Report on the Research and Teaching Activities of the Ontario Chair in Green Chemistry and Engineering at Trent University, 2013-2014

The Ontario Research Chair in Green Chemistry and Engineering at Trent University was slated to have the following research related focus over the course of the program (text in italics is reproduced pasted from the original application to COU):

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.*

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.*

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.*

In 2013-2014, the research group made more progress than in any other year since the inception of the Ontario Research Chair in Green Chemistry and Engineering research program, as evidenced by the number of publications and patents outlined below. Despite this, 60 –70 % of our work is currently delayed from publication due to the need to file patents. Four (4) patents were filed during the reporting period and seven (7) additional patent applications are currently being prepared. Given the confidentiality considerations around patents that are currently being filed, this report refrains from discussing the work implicated, and instead focuses on the published work and patents filed, as discussed below.

Five peer-reviewed publications [2, 5, 9,11,13] (refers to the numbered list of publications) were published and three patents [17, 18, 20] were filed during the reporting period which relate to fundamental objective three. Publication [2] and patents [17-18] relate to our work on highly functional, totally biobased thermoplastics which performs as well and in some instances even better than their petrochemically based counterparts.

This work is one of the culminations of the previous four years of effort under the Chair's program. Publication [5] relates to biomedically active polyesters synthesized using CLICK chemistry approaches, partially from biobased lipid sources (maximum 30 percent non-biobased materials were used). Graduate Student Michael Floros, who spearheaded the work, received a major award from the American Oil Chemists' Society at its annual meeting in San Antonio, Texas in 2014 for this work. Publications [9, 11, 13] relate to our work with totally biobased polyester thermoplastics. These polyesters are as strong as high density polyethylene, but retain all of the desirable polyester characteristics, especially with regards to biodegradation. This work, now

published, was patented during the last reporting period. Patent [20] seeks intellectual property protection for work that establishes protocols, structure and functionality of a new green polyol and its related polyurethanes, which are produced from the by-products of the metathesis of palm oil to produce green hexane. The work was held back from publication this year due to the need to apply for patent protection. The polyol allows us to prepare industry-leading polyurethane foams in terms of performance and costs. This work is under active commercialization efforts currently by our main industrial partner, Elevance Renewable Sciences Inc.

Four peer-reviewed publications [3, 8, 10, 15] were published and one patent [19] filed for work done under fundamental objective one. Publications [3, 10 and 15] relate to our on-going work focused on the design of edible lipid systems with zero trans fats and lowered saturated fats. Significant progress was made this year in the understanding of how structured isomers of triacylglycerides interact as a function of symmetry, chain length mismatch and unsaturation, and the extent to which structure of such mixtures can be templated by the use of processing conditions, so as to deliver a range of desirable functionalities. Publication [8] and patent [19] relate to our work focused on the synthesis of totally biobased waxes from vegetable oils which perform as well as or in some instances better, than waxes made from petrochemical sources.

Four peer-reviewed publications [4, 6, 7, 12] were published for work done under fundamental objective two. Publications [4, 7] relate to ongoing work, already patented during the last reporting period, which establishes the structure and function relationships between a series of linear and branched monoesters and their lubricating properties, such as low temperature fluidity, viscosity – temperature profiles, thermal degradation and chemical stability. The work joins a body of work already published which examines symmetry, chain length mismatch, unsaturation, degree, position and type of branching on the physical properties of lubricating compounds. Superior lubricants with industry-leading low temperature fluidity properties were designed from this work and are under commercialization considerations. Publication [6] details the synthesis of a series of entirely biobased esters with very high enthalpies of crystallization and controllable melt temperatures, suitable for utilization as phase change materials, especially in food applications. Publication [12] details the synthesis of a range of novel diols, diacids and diisocyanates from lipid based materials, useful for application in a range of polymers, lubricants and other high value chemicals.

Publications [1, 14, 16] relate to fundamental objective three, and were published in conjunction with our Brazilian [1] and Indian [14, 16] collaborators. Publication [1] is a review of the potential of using cashew nut shell liquid as a potential replacement for phenolic resins. Publications [14 and 16] are focused on the production of nanocomposite biobased materials.

The research deliverables of the Chair’s program as detailed in the original research program have all been met and significantly exceeded. There are no areas of the proposed research program that have not been addressed by the team, and in several instances these areas have resulted in the filing of very valuable intellectual property.

Furthermore, at least two of the areas of endeavor and in which the team has developed IP are being actively pursued as commercial endeavors.

Manuscripts published in 2013-2014:

1. Telascrêa, M., A.L. Leão, M.Z. Ferreira, H.F.F. Pupo, B.M. Cherian and **S. S. Narine**, (2014), *Use of a Cashew Nut Shell Liquid Resin as a Potential Replacement for Phenolic Resins in the Preparation of Panels – A Review,* Molecular Crystals and Liquid Crystals, 604(1): 222-232.

2. Li, S., J. Jose, L. Bouzidi, A.L. Leão and **S.S. Narine**, (2014), *Maximizing the Utility of Bio-based Di-isocyante and Chain extenders in Crystalline Segmented Thermoplastic Polyester Urethanes: Effect of Polymerization Protocol,* Polymer, 55: 6764-6775.

3. Baker, M., L. Bouzidi, N. Garti and **S.S. Narine**, (2014), *Multi-Length-Scale Elucidation of Kinetic and Symmetry Effects on the behavior of Stearic and Oleic TAG. II. OSO and SOO*, Journal of the American Oil Chemists' Society, 91(4): 1685-1694.

4. Bouzidi, L., S. Li and **S.S. Narine**, (2014), *Lubricating and Waxy Esters. VI. Effect of Symmetry about Ester on Crystallization of Linear Monoester Isomers*, Symmetry, 6(3): 655-676.

5. Floros, M.C., A.L. Leão and **S.S. Narine**, (2014), *Vegetable Oil Derived Solvent, and Catalyst Free "Click Chemistry" Thermoplastic Polytriazoles.* BioMed Research International, 2014:792901-14.

6. Floros, M.C. and **S.S. Narine**, (2014), *Saturated Linear Diesters from Stearic Acid as renewable Phase change Materials,* Materials Letters, 2014: 252-255.

7. Li, S. & L. Bouzidi and **S.S. Narine**, (2014), *Lubricating and Waxy Esters, V. Synthesis, Crystallization, and Melt and Flow Behaviours of Branched Monoesters Incorporating 9-Decenoic Acid*, Industrial and Engineering Chemistry Research, 53(31): 12339-12354.

8. Li, S. & L. Bouzidi and **S.S. Narine**, (2014), *Synthesis, Crystallization and Melting Behavior of Metathesis-Like Triacylglycerol Oligomers: Effects of Saturation, Isomerism and Size*. Industrial and Engineering Chemistry Research. 53(38): 14579-14591.

9. Jose, J., G. Pourfallah, D. Merkley, S. Li, L. Bouzidi, A.L. Leão and **S.S. Narine**, (2014), *Thermoplastic polyesters and co-polyesters derived from vegetable oil: synthesis and optimization of melt polycondensation for medium and long chain poly(w-hydroxyfatty acids) and their ester derivatives*, Polymer Chemistry, 5(9): 3203-3213.

10. Baker, M., L. Bouzidi, N. Garti and **S.S. Narine**, (2014), *Multi-Length-Scale Elucidation of Kinetic and Symmetry Effects on the behavior of Stearic and Oleic TAG: I. SOS and SSO*, Journal of the American Oil Chemists' Society, 91(4): 559-570.

11. Jose, J., S. Li, L. Bouzidi, A.L. Leão and **S.S. Narine**, (2014), *Mechanical and thermal properties of thermoplastic random co-polyesters made from lipid derived medium and long chain poly(w-hydroxyfatty acids*, Journal of Applied Polymer Science, 131(13): 40492(1-8).

12. Raghunanan, L., J. Yue and **S.S. Narine**, (2014), *Synthesis and Characterization of Novel Diol, Diacid and Di-isocyanate from Oleic Acid*, Journal of American Oil Chemists' Society, 91(2): 349-365.

13. Jose, J., G. Pourfallah, A.L. Leão and **S.S. Narine**, (2014), *Influence of monomeric and polymeric structure on physical properties of thermoplastic polyesters derived from hydroxyfatty acids*, Polymer International, 63(11): 1902-1911.

14. Abraham, E., B. Deepa, L.A. Pothen, M. John, R. Anandjiwala, S. Thomas and **S.S. Narine**, (2013), *Physicomechanical Properties of Nanocomposites Based on Cellulose Nanofibre and Natural Rubber Latex*, Cellulose, 20(1): 417-424.

15. Bouzidi, L., T.S. Omonov, N. Garti and **S.S. Narine**, (2013) *Relationships between molecular structure and kinetic and thermodynamic controls in lipid systems. Part I: Propensity for oil loss of saturated triacylglycerols*, Food & Function, 4(1): 130-143.

16. Abraham, E., B. Deepa, L.A. Pothen, J. Cintil, S. Thomas, M.J. John, R. Anandjiwala and **S.S. Narine**, (2013), *Environmental Friendly Method for the Extraction of Coir Fibre and Isolation of Nanofibre*, Carbohydrate Polymers, 92(2): 1477-1483.

Patents Filed in 2013-2014:

17. U.S. Provisional Patent Application #62051740, (filed 2014), "*Synthesis and Molecular Weight Control of Lipid Derived Aliphatic Polyester Diols*," **S.S. Narine**, S. Li, J. Jose, S. Shetranjiwalla and L. Bouzidi.

18. U.S. Provisional Patent Application #62051821, (filed 2014), "*Bio-based Diisocyanate and Chain Extenders in Crystalline Segmented Thermoplastic Polyester Urethanes*," **S.S. Narine**, S. Li, J. Jose and L. Bouzidi.

19. U.S. Provisional Patent Application # 61/989722, (filed 2014), "*Triacylglycerol Oligomers*," **S.S Narine**, S. Li and L. Bouzidi

20. U.S. Provisional Patent Application #61971475, (filed 2013), "*Metathesized Triacylglycerol Polyols For Use In Polyurethane Applications And Their Related Physical Properties*," **S.S. Narine**, P. Pillai, S. Li, L. Bouzidi and A. Mahdevari.

Conferences attended:

1. **Suresh S. Narine,** Structure and Function of Lipid based molecules – symmetry as a source of functional differences, November 7, 2014, University of Strasbourg, Strasbourg, France, Talk Delivered by Suresh Narine. Invited Talk.

2. **Suresh S. Narine**, *The Lipid Biorefinery: Lubricants, Waxes, Fine Chemicals, Polymers and Mor*e, November 5, 2014, University of Leuven, Kortrijk, Belgium, *Talk Delivered by Suresh Narine.* **Invited Talk.**

3. **Suresh S. Narine**, *Potential of Natural Resources in the Guyana Contex*t, August 8, 2014, Institute of Chartered Accounts of Guyana (ICAG) Annual Conference 2014, Georgetown, Guyana. *Talk Delivered by Suresh Narine.* **Invited Talk. Keynote Address.**

4. **Suresh S. Narine**, *Natural Resources, Economic Growth and Sustainability: Mutually Exclusive?*, June 24, 2014, ICAC 32nd Caribbean Conference of Accountants, Paramaribo, Suriname. *Talk Delivered by Suresh Narine.* **Invited Talk. Keynote Address.**

5. L.C. Raghunanan, S. Li, Laziz Bouzidi and **Suresh S. Narine**, *Influence of Structure on the Physical Properties of linear aliphatic biobased esters*, May 4-7, 2014, 105th AOCS Annual Meeting and Expo, San Antonio, United States. *Talk Delivered by Latchmi Raghunanan.*

6. Michael Tessier, Mark Baker, Laziz Bouzidi and **Suresh S. Narine**, *Using Monte Carlo Analyses to Model Thermal Data from Lipid Crystallization Studies*, May 6-7, 2014, 24th Canadian Thermal Analysis Society (CTAS) Annual Workshop and Exhibition, Mississauga, Canada. *Talk Delivered by Michael Tessier.*

7. M. J. Tessier, M. Baker, S. Joseph, S. McConnel, L. Bouzidi and **Suresh S. Narine**, *Software Tools for Improved Understanding of Lipid Crystallization*, May 4-7, 2014, 105th Annual Meeting and Expo, San Antonio, United States. *Talk Delivered by Laziz Bouzidi.*

8. Michael C Floros and **Suresh S. Narine**, Antimicrobial Properties of a Lipid Derived Thermoplastic Polytriazoleaocs, May 4-7, 2014, 105th AOCS Annual Meeting and Expo, San Antonio, United States. *Talk Delivered by Michael Floros*.

9. **Suresh S. Narine**, *The Lipid Biorefinery: Lubricants, Waxes, Fine Chemicals, Polymers and Mor*e, May 4-7, 2014, 105th Annual Meeting and Expo, San Antonio, United States. *Talk Delivered by Suresh Narine*. **Invited Talk.**

Number of students supervised in the year:

Master's	3
Doctoral	6
Postdoctoral Fellows	1
Undergraduates who participated in the research program	5
Other: Visiting Scholars	2

Members of the Research Team:

Principal Investigator

1. Dr. Suresh Narine, Program Director and Professor

   Professor Narine is responsible for the entire program management and for setting and managing research milestones and deliverables, and for liaison with the Research Advisory Committee.

Research Associates

2. Dr. Laziz Bouzidi, Materials Science, Condensed Matter Physics, Surface and Interface Science

   Dr. Bouzidi assists Professor Narine in the management of deliverables related to fundamental objective 1 (see section on research above) and associated applied objectives and is also actively engaged in the actual research deliverables and in helping to supervise graduate students.

3. Dr. Shaojun Li, Organic Chemistry, Polymer Science:

   Dr. Li assists Professor Narine in the management of deliverables related to fundamental objective 2 (see section on research above) and associated applied objectives and is also actively engaged in the actual research deliverables and in helping to supervise graduate students.

Post-doctoral Fellows

4. Dr. Jesmy Jose, Physical Properties, Polymers

   Dr. Jose is involved with the evaluation of structure and physical properties of polymers prepared under fundamental objective 3 (see section on research above) and associated applied objectives.

5. Dr. Jinhua Zhang, Chemistry, Polymers

   Dr. Zhang is involved with the synthesis of polymers to be used in the production of an intelligent coating for fertilizers. This is part of a collaboration with Agriculture Canada, University of Alberta, Carleton University and two private sector companies.

Research Technician

6. Peter Andreas

   Mr. Andreas is our laboratory manager, and is in charge of safety, calibration, supply management, equipment repair and training for equipment operation. He supports all research activities in our laboratories.

Graduate Students:

There are nine (9) graduate students currently in the research program, either solely supervised or co-supervised by Professor Narine; two students have already graduated from the program during 2013-2014. Students' projects are all related to Biomaterials, but range widely in terms of focus:

Graduated 2013 – 2014

1. **Ghazaleh Pourfallah**, MSc. January 2013. *Structure and functionality of green polyesters from lipids.* Supervised by Dr. Narine, Ms. Pourfallah is originally from Iran. She is currently pursuing a Ph.D. in Australia.

2. **Emily Morrison**, MSc. 2014. Learning from One Another: *A Comparative Study between Canada and Brazil on University Technology Transfer through Biomaterial Spinoff Development*. Supervised by Dr. Narine*. Emily Morrison* is now an Economic Development Officer for Durham Region.

Current

1. Prasanth Kumar transferred from the MSc. into the Ph.D. program in Materials Science and is originally from MG University in Kerala, India – a dhemist, he is working on lipid-based polyols and polyurethane foams and is supervised by Dr. Narine.

2. Latchmi Singh transferred from the MSc. into the Ph.D. program in Materials Science and is a Chemist from the University of Trinidad and Tobago and from the University of the West Indies. She is working on the synthesis of green lubricants and is supervised by Dr. Narine.

3. Shegufa Merchant transferred from the MSc. into the Ph.D. program in Environmental and Life Sciences and is a chemist, who is working on the synthesis of hybrid polymers – silica and lipid based polyester urethanes; this represents a collaboration between Professor Vreugdenhil's group and Professor Narine's group. Shegufa is from Toronto, India and the Persian Gulf.

4. Michael Floros transferred from the MSc. into the Ph.D. program in Materials Science and is a chemist and is working on CLICK and anti-microbial polymer films. Mike is from Aurora, Ontario and is supervised by Dr. Narine.

5. Thien Nguyen Quoc is a Ph.D. student in the Environmental and Life Sciences graduate program and is from Vietnam, working with Professors Neil Emery and

Suresh Narine on modification of soybeans so as to influence the fatty acid profiles to be more industrially beneficial to producing green chemicals.

6. Kira Ramphal is a MSc. student in the Environmental and Life Sciences graduate program, working with Professors Narine and Emery on the cultivation of novel strains of algae which produce stearidonic acid, and the use of hormonal pathways to cause variations in fatty acid profiles. Kira is from Scarborough, Ontario.

7. Michael Tessier is a MSc. student in Materials Science, who is working on lipidic Phase Change Materials for energy storage and is supervised by Professor Narine. Mike is a Physicist from Trent University and originally from Peterborough.

8. Benjamin Musclow is a MSc. student in Materials Science, who is working on polymeric coatings for the triggered release of urea fertilizers. He supervised by Dr. Narine and is a Peterborough native with a BSc. degree from Trent University.

9. Athira Mohanan is a MSc. student in Materials Science seeking to transfer to the Ph.D. program. She is working on the multi-length scale phase behavior of binary eutectic-forming lipid molecules and is supervised by Dr. Narine. She is a physicist who is originally from Mahatma Ghandi University, Kerala, India.

Exchange Students and Visiting Scholars 2013-2014:

1. Hernane da Silva Barud, Visiting Professor, University of Araraquara (UNIARA), Brazil

2. Sangeetha Nair, Visiting Professor from Mahatma Ghandi University, India

Summer and Undergraduate Students 2013-2014:

1. Kaitlyn Pinkett, Trent University Undergraduate, working on CLICK Chemistry Polymers

2. Sunil Mahato, University of Virginia Undergraduate, working on Crystallization of Lipids

3. Mark Baker, University of Western Ontario Undergraduate – working on Materials Science, Phase Behavior of Methyl Esters and Triacylglycerols

4. Benjamin McPhail, Trent University Undergraduate, working on Materials Science, CLICK Chemistry Polymers

5. Jennifer Morgan, Trent University Undergraduate, working on Materials Science, Modification of Nanocellulose for Enhanced Miscibility in Hydrophobic Polyurethane Matrices.

Linkages and Networks:

1. Industry

The following companies toured the facilities at Trent and held discussions with our team:

1. Grain Farmers of Ontario – this organization represents some 23, 000 farmers in Ontario whose markets are affected by our research activities. They are a major funder of our program and visited and interacted with the research team four times during this reporting period.

2. Elevance Renewable Sciences – this is our other main industrial partner, with multiple projects underway. We have monthly meetings with this group.

3. Swish – a local industry which manufactures cleaners and the research group met approximately three times during the reporting period to investigate possible collaborations.

4. Northwater Capital – Toronto-based intellectual capital investment firm. This firm has now become a funder of our research program and we met with them approximately three times during the reporting period. We are currently in the process of filing two joint patents with this company.

5. Ecosynthetix, Burlington-based bio-based Biomaterials Company. We interacted with their Vice-President twice during the reporting period, to discuss possible collaboration.

2. Government Ministries

Staff from the Ontario Ministry of Agriculture, Food and Rural Affairs toured our facilities and held feedback discussions with our staff:

3. Enabling Organizations

Ontario Bioproducts A team has toured our facilities and engaged with our staff. The Bioproducts A Team is a specialized business-savvy biomaterials team providing solutions for industry. This organization was put together by a number of university professors working in the biomaterials area, under the leadership of Ontario Agri-Food Technologies (OAFT). We have been an integral part of this team, and have had numerous meetings with our counterparts across the country.

4. Universities

In addition to the above stakeholders, including the universities represented in the Ontario Bioproducts A team, we have also developed close collaborative and communication relationships with the following Professors at other universities:

1. Professor Mohini Sain, University of Toronto (we have had numerous visits from Professor Sain and his group and have visited his facilities at University of Toronto numerous times).

2. Professors Misra and Mohanty, University of Guelph (we have had several meetings with these stakeholders, from the University of Guelph, and have participated in their workshops).

3. Professor Leonardo Simon, University of Waterloo (Professor Simon visited our laboratory and interacted with our team, and Professor Narine also visited Professor Simon's laboratory at the University of Waterloo - the two groups committed to working on collaborative projects).

5. International Collaboration Activities

A number of international collaborations have been set up a part of the Chair's program:

1. India

   Mahatma Ghandi University, Kerala, India

   Activity Description: Regular graduate student exchanges and a number of collaborative projects related to bioplastic/nanofibre composites are being actively pursued.

2. Brazil

   Universidade Estadual de Paulista (UNESP), Botucatu, Brazil

   Activity Description: The collaboration with the Universidade Estadual de Paulista (UNESP) in Botucatu, Brazil, is focused on projects related to biomedical plastics for body implantation and bioplastics/fibre composites. Student and faculty exchanges have begun around a joint research project between the University of Toronto, UNESP, and Trent University, focused on the study of lightweight bio-sourced plastics for automotive applications (in addition to student and faculty exchanges, Trent University through the Chair's program, the University of Toronto, and UNESP has been successful in securing funding from the Canada-Brazil Research Partnerships Program, and this is resulting in increased collaboration among these universities).

3. Malaysia

   Activity Description: Collaboration is with the Malaysian Palm Oil Board (MPOB), focused on materials for the edible and industrial uses of palm oil. The collaborative projects are between Professor Narine and Dr. Hazima Binti Abu Hassan, Director, Malaysian Palm Oil Board, Kuala Lumpur. There have been multiple visits between the two facilities and a number of projects are underway.

4. Barbados

   University of the West Indies, Cave Hill, Barbados. Major collaborative projects are underway in the areas of green chemistry between UWI and Trent, and Professors Narine and Tinto.

5. Israel

Hebrew University, Jerusalem, Israel

Activity Description: There is a research program in collaboration with the Casali Institute for Applied Chemistry at the Hebrew University in Jerusalem, Israel. Collaboration is focused on crystallization of lipids and specialty waxes, gels and polymers (we have had faculty visits from this university and Professor Narine has also visited the Hebrew University. A number of crystallization-based projects have been established).

6. Guyana

   Activity Description: The Chair's program is closely aligned with projects at the Institute of Applied Science and Technology (IAST) in Guyana, South America, which is also directed by Professor Narine. Under the rubric of a memorandum of understanding between Trent University and the IAST, there are regular exchanges between graduate students enrolled in the Chair's program and the institute.

Measures to publicize and share research with public and policy makers:

Interviews and Media Relations

During the reporting period, most of the media interactions occurred in Guyana:

1. 2013-08-26 – Activated carbon from coconut shells, a viable alternative to mercury – 10th Biannual Mining and Quarrying Conference at the Guyana International Conference Centre.

2. 2013-08-14 – Guyana faces dark future without hydropower – National Economic Forum at Guyana International Conference Centre, Liliendaal.

3. 2013-07-25 – Seeking Stakeholders' Input on how IAST can service the Private Sector – Meeting hosted at the University of Guyana Board Room by IAST

4. 2013-07-18 – The importance of collaborating with the Private Sector – Meeting hosted at IAST's Turkeyen headquarters.

5. 2013-04-15 – The importance of an Energy Policy – National Economic Forum held at the Guyana International Conference Centre.