Challenges in Sustainable Polymeric Materials

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INTRODUCTION

The term "sustainability" is loaded with connotations in many different disciplines, from economics and social sciences to chemistry and engineering. The most widely accepted definition of the term is derived from a UN report more than 20 years old,[1] an inspiring and sweeping document that captured the problem and its challenges on a global scale, but did not provide the corresponding details to develop clear metrics or measurements of our progress towards a more sustainable future. Furthermore, the three commonly accepted main components of sustainability, economics, society and the environment, have complex interdependencies and subjective criteria, complicating the problem. Of course, this has not prevented the development of many decision tools and processes for quantifying the sustainability of chemicals, materials and products. New tools will even determine the sustainability of whole systems (such as buildings or regional markets). The reliability of these tools is only as good as the data available to populate the models, and that data, where it exists, is often not consistent or reliable. It is critical that, while policies, frameworks and regulations for sustainability are crafted at high levels, the corresponding measurements, data and methods are developed in the lab and field to provide meaningful, effective comparisons and solutions.

> **Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.**
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> *-"Our Common Future" UN World Commission on Environment and Development, 1987*

Polymer science and engineering have prominent roles in addressing many sustainability-related challenges identified in reports from the National Academy of Engineering[2] and the Royal Society of Chemistry,[3] among others. These challenges include conservation of scarce natural resources, conversion of biomass feedstocks, diagnostics for human health, drinking water quality, energy conversion and storage, solar energy, and sustainable product design. With the challenge of discovering, developing and marketing sustainable products, the chemical and materials industries are both supplier and customer of new sustainable technologies. The polymer industry is a major consumer of new technology in the areas of biomass conversion and product design. Product design can include the incorporation of alternative/renewable starting materials, improved manufacturing processes, higher performing, tailored materials and advances in recovery, recycling and degradation post-use.

This summary describes new work in our group using high throughput and combinatorial methods along with conventional measurements to advance understanding and promote the use of biomass feedstocks (polyesters) and enzyme catalysis as a "green chemistry" synthetic method. It will also summarize a suite of new measurement techniques aimed at improving our understanding of the mechanical properties of thin films that impact performance. These methods are designed to enable improved product design.

MICROREACTORS AND ENZYMATIC CATALYSIS

For the last ten years, the NIST Combinatorial Methods Center (NCMC) has been dedicated to the development of high throughput and combinatorial methods for the characterization and measurement of materials and materials processes.[4] As part of that program, microfluidic technology was adapted to prepare devices containing channels in which polymer synthesis could be controlled on very small-length scales, matched to many of the complementary characterization techniques that had been developed in the Center. The use of microfluidic devices, a subset of devices referred to as microreactors, provides a number of advantages including dramatic reduction in the scale of reactions, which reduced the amount of chemical waste and safety hazards often associated with organic chemistry. Improved heat transfer and controlled mixing also improve safety and, in some cases, the precision and repeatability of associated measurements, and properties of the products.

One example of these benefits was the development of a new approach to measuring reactivity ratios. Reactivity ratios provide critical information about the statistical distribution of comonomers in polymer chains produced by chain growth mechanisms. Conventional measurements are straightforward, but tedious, producing large quantities of waste because reactions must be stopped at very low conversion and products are isolated by precipitation. Using a microreactor, which confined the solution volume to a few 100 μL, and a technique called surface initiated polymerization, polymer chains were isolated by covalently attaching them to a surface, eliminating the need to precipitate the products.[5] This effectively eliminated both major sources of waste in the process, while eliminating significant sources of error.

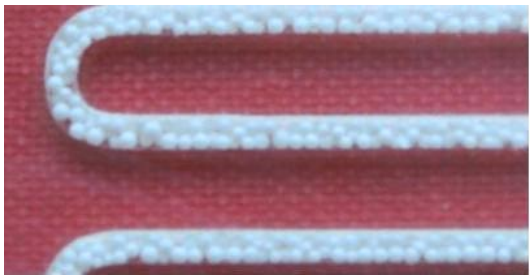

Figure 1: Microfluidic channels packed with polymethylmethacrylate beads loaded with physisorbed lipase for polyester synthesis.

More recently, we have used microreactor technology to investigate enzymatic catalyzed polymerization of polyesters. Enzymes are a potential replacement for classical transition metal catalysts, which are often comprised of precious metals and may have serious health risks. In order to compete with classical catalysts economically, enzymes must be recoverable and recyclable, which has led to the use of immobilized-enzymes on solid supports. We have developed a platform to study the use of solid supported enzymes in continuous flow polymerization reactors and chose lipase catalyzed

polyester synthesis as a model system because there is a reasonable literature base upon which to compare data, and polyesters have received significant attention in recent years as a potentially bio-sourced polymer.

Results showed an order of magnitude increase in the rate of reaction along with molecular masses as much as 30% higher than in conventional batch reactions.[6] Side reactions such as cyclization were also observed using mass spectrometry and chromatography, However, more systematic comparisons of temperature and water content showed that the microreactor method produced more consistent data, with dramatically reduced consumption of starting materials and less waste.

Ongoing investigations include the lifetime of the catalyst under flow and improving measurements of enzyme sorption processes that affect both performance of the flow reactors and contamination of the products.

THIN FILM MECHANICAL TESTING

Other work that has been carried out on the part of the NCMC includes a suite of methods to address the challenge of measuring the mechanical properties of thin films and coatings, and how they might change over time, using high-throughput methods. Traditional methods for testing materials in thin film geometries are either time-consuming or qualitative in nature. As new materials are developed from a broad array of sustainable or renewable sources, quantitative high-throughput methods can enable absolute determinations of whether the properties of these alternative materials are equivalent or superior to petroleum-based materials, while concurrently shortening overall time-to-market. The use of thin films as model systems can also facilitate accelerated tests of material property changes as a function of environmental factors and/or degradation due to the short path lengths and the elimination of through-thickness gradients.

An example of these high-throughput measurement approaches is a metrology based on the wrinkling of thin and ultrathin films and coatings.[7] The measurement of modulus in such thin films is challenging for conventional methods, such as indentation-based approaches, due to uncertainties associated with indentation depth and the proximity of the substrate. Using a wrinkling instability that occurs in bilayer laminates, we were able to rapidly and accurately measure the elastic modulus of sub-micrometer films. We have demonstrated that this technique and film properties are sensitive to film porosity, the presence of nanoparticles, compositional changes, and crosslink density, all of which are critical to designing multifunctional coatings and adhesives.

Additionally, we recently developed a high-throughput measurement approach based on the indentation of an independent array of spheres to measure the creep compliance at multiple points on a polymer film or coating.[8] Samples with gradients in composition and temperature were used to illustrate this technique's ability to measure viscoelastic properties under unique conditions for each indentation. Methacrylate photopolymer systems were measured at different compositions and crosslink densities simultaneously within the indenter array to increase the measurement throughput, with a measured creep compliance ranging from 10^{-9} Pa^{-1} to 10^{-5} Pa^{-1}. We have also shown that this approach can detect the strength or adhesion of buried interfaces,

with fluorinated interfaces exhibiting up to a 30% change from an ideal bonded indentation due to the presence of a weak interface. Moreover, temperature gradients allow acquisition of large data sets for time-temperature superposition, enabling accelerated tests on materials and films that aid in predicting property changes over long times. Ongoing studies are focused on probing the effect of interfacial degradation on the measured compliance of thin polymer films.

Collectively, these high-throughput measurement techniques will enable researchers to correlate the structure and dynamics of materials at surfaces and buried interfaces to their macroscopic mechanical properties, allowing predictive modeling of material life-time as well as the effects of degradation on performance. This suite of tools will enable industry to develop sustainable practices through reducing use or restoring performance of polymer coatings and adhesives.

SUMMARY

These new measurements and methods in polymer chemistry and thin film mechanics are designed to enable rapid assessment of the capabilities and limitations of replacement materials and processes. In general, the development of quantitative, fundamental metrics addressing the scientific issues relevant to improved polymer sustainability lowers the barrier to identification and adoption of new technologies.

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