1.0 Overview of Results and Accomplishments

Overall Objectives of the Research Chair in Green Chemistry and Engineering Research Program

The objectives of the research program were grouped under three fundamental objectives, and a number of applied objectives. The fundamental objectives were envisioned to remain valid throughout the program; applied objectives were designed to be changed by the Research Advisory Committee (RAC), in response to emerging opportunities arising from the fundamental objectives, markets, competitive intelligence, new knowledge in the field, etc. The objectives of the original research program:

Fundamental Objective 1) A fundamental understanding of the crystallization of lipid and modified lipid networks to direct the modification of natural molecular ensembles and processing conditions in order to design crystal network structures with specific physical properties in a stable thermodynamic state. The research proposal detailed three different types of lipid-derived chemical compounds to be focussed on (CLASSES 1 – 3).

Applied Objective 1: Development of shortenings, margarines, and confectionery lipid networks which contain significantly reduced (or zero) trans fatty acids, as well as reduced saturated fatty acids and which deliver solid-like characteristics with maximum, healthful oil.

Applied Objective 2: Development of unique, non-toxic, biodegradable, cost competitive vegetable-oil replacements for functional waxes for various commercial uses.

Fundamental Objective 2) Development of chemical modification techniques that can alter the chemical functionality of lipids, so as to produce high value chemicals, functional monomers and functional supra-molecular assemblies, including nano-scale delivery systems. The research proposal detailed five different types of chemical compounds to be synthesized (CLASSES 1 – 5).

Applied Objective 3: Development of unique non-toxic, biodegradable, cost effective and environmentally friendly lipid-based lubricants that exhibit excellent lubrication properties.

Fundamental Objective 3) A fundamental understanding of the inter-relationships between the chemical functionality of monomers, processing conditions, derived structural hierarchies, and the resultant physical functionality of the polymer networks created from lipid-derived monomers.

Progress Made over 5 Year Period of the Chair's Program

Fundamental Objective 1

CLASS 1 Compounds (triacylglycerides or TAGs)**: 33 different TAGS were synthesized.** The interaction of the various TAG molecules in commercially produced and utilized lipids are still poorly understood, although they play crucially important roles in determining the health impacts of fat-containing foods, and their interactions determines the physico-chemical functionality which motivate their use in both food and non-food applications. Our work has added important perspectives to this understanding, and generated intellectual property with significant commercial promise. The pure phase transformation behavior of 1,3 –dioleyl-2-stearoyl-sn-glycerol (OSO); 1,2 –dioleyl-2-stearoyl-sn-glycerol (OOS); 1,3 –distearoyl-2-oleyl-sn-gycerol (SOS); 1,2-distearoyl-3-oleyl-sn-glycerol (SSO); 1,2,3-propanetriyl trioctadecanoate (SSS); 3-palmitoyl-1, 2-distearoyl-*sn*-glycerol (PSS) and 1, 2-dipalmitoyl-3-stearoyl-*sn*-glycerol (PPS) were studied. The binary phase transformation behavior of PSS and SSS; 1,3 dipalmitoyl-2-stearoyl-sn-glycerol (PSP) and 1,2-dipalmitoyl- 3-stearoyl-sn-glycerol (PPS); 1, 3-dilauroyl-2-stearoyl-sn-glycerol (LSL) and 1, 2 – dilauroyl-3-stearoyl-sn-glycerol (LLS) and 1, 3 dicaproyl- 2-stearoyl-sn-glycerol(CS) and 1,2–dicaproyl- 3-stearoyl-sn-glycerol(CCS) were also elucidated. The time-resolved phase transformation behavior of a TAG was elucidated in detail, using standard XRD, for the first time. The work above has allowed us to contribute an understanding of how symmetry and chain-length mismatch of TAGs in a molecular ensemble affects both crystallization as well as important physical functionality parameters such as hardness and melting and highlighted the influence of the viscosity of the TAG ensemble in the liquid state to the resulting crystallization pathway and development of structural hierarchy.

Cross-metathesis of vegetable oils with various olefins is currently used to produce modified TAGs, petrochemical replacements and entirely new chemicals in a biorefinery approach, especially pioneered by our industrial partners, Elevance Renewable Sciences. A thorough study of the crystallization, melting, phase transformation behavior and physical properties of these modified TAGs are yet to be investigated in the field. We have completed a study of the crystallization, structure and physical properties of 3-stearoyl-1, 2-didecenoyl-*sn*-glycerol (SDD), 3-decenoyl-1, 2-distearoyl-*sn*-glycerol (DSS), 1,3-didecenoyl-2-stearoyl-sn-glycerol (DSD), 1,3-distearoyl-2-decenoyl-sn-glycerol (SDS) and propane-1,2,3-triyl tris(dec-9-enoate) (DDD) and found remarkably useful properties for a variety of applications; these are typical modified TAGs produced when a vegetable oil is cross metathesized with ethylene or 1-butene. A number of recently filed patents exploits this knowledge to produce functional waxes.

A database relating molecular structure, processing conditions, derived hierarchies of structure and physical properties was built and integrates our own work, text-mining, query and data-mining from the literature, and visualization capabilities. This tool has helped to extract relationships not otherwise readily obvious. In part, this work has demonstrated that lipid networks grow via specific growth modes, which can be selected for by the choice of the crystallizing molecules and processing conditions.

CLASS 2 Compounds: a) Jojoba-like monoesters (JLEs) and b) Diesters

a) Seven (7) JLEs were synthesized. The crystallization, melting, evolution of solid fat content, crystallographic structure, thermo-gravimetric stability and viscosity-temperature behavior of these compounds were studied as a function of chain length and symmetry. It was found that their physical properties were predictive as a function of structure. This is the first comprehensive study of the relationships between molecular structure (symmetry, chain lengths and chain length mismatch), viscosity, crystallized structures and crystallization kinetics of lipid-based monoesters, and the work has led to the design of superior renewable lubricant base oils.

b) Fifty-seven (57) diesters were synthesized. Synthesis routes were developed and crystallization, melting, evolution of solid content and crystallographic structure was studied as a function of chain length, symmetry and odd/even carbon numbers. Physical properties were found to be predictable as a function of structure. The unsaturated compounds crystallized at lower temperatures than their monoester counterparts with a similar number of carbons and presents further opportunity to design superior, high-viscosity lubricants. Furthermore, chemical and thermal stability of the diesters synthesized was predictively related to their structure. The diester E-didec-9-enyl octadec-9-enedioate, was studied in detail, and included in the lubricant patents filed. As with aliphatic monoesters, this is the first comprehensive study of linear lipid based diesters. Our study of saturated aliphatic diesters motivated the investigation of this class of compounds as potential phase change energy storage materials. We conducted a study on the potential of using similar materials in mixtures to store energy and improve the efficiency of Compressed Air Energy Storage (CAES) facilities and found them to be very suitable. Three patents have now been filed: the synthesis and use of the diester compounds, the use of the diesters as energy storage materials in food storage, and their use in CAES facilities.

CLASS 3 Compounds: Branched derivatives of a) TAGs and b) mono and di-esters

a) No branched TAG derivatives synthesized. A comprehensive, reproducible toolbox for testing of the structure and physical properties of waxes was developed and TAG based, TAG-oligomer based and petroleum derived waxes investigated. It was concluded that for competitive purposes, the investigation of the wax-like properties of oligomers of TAGs and their derivatives was more urgent. Therefore, TAG oligomers (a new class of compounds, additional to what was described in the research proposal: CLASS 6), were synthesized under Fundamental Objective 2, and their phase behavior, structure and physical properties investigated. Intellectual property was also developed as a result of this work; enabling the production of functional waxes with tunable properties from TAG oligomers.

b) Twenty-five (25) branched derivatives of seven (7) monoesters, eight (8) branched derivatives of the diester E-didec-9-enyl octadec-9-enedioate and three (3) branched derivatives of 1,6-hexyl dioleate were studied in detail with respect to crystallization, melting, evolution of solid fat content, crystallographic structure, thermo-gravimetric stability and viscosity-temperature behavior. The physical properties and supra-molecular structure of these branched derivatives were investigated as a function of number and length of branching, number and position of hydroxyl groups, symmetry and base monoester chain lengths. These compounds were found to have extremely low temperatures of crystallization; as low as -90 °C. They also demonstrated predictive and superior viscosity-temperature profiles and high thermal stabilities.

Applied Objective 1

One of the significant barriers to zero-trans, lowered saturated fatty acid solid edible products such as shortenings, margarines and confections is the inability of the tenuous solid network formed to bind the increased amounts of liquid oil present. As a result, the products “oil off” and phases separate. Based on the phase behavior studies conducted under fundamental objective 1, the team conducted an analysis of the thermodynamic and kinetic basis of the oil binding capacity of specific saturated TAGs. This work resulted in a fundamental understanding of the way these TAGs bind oil, and a comparative ranking of their function in binding oil. This work was supported by the development of a new method for measuring oil binding capacity. This work has helped tremendously in assisting our team with oil binding issues in waxes, and supported the development of the filed patents on waxes. Furthermore, our team is working with Archer Daniels Midland and with high-oleic acid soybean oil feedstock in developing a range of commercial products utilizing this knowledge.

Applied Objective 2

The development of vegetable oil-based waxes based on natural triacylglyceride architecture results in limited functionality. A comparative assessment of seven commercially available waxes by the comprehensive toolbox we developed demonstrated that natural TAG-based waxes rank at the bottom of the performance range. A comparative assessment of waxes from soybean oil and paraffin supported this conclusion. However, TAG-oligomer based waxes demonstrated the potential to offer a platform which may be able to compete with performance waxes. Therefore a series of TAG oligomers with varying degrees of *cis/trans* ratios and degree of oligomerization were synthesized and evaluated. One study focussed on the structure and wax functionality of highly *cis* TAG oligomers. The results motivated studies focussed on TAG dimers and quatrimers with specific *cis*/*trans* ratios, which led to technology that allows competitive, high performance waxes to be produced. Being able to produce specific oligomers requires an understanding of metathesis of unsaturated TAGs in vegetable oils – the team has investigated the control of product composition of metathesized triolein as a function of reaction conditions. In addition to the work on oligomers of TAGs, recent work by the group on metathesis-modified TAG systems has led to technology which has produced beeswax analogues. This work exploited fundamental work discussed above under fundamental objective 1, and further utilized fractionation approaches to develop competitive beeswax replacements.

Fundamental Objective 2

Synthesis of five classes of compounds was targeted in the original research plan. The numbers of each class of compounds synthesized are summarized in the table below. Of note, an additional 6 classes of compounds have been synthesized apart from the original five classes envisioned in the research plan. Classes 6, 7 and 8 were motivated by Applied Objective 2; i.e. the design of functional, non-toxic waxes from vegetable oils. Class 9 was motivated by a new applied objective discussed and approved by the Research Advisory Committee; the synthesis of polyols and polyurethane foams from by-products of cross-metathesis reactions of ethylene and butene with vegetable oils such as soybean, canola and palm. Class 10 was motivated by work under fundamental objective 3, focussed on the synthesis of superior thermoplastic polyesters from lipids. Class 11 was motivated by work conducted under fundamental objective 3, focussed on pursuing an understanding of the relationships between structure and function of lipid-derived polyesteramides. Classes 12 and 13 were motivated by our work on CLICK thermoplastics, conducted under fundamental objective 3.

Class #		**Name**	**# Synthesized**
1		Triacylglycerides (TAGs)	33
2	2a	Jojoba-like monoesters (JLEs)	7
	2b	Jojoba-like diesters (JLDs)	57
3	3a)	Branched triacylglycerides	None
	3b) i)	Branched derivatives of JLEs	25
	3b) ii)	Branched derivatives of JLDs	13
4	4a	Simple aliphatic diols	3
	4b	Diester and tetraester diols	2
	4c	Polyester diols	13
5	5a	Diisocyanates	23
	5b	Poly-diisocyanates	6
6		TAG Oligomers	23
7		Linear Jojoba-like oligomers	6
8		Modified TAGs	6
9		TAG polyols	26
10		ω-hydroxy fatty acids and methyl esters	8
11		Amines	4
12		Diazides	1
13		Dialkynes	3

Applied Objective 3

Significant progress was made on this applied objective, based on the team's work with jojoba-like monoesters and their branched derivatives and branched derivatives of the diester E-didec-9-enyl octadec-9-enedioate, resulting in the filing of two patents to protect the findings. This family of compounds demonstrate superior viscosity-temperature profiles compared to the state of the art for lipid-derived and synthetic lubricants, industry-leading cold flow characteristics (with crystallization temperatures sometimes lower than -90 °C), high thermal stability and high hydrolytic and oxidative stabilities. As envisioned in the research plan, this work has been extended to linear diesters and their branched derivatives. ERS has already commercialized two very successful renewable lubricant formulations in 2014, and we are currently engaging with them to develop strategy for commercialization of the learning from our work.

Fundamental Objective 3

Polyurethanes and Nano-Composites: Using a novel lipid-derived diisocyanates developed by the team whilst at the University of Alberta, a study was made of the structure and function of entirely lipid-based thermoplastic polyurethanes (TPU). This thermoplastic demonstrated promising strength and thermal properties but very poor elongation at break. The team therefore focussed on enhancing the physical properties of thermoplastics through the incorporation of nano-scale cellulose in the polymeric matrix and was successful in demonstrating that the elongation at break could be significantly improved by the inclusion of nanocellulose in the matrix. A subsequent multidisciplinary collaboration with colleagues in India and Brazil resulted in the contribution of a number of publications to the field of nano-scale polymeric composites. A novel, long-chain unsaturated diisocyanate was also synthesized entirely from lipids using green reaction conditions, and another set of entirely lipid-based polyurethanes produced. A focus on the synthesis of polyols and of thermoset polyurethanes was continued with a focus on modified triacylglycerides produced through the cross-metathesis of vegetable oils with ethylene and butene; this approach has resulted in the synthesis of polyols which produce superior flexible and rigid polyurethane foams, and filing of multiple patents.

Polyester(amides) and Polyester(urethanes): In an effort to extend the properties of both polyesters (typically low mechanical strength and thermally labile) and polyamides (limited biodegradability), aliphatic diols, with zero, two, four and six ester groups were synthesized from lipids and utilized in the synthesis of thermoplastic polyesteramides. This work established predictive relationships (un-established before) between the structure and physical properties of the polyesteramide films that are important to the design of polyesteramides with specific functionality. Furthermore, it was found that the polyesteramides produced were superior to all others derived from lipids reported in the literature, and comparable to the properties displayed by petroleum-derived polyesteramides. To similarly extend the properties of both polyesters and polyurethanes, a series of five polyesterdiols were prepared, with molecular weights ranging from 534 to 1488 and utilized with lipid-derived diisocyanates to produce polyesterurethanes. This work established predictive relationships between crystalline structure and physical properties and soft/hard segment ratios, ratios of ester to urethane bonds, and relative chain lengths of the polyester segments. The work also resulted in superior polyesterurethane thermoplastic coatings, compared to those reported in the published literature. The findings suggested additional strategies to maximise physical functionality by modifying structure, and so this work has resulted in efforts to modify the structure of the polyurethane hard and soft segments, this latest work producing polyester urethanes with vastly superior strengths and elongations at break. The work has been protected by the filing of several patents.

Polyesters: The group has focussed earlier on use of lipids in the ring opening polymerization of polycaprolactone and polynonanolactone. This early work led to a renewed interest in lipid-based polyesters which could be developed into high-strength polymers, and recently the group has been successful in designing polyesters from lipids with strengths as high as 750 MPa, and resulting in the filing of several patents**.** In addition, we have recently investigated the effect of chain length mismatch and molecular structure on lipid-derived polyesters produced using green CLICK chemistry approaches**.**

2.0 Five Year Data Summary

Indicator	Results
Publications; patents (if applicable)	# of Peer Reviewed Journal Articles Co-Authored by Chair: 65
	# of book chapters, authored or co-authored by the Chair: 6
	# of patent applications filed: 58
Students supervised over the five years	# of Master's students: 8
	# of doctoral students: 7
	# of postdoctoral fellows: 7
	# of undergraduate students who participated in the research program: 18
	# of visiting students/scientists who participated in the program: 7
Conferences	# of conferences attended: 92
	# of conferences where Chair gave a presentation or paper: 36
	# of conferences where members of the research team gave poster/oral presentations: 56
	- With universities and other PSE institutions in Canada (specify):

Partnerships: engagement and linkages developed across the years	• University of Toronto • University of Guelph • McGill University • University of Waterloo • UOIT
	- With universities and other PSE institutions abroad (specify): • Mahatma Ghandi University, India • Malaysian Palm Oil Board, Malaysia • Hebrew University of Jerusalem, Israel • University of the West Indies, Barbados, Jamaica and Trinidad • UNESP, Brazil • University of Guyana, Guyana • Institute of Applied Science and Technology, Guyana
	- With government organizations and agencies, in Canada and abroad (specify): • Ontario Ministry of the Environment and Climate Change • Ontario Ministry of Agriculture, Food and Rural Affairs • Environment Canada • Soy 20/20 • Ontario Bioproducts A Team • Ontario Agri-Food Technologies • Alberta Bio-Innovate • Ontario Centres of Excellence
	- With business and industry (specify companies or associations): • Elevance Renewable Sciences • Northwater Capital • Grain Farmers of Ontario • Archer Daniels Midland • Bunge Oil • DuPont • Pepsico • Bayer • Charlotte Products • Woodbridge Foams

Dissemination of research results; outreach to public and public policy makers; courses based on the research	Identify symposia, workshops, meetings with government officials, etc.:
	• Carbon Conversations (Symposia series organized by Chair)
	• Annual meetings with:
	  o Ontario Ministry of the Environment and Climate Change
	  o Ontario Ministry of Agriculture, Food and Rural Affairs

	Identify undergraduate or graduate courses taught based on the research: • MTSC 6270H Topics in Materials Science II – Intermolecular and Surface Forces • MTSC 6240H – Topics in Biomaterials: Lipid Based Materials - Green Chemistry and Materials Physics

3.0 Variances between Research Program and Original Terms of Reference

Three major deviations from the research proposal occurred, all sanctioned by the Research Advisory Committee. These relate to Applied Objective 2 and supporting work in Fundamental Objectives 1 and 2, and the creation of two entirely new Applied Objectives (#4 and #5), with related activities in Fundamental Objectives 1 and 2 and 2 and 3,respectively.

Deviations in Applied Objective 2 and related deviations in Fundamental Objectives 1 and 2:
Focus was switched from TAGs and their branched derivatives to TAG-oligomers, jojoba-like oligomers and metathesis-modified TAGs for the purpose of designing functional waxes. Described above under Applied Objective 2, this necessitated the synthesis of three new classes of compounds (Classes 6, 7 and 8). Significant progress including multiple patents and publications was recorded for these areas.

New Applied Objective 4 - structured lipids for cold flow modification of biodiesel
The use of biodiesel is limited in cold climates during winter months, due to the crystallization of saturated methyl esters present, leading to a restriction of the fluidity of the fuel and to clogging of fuel filters by the crystalline particles. It was found by our ERS partners that products from self-metathesis of vegetable oils results in amalgams capable of modifying the cold flow behavior of biodiesel mixtures, specifically; the lowering of the cloud and pour points of biodiesel mixtures. Our team was able to determine which chemical moieties within self-metathesized soybean oil were responsible for the modification of the biodiesel crystallization, and was able to determine the mechanism by which these compounds alter the crystallization behavior of biodiesel. A series of patents were filed on the technology.

New Applied Objective 5 – Polyurethane Foams from Metathesis-Modified Triacylglycerides
Cross-metathesis of vegetable oils with olefins can produce high-value olefinic chemicals which are useful and valuable petrochemical replacements. This process results in the creation of modified triacylglycerides, some with significantly shortened, double-bond terminated fatty acids at the stereospecific locations which originally contained unsaturated fatty acids. The mixture of modified triacylglycerides does not occur naturally and therefore their chemistry, structure, and physical properties need to be developed. This applied objective seeks to produce polyols from the modified triacylglycerides and polyurethane foams from the polyols. This objective addresses an important commercial opportunity – Elevance Renewable Sciences and Wilmar currently processes 400 million lbs. of palm oil in their biorefinery in Indonesia. Adding value to the modified triacylglycerides produced in these plants is important to the profitability of the biorefinery. Significant progress has been made, with five filed patents and multiple publications.