original oil. Essential oils are considered to have excellent antimicrobial and anti-inflammatory properties and if we can retain these in fabricated polymers the scope of their application is tremendous. Further research is needed to conduct more bio-medical studies.

In the interim it is recommend that this report be provided to the industry peak body – the Essential Oil Producers Association of Australia for dissemination of these exciting preliminary results to stakeholders.

In order to support future development in the Fabrication of Electronic Materials from Australian Essential Oils, James Cook University has established the basic facilities and infrastructure to pursue advanced and systematic research in this area. Industry support is critical in advancing this area of research. Only through such collaborations can novel applications for essential oils truly be investigated and applied. Further funding would enable such research to continue and effectively contribute to industry.

References

1. Colton B (1999),Emerging Opportunities in Agricultlure, The Australian New Crops Newsletter, Issue No 11, January 1999.

2. Rural Industries Research and Development Corporation (2008), Essential Oils and Plant Extracts: Five Year R&D Plan 2008-2013, RIRDC Publication No 08/053

3. Rural Industries Research and Development Corporation (1995), Proceedings of the Essential Oils Planning Workshop, Hobart, Occasional Paper, No. 96/1.

4. New Scientist (2008), Smart contact lens feels the pressure of glaucoma, Internet site: http://www.newscientist.com/article/dn14285-smart-contact-lens-feels-the-pressure-of-glaucoma.html

Fabrication of Electronic Materials from Australian Essential Oils

by Mohan Jacob and Kateryna Bazaka

RIRDC Pub. No. 10/193

This RIRDC research was undertaken to facilitate an expansion of the Australian essential oils industry through the development of novel applications in the electronic and bio-materials industries.

The findings presented provide value across the Australian essential oils industry and more particularly to the growers involved in the production of tea tree, lavender and other essential oils.

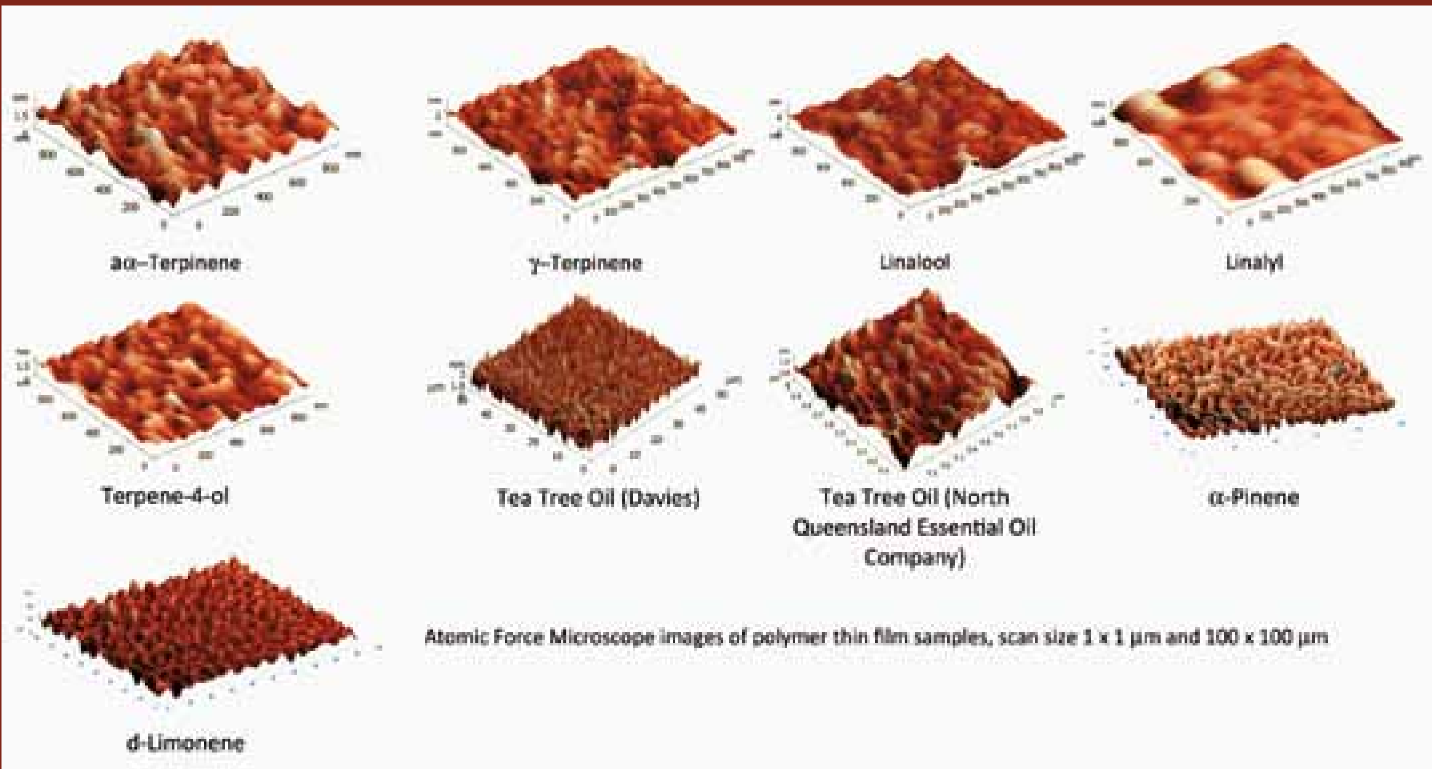
Several essential oils, namely tea tree oil, sandalwood oil, eucalyptus oil, alpha-pinene, d-limonene, lavender oil (a separate PhD project) and five major components of tea tree oil were tested. With the exception of sandalwood oil, all oils investigated were successfully polymerised.

Importantly, this research determined that it is possible to use an environmentally friendly, inexpensive process of polymerisation to fabricate materials from essential oils in a reproducible manner with properties required by the optics, electronics, protective coatings, and bio-material industries.

This report is an addition to RIRDC's diverse range of over 2,000 research publications and forms part of our Essential Oils and Plant Extracts Program, which aims to support the growth of a profitable and sustainable essential oils and natural plant extracts industry in Australia.

Most of RIRDC's publications are available for viewing, downloading or purchasing online at www.rirdc.gov.au.

Purchases can also be made by phoning 1300 634 313.



Atomic Force Microscope images of polymer thin film samples, scan size 1 x 1 μm and 100 x 100 μm

Most of RIRDC's publications are available for viewing, free downloading or purchasing online at www.rirdc.gov.au.

Purchases can also be made by phoning 1300 634 313.

www.rirdc.gov.au

Contact RIRDC:
Level 2
15 National Circuit
Barton ACT 2600

PO Box 4776
Kingston ACT 2604

Ph: 02 6271 4100
Fax: 02 6271 4199
Email: rirdc@rirdc.gov.au
web: www.rirdc.gov.au
Bookshop: 1300 634 313