Narrative of Research and Teaching Activities of the Ontario Chair in Green Chemistry and Engineering Activities at Trent University: 2011 - 2012

This narrative examines the activities of the Ontario Research Chair in Green Chemistry and Engineering at Trent University, Professor Suresh Narine, under three headings - teaching, outreach and research activities.

1.0 Teaching Related Activities:

The Ontario Research Chair in Green Chemistry and Engineering at Trent University was slated to have the following teaching related activities from 2011 (text in *italics* are cut and pasted from the original application to COU):

The proposed Chair will have the following teaching responsibilities:

Undergraduate

- *Department of Physics, first year course, 2010: "Physics for the Life Sciences".*
- *Departments of Physics and Chemistry, fourth year course, 2011: "Physics and Chemistry of Colloidal Biomaterials"*
- *Department of Chemistry, fourth year course, 2012: "Techniques in Green Chemistry: Organic Synthesis Reactions Suitable for the Conversion of Lipid Molecules into Toxin-Free Polymers."*
- *Development in 2013 of a Trent Centre for Community Based Education community-based course: "Biomaterials- Chemistry, Ethics, and Economics".*
- *Supervision of senior undergraduate students (up to 10 per year) in project-based courses.*

Graduate

- *Materials Science and Environmental and Life Sciences Graduate Programs, 2010, "Biomaterials"*

Professor Narine was successful in securing two major research Chairs in 2011 - the Ontario Research Chair in Green Chemistry and Engineering and the Senior NSERC/GFO/ERS Industrial Research Chair in Lipid Derived Biomaterials. Due to the unusual amount of research activity and research administration that Professor Narine is engaged in as a result of holding two major research chair positions, ***his teaching load at Trent University has been reduced to zero***.

1.1 Courses Offerred

Despite this teaching reduction, in 2012, Professor Narine taught the graduate level course: **Topics in Biomaterials: Lipid Based Materials - Green Chemistry and Materials Physics**. This course was offered to graduate students in the Materials Science graduate program at Trent University and University of Ontario Institute of Technology (UOIT), graduate students in the Environmental and Life Sciences graduate program at Trent University and graduate students in the Sustainable Studies graduate program, and to senior undergraduates from Trent University.

The senior undergraduate course **"Techniques in Green Chemistry: Organic Synthesis Reactions Suitable for the Conversion of Lipid Molecules into Toxin-Free Polymers"** is being developed in conjunction with Professor Andrew Vreugdenhil.

1.2 Undergraduate Students Supervised

Six high school/undergraduate students were supervised in 2011 - 2012:

1. Christopher Anzenberger, 3rd year Undergraduate Chemistry Student, Trent University
2. Shawna Miles – 3rd year Undergraduate Physics Student, Trent University
3. Mark Baker – 3rd year Undergraduate Physics Student, University of Western Ontario
4. Brandon Harilall – 2nd year Chemical Engineering Student, University of Waterloo
5. Sabin Ciotir – Grade 12 Student, Adam Scott High School, Peterborough, Ontario
6. Pablo Ferreira – 3rd year Computer Science Student, Universidade Estadual de Paulista, Brazil

Two Exchange Students were supervised in 2012, both from Brazil, funded through a joint Brazil-Canada Research Partnerships Grant with University of Toronto, Trent University and Universidade Estadual de Paulista (UNESP),

1. Janaina Freitas Bortolatto – Ph.D. Student
2. Ivi Martins de Carvalho – Ph.D. Student

1.3 Graduate Supervision

There are ten (10) graduate students in the research program, either solely supervised or co-supervised by Professor Narine. Their projects are all related to Biomaterials, but range widely in terms of focus:

1. **Jiaqing Zuo,** MSc. Graduated, April 2011. Jiaqing worked on lipid based thermoplastic polyesteramides, successfully defended her thesis, and co-authored one publication in the high impact factor journal Polymer.

2. **Prasanth Kumar** is an MSc student in Materials Science, also seeking to transfer into the Ph.D. program, also from MG University in Kerala - a Chemist, he is working on lipid based polymers and polymer composites.

3. **Latchmi Singh** is an MSc. student, also seeking to transfer into the Ph.D. program, she 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.

4. **Shegufa** Merchant is an MSc. student in Materials Science who will be seeking to transfer into the Ph.D. program, also. She is a chemist, who will be working on the synthesis of hybrid polymers - silica and lipid based hybrid materials, and this represents a collaboration between Professor Vreugdenhil's group and Professor Narine's group. Shegufa is from Toronto, India and the Persian Gulf.

5. **Michael Floros** is an MSc. student in Materials Science who will also be seeking to transfer into the Ph.D. program. He is a chemist and is working on anti-microbial polymer films. Mike is from Toronto.

6. **Ghazaleh Pourfallah** is doing an MSc. in the Materials Sciences Program. She is a chemist who is working on omega hydroxy polyesters derived from lipids. Ghazaleh is from Iran.

7. **Nguyen Quoc Thien** is from Viet Nam and is 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.

8. **Emily Morrison** is an MSc student in the Masters in Sustainability program beginning in January 2012, working with Professors Narine and Zohar on a critical analysis of the policy environment governing biomaterials, and its impact on the commercialization of such materials.

9. **Kira Ramphal** is an MSc. student in the Masters program in ENLS, who began in May, 2012. She is 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.

10. **Michael Tessier** is an MSc. student in the Masters program in Materials Science, who joined the program in September, 2012. He is working on lipidic Phase Change Materials for energy storage and is supervised by Professor Narine.

2.0 Outreach Activities:

The Ontario Research Chair in Green Chemistry and Engineering at Trent University was slated to have the following outreach activities from 2011 (text in *italics* are cut and pasted from the original application to COU):

In addition to the plans for technology transfer and commercialization with our commercial partners outlined above, the Chair will also commit to establishing a multi-stakeholder network with representatives from the Ontario Ministry of Agriculture, Food and Rural Affairs, the Ontario Ministry of the Environment, the Ontario Ministry of Natural Resources, Environment Canada, Primary Producers, Processors, Academics and other stakeholders, who will be engaged annually and semi-annually through an annual workshop and 2-3 seminars per year. The intent would be to allow the research advisory committee for the Chair to be guided by interactions with this stakeholder community and to allow the stakeholder community to be informed of new products, processes and understanding developed by the Chair's program.

Outreach activities did not take the form of a workshop organized at Trent University, as there were multiple opportunities to interact with almost all of the stakeholder groups identified above, at multiple workshops, seminars and individual meetings, laboratory tours and conference call updates during 2011 and 2012. The idea of a workshop has been replaced by a multi-stakeholder symposium, called the Carbon Conversations, established by Professor Narine and the Trent Centre for Biomaterials Research at Trent University.

In March 2012, the Trent Centre for Biomaterials Research launched the inaugural Carbon Conversation. These conversations are designed to occur multiple times a year, and engages a broad spectrum of stakeholders - students, scientists, artists, policy makers, consumers, industry, environmentalists, etc. The Carbon Conversations Symposium Series replaces the idea of the workshops that were originally slated to engage stakeholders in the Chair's activities.

Specifically, the following stakeholder groups were engaged during 2011 - 2012:

2.1 Industry

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

1. Grain Farmers of Ontario (we held a mini-symposia for the GFO in 2012, with 26 poster presentations presented by the staff and students of the Trent Centre for Biomaterials Research). this organization represents some 23, 000 farmers in Ontario whose markets are affected by our research activities.

2. Elevance Renewable Sciences ((multiple meetings, toured facilities, held discussions on collaboration, this is our main industrial partner, with multiple projects underway).

3. Swish, a local industry which manufactures cleaners, met and engaged with the TCBR on potential partnerships to produce greener cleaners.

2.2 Government Ministries

Staff from the following government ministries toured our facilities and held feedback discussions with our staff:

1. Ontario Ministry of Agriculture, Food and Rural Affairs - we continue to have regular updates with this Ministry, and had a visit from Mr. Rajib Hazarika in 2012.

2. Ontario Ministry of the Environment - staff from the Ministry visited Trent in March, 2012, to attend the inaugural Carbon Conversations Symposium and then toured the laboratories of the Trent Centre for Biomaterials research and interacted with Dr. Narine, staff and students.

2.3 Enabling Organizations

The following organizations have also toured our facilities and engaged with our staff:

1. Ontario Bioproducts A team - 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 the OAFT. We have been an integral part of this team, and have had numerous meetings with our counterparts across the country.

2.4 Universities

In addition to the above stakeholders, including the list of Universities represented in the Ontario Bioproducts A team, we have also developed close collaborative and communication relationships with the following 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 (similarly, we have had numerous 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).

2.5 Seminars and Presentations

In addition to the above outreach efforts, Professor Narine and the rest of the staff have been very active in terms of presenting our work at national and international conferences:

2.6 International Collaborations

An impressive array of international collaborations have been set up as part of the Chair's program:

1. Mahatma Ghandi University, Kerala, India (a number of student and faculty exchanges have occurred, and this is set to continue as we embark on collaborative projects with this university).

2. Universidade Estadual de Paulista (UNESP), Botucatu, Brazil (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. Hebrew University, Jerusalem, Israel (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).

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

5. The TCBR also has close collaborative projects with the Malaysian Palm Oil Board, and Professor Narine and Dr. Hazima Binti Abu Hassan, Director, Malaysian Palm Oil Board, Kuala Lumpur, have visited each other's facilities and have various projects underway.

3.0 Research Activities:

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* are cut and 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.*

The above three objectives are referred to as fundamental objective 1, 2, and 3, respectively in the text that follow. Significant progress has been made in all three of the above objectives, and are reflected in the published work cited below.

Publications (5), (6), (7), (8), (9), and (11), and the patent filed in (17) all address fundamental objective #1. In publications (5), (6), and (7), the impact of specifically structured triacylglycerides on the physical functionality of crystallized lipid networks are examined. In particular, publication (5) establishes, for the first time, two parameters, one kinetic and one thermodynamic, which can be utilized to predict the capacity of a crystallized lipid network to bind liquid oil. This is of particular importance to the complete removal of trans fats from lipid-containing products, but also, *the reduction of saturated fat* in such products. As one removes the trans fats and reduces the saturated fats from products such as margarines, shortenings, confectionery fats and such products as ice-cream and peanut butter, the resulting effect is that

these products soften due to an increased liquid oil content (trans fats and saturated fats pack easily into solid crystal lattices due to their straight molecular architecture, whereas unsaturated fat molecules are less likely to pack because of kinks introduced into the molecular architecture due to the presence of double bonds). However, trans as well as saturated fats have been implicated in a deterioration of our cardiac health. Therefore, it is imperative that we reduce the amount of trans and saturated fats in our diet, but to ensure that we can continue to deliver the solid-like expectations that consumers expect, effective strategies to deliver unsaturated lipids in a solid, plastic-like matrix are important. One such strategy is to develop ways of crystallizing uniquely structured triacylglycerides which can be sourced from normal, everyday oilseed crops, which however crystallize in specific matrices that have a high capacity to bind liquid oil. Publication (5) not only established two effective parameters for predicting the oil binding capacity of specifically structured triacylglyceride molecules, it also relates these parameters to structural elements of the molecules themselves and to measurable hierarchies of the crystallized network. The impact of this work we expect will be significant, and will result in the offering of healthier lipid-based products, some of which we are also working on with commercial partners. Publications (6) and (7) examines the specific phase transition behavior of the triacylglycerides SSS, PSS and PPS, which were implicated in publication (5) as some of the more important molecules in binding oil in a crystallized network of lipid molecules. Publications (5), (6), and (7) adds to the work that was accomplished in 2010 – 2011 and reported on, under fundamental objective #1, in a continuous fashion.

Publications (8), (9) and (11) arises out of activities in both fundamental objectives #1 and #2, as does the patent listed in (17). Publications (8) and (9) are two in a series of publications related to the patent that our group filed in 2011, on superior lubricants derived from vegetable oil. The work, which developed an entirely new class of compounds which are oxidatively stable, resists hydrolysis, is thermally resistant, and is resistant to solidification at temperatures as low as -90°C, depended on activities in fundamental objective #2 to develop the synthetic methods to produce the new compounds, and on activities in fundamental objective #2 to examine the solidification, glass transformation, and crystallization tendencies of these compounds, as a function of their molecular architecture. In addition to new knowledge on how chain length, symmetry, and presence of functional groups and esters affect viscosity profile, thermal and oxidative stability and hydrolytic stability, significant new understanding has been created with respect to packing efficiencies and the effect of steric hindrance on crystallization and solidification (glass transformation) of linear monoesters and their branched derivatives.

Publication (11) and the filed patent (17) are related to a new direction for the group that we pursued in 2012, related to both fundamental objectives #1 and #2. Our commercial partners discovered that additional of small percentages of self-metathesized vegetable oils were very effective in lowering the crystallization temperature of biodiesel prepared from vegetable oil. Biodiesel contains saturated methyl or ethyl (rarer) esters, and these, due to their propensity to pack easily into crystalline lattices at sub-ambient temperatures, present significant challenges

for the low-temperature fluidity of biodiesel during the fall, winter and spring months in temperate countries. Various approaches have evolved to handle this problem – by far the most elegant and inexpensive without sacrificing the cetane rating of the fuel would be to develop effective additives which could be added in very small percentages so as to not interfere with the fuel or the combustion in the engine, but would effectively improve the low-temperature fluidity of the fuel. Although our commercial partners noted significant performance-related improvements with the self-metathesized soybean oil, it was unclear which of the multiple (as many as thousands, classified into as many as 10 – 12 different types of compounds) compounds were responsible for the behavior noted. In an attempt to first understand which compounds were responsible, then to understand the mechanism which was employed in the action of these compounds, we began a series of investigations. We were able to determine the class of compounds implicated, as well as to determine the mechanism by which they restrict the crystallization of the saturated compounds in biodiesel. A significant number of publications were held back from this work, due to the need to patent the work first. Publication (11) examines how the yields of these specific compounds may be maximized when an unsaturated vegetable oil is self-metathesized. Other publications will follow early in 2013.

Publications (1) – (4), (10) and (12) – (16) are all related to fundamental objective #3. Publication (10) is a continuation of our important work aimed at an understanding of the relationship between functional group, chain length, and various types of bonding imparted by controlling lipid-based monomeric structure, and the functionality of the resulting thermoplastic polymer. This publication is one more in a series that has been published in the journal Polymer, and we believe this series of work is laying the foundation of a fundamental understanding of the limits of functionality that can be extracted from lipid-based polymers, and the structural changes that are necessary to derive certain changes in functionality.

Publications (1) – (4) and (12) – (16) is a result of the exciting collaboration we have made with the Mahatma Ghandi University of India and the UNESP of Brazil (Professors Sabu Thomas and Alcides Lopes Leao, respectively). This is in the area of lipid-based polymers combined with nano-scale cellulosic fibres. The addition of these fibres can drastically and impressively extend the physical properties of the resultant composites, as a perusal of some of the publications listed will explain. This work will continue into 2013.

Manuscripts published in 2012

1. Abraham, E., Deepa, B., Pothen, L.A., John, M., Anandjiwala, R., Thomas, S. & **Narine, S.S.**. (In Press, 2012). *Physicomechanical Properties of Nanocomposites Based on Cellulose Nanofibre and Natural Rubber Latex,* Cellulose.

2. Abraham, E., Deepa, B., Pothen, L.A., Cintil, J., Thomas, S., John, M.J. Anandjiwala, R. & **Narine, S.S.** (In Press, 2012). *Environmental Friendly Method for the Extraction of Coir Fibre and Isolation of Nanofibre,* Carbohydrate Polymers.

3. Abraham, E., Elbi, P. A., Deepa, B., Jyotishkumar, P., Pothen, L. A., **Narine, S. S.,** & Thomas, S. (2012). *X-ray diffraction and biodegradation analysis of green composites of natural rubber/nanocellulose*, Polymer Degradation and Stability, **97 (11),** 2378-2387.

4. Floros, M., Hojabri, L., Abraham, E., Jose, J., Thomas, S., Pothan, L.A., Leao, A,L. and **Narine, S.S**. (2012), *Enhancement of Thermal Stability, Strength and Extensibility of Lipid-Based Polyurethanes with Cellulose-based Nanofibres*, Polymer Degradation and Stability, **97 (10),** 1970-1978.

5. Bouzidi L., Omonov, T.S., Garti, N. and **Narine, S.S.** (2012), *Relationships between molecular structure and kinetic and thermodynamic controls in lipid systems. Part I: - Propensity for oil loss of saturated triacylglycerols,* Food & Function, DOI: 10.1039/C2FO30164D.

6. Bouzidi, L. and **Narine, S.S.** (2012), *Relationships between molecular structure and kinetic and thermodynamic controls in lipid systems. Part II: Phase behavior and Transformation path of SSS, PSS and PPS Saturated Triacylglycerols – Effect of Chain Length Mismatch*, Chemistry and Physics of Lipids, **165 (1)**, 77 - 88.

7. Bouzidi, L. and **Narine, S.S.** (2012), *Relationships between molecular structure and kinetic and thermodynamic controls in lipid systems Part III: Crystallization and phase behavior of 1- palmitoyl 2-, 3-stearoyl-sn-glycerol (PSS) and tristearoylglycerol (SSS) binary system*, Chemistry and Physics of Lipids, **165 (1)**, 105 - 119.

8. Bouzidi, L., Li, S., Di Biase,S., Rizvi, S.Q. and **Narine, S.S.** (2012), *Lubricating and Waxy Esters, I: Synthesis, Crystallization and Melt behavior of Linear Monoesters,* Chemistry and Physics of Lipids, **165 (1)**, 38 - 50.

9. Laziz Bouzidi, Shaojun Li, Steve DiBiase, Syed Q. Rizvi, Peter Dawson and **Suresh S. Narine**, (2012), *Lubricating and Waxy Esters II: Synthesis, Crystallization, and Melt Behavior of Branched Monoesters*, Industrial and Engineering Chemistry Research, **45**, 14892 – 14902.

10. Hojabri, L., Jose, J., Leao, A. L., Bouzidi, L.,and **Narine,S.S.**(2012). *Synthesis and physical properties of lipid-based poly(ester-urethane)s, I: Effect of varying polyester segment length.* Polymer, **53**, 3762-3771.

11. Li, S, Hojabri, L and **Narine, S. S.,** (2012), *Controlling Product Composition of Metathesized Triolein by Reaction Concentrations*, Journal of American Oil Chemists' Society, **89(11)**, 2077 - 2089.

12. de Olyveira, G.M., Costa, L.M.M., Leão, A.L., de Souza, S.F., Cherian, B.M., de Carvalho, A.J.F., Pessan, L.A. and **Narine, S.S.** (2012), *LDPE/EVA Composites for Antimicrobial Properties*, Molecular Crystals and Liquid Crystals, **556**,168 – 175

13. Cherian. B.M., Leão, A.L., Caldeira. M., Chiarelli, D., de Souza, S.F., **Narine, S.S.** and Chaves, M.R.(2012) *Use of Saponins as an Effective Surface Modifier in Cellulose Nanocomposites*, Molecular Crystals and Liquid Crystals, **556(1),** 233 - 254.

14. Leão, A.L., Cherian,B.M., de Souza, S.F., Sain,M., **Narine,S.S.,** Caldeira, M.S. and Toledo, M.A.S. (2012) *Use of Primary Sludge from Pulp and Paper Mills for Nanocomposites*, Molecular Crystals and Liquid Crystals, **556(1)**, 254 – 263

15. Leao,A.L., Cherian, B.M., de Souza, S.F., Sain, M. and **Narine, S.S.** (2012). *New Developments for Lignocellulosics-Nanocomposites with Low Carbon Footprint*, MRS Proceedings, 1386, mrsf11-1386-d01-02 doi:10.1557/opl.2012.326

Book Chapters Published in 2012

16. Cherian, B.M., de Olyveira, M.G., Costa, L.M.M., Leao, Al.L., Morais, M., de Souza, S.F. and **Narine, S.S.**, (2013), *Biocomposites for Natural Food Packaging*, in Advances in Food Science and Technology, *Eds.* Visakh, P.M., Thomas, S., Iturriaga, L.B. and Ribotta, P.D., Scrivener Publishing LLC, pp. 265 – 300.

Patents Filed in 2012

17. U.S. Patent Application (Filed April 2012) "*Phase Behaviors and Properties of Certain Triacylglycerols and Fatty Acid Methyl Esters"* , **Suresh S. Narine,** Bruce Darling, Mark Baker and Laziz Bouzidi.