



Thermoplastic Elastomers and Thermosets Derived from Vegetable Oils

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A great challenge to overcome is the replacement of traditional petroleum-based polymers with materials derived from sustainable, alternative resources. Vegetable oils are an attractive substitute for petroleum sources for the derivation of polymers, due to their abundance, low cost, and lack of toxicity. We are developing two classes of polymers derived from vegetable oils: thermoplastic elastomers and thermosets.

Of particular interest is the design of nanostructured polymers from sustainable sources with well-defined molecular characteristics and competitive properties to petroleum-derived materials. We are developing triblock copolymers with hard, glassy outer blocks and a soft, rubbery midblock which can act as thermoplastic elastomers and pressure sensitive adhesives. We have utilized reversible addition fragmentation chain transfer polymerization for polymerizing fatty acrylates, for the production of triblock copolymers. The thermal and mechanical properties of the polymers are readily tuned by varying the composition of fatty acids used as the raw material source for the polymers.

Epoxy resins have been synthesized containing epoxidized soybean oil (ESO) and traditional petroleum-derived epoxy resin components (the diglycidyl ether of bisphenol A, DGEBA, and methylene dianiline). Significantly higher curing temperatures are required for ESO as compared to DGEBA. Increasing the concentration of ESO in the resin significantly decreased the glass transition temperature. However, epoxy resins with high ESO content (60-100 wt% relative to the total epoxide-bearing molecules in the mixture) exhibited a second, higher temperature peak in the derivative of the thermogravimetric analysis weight loss curve. Significant differences were observed in the hydrolytic degradation characteristics of the polymers at 80 °C in sodium hydroxide (NaOH) solutions. The presence of degradable cleavage points throughout the network structure may provide a valuable route for recycling these materials after their useful lifetime.



The Importance of Chemical Control to Afford Functionally-Sophisticated and Biologically-Active Nanoscopic Macromolecules as Discrete Objects and Supramolecular Assemblies

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The evolution of nanostructured materials that originate from the supramolecular assembly of macromolecular building blocks, from relatively simple overall shapes and internal morphologies to those of increasing complexity, is driving the development of synthetic methodologies that allow for the preparation of increasingly complex macromolecular structures. Moreover, the inclusion of functional units within selective compartments/domains is of great importance to create (multi)functional materials. We have a special interest in the study of nanoscopic macromolecules, with well-defined composition, structure and topology, as components that are programmed for the formation of sophisticated nanoscopic objects in solution. Combinations of controlled radical and ring opening polymerizations, chemical transformations, and supramolecular assembly are employed to construct such materials as functional entities. This presentation will highlight our recent work involving the construction of polymers and nanostructured materials, in some cases being derived from natural products and including biologic-synthetic hybrid materials, which exhibit unique mechanical and/or biological activities, including for instance therapeutic effects to treat inflammation, infectious diseases or cancer, or properties designed for orthopedic device applications.



Novel Mixed Matrix Membranes for Gas Separations

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Mixed Matrix Membranes (MMM) combine the advantages of pure inorganic and pure polymer membranes. The goal is to maintain the flexibility of membranes but add the selectivity of nanoporous molecular sieves. Early efforts with MMMs based zeolites and polymers revealed some of the challenges associated with this strategy. The most significant problem arises from poor wetting of the inorganic particle which creates non-selective voids. The advent of metal organic frameworks (MOF) seem to provide some solutions to the problems associated with zeolite based MMMs. The organic nature of the MOF linkers should help improve the compatibility with the polymer matrix. In fact, MOF loadings of 100% (w/w) have been achieved while maintaining some measure of flexibility. While the wetting of the additive particles was improved with MOFs there are still problems with aggregation at such high loadings which results in non selective voids at the particle boundaries. So taking a lesson from organic heterojunction energy storage devices we prepared polymer blends of a highly selective polymer and a highly permeable polymer that phase separate. The domains of the highly permeable polymer are separated with very thin continuous veins of selective polymer that a gas molecule must pass through. For an MMM of this design, the goal would be to have the MOF nanoparticles localize at the interface of the two polymers. Interestingly, the MOF nanoparticles were discovered to have a profound effect on the microstructure of the MMM blend. It was found that the size of the phase separated polymer domains could be controlled by the MOF loading. Results for this new type of MMM will be presented.

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Non-covalent functionalization, dispersion, and processing of pristine graphene

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Graphene, i.e. single-layer graphite sheets, show extraordinary promise for the development of polymer nanocomposites with targeted properties. This work focuses on the central concept of producing graphene from graphite without covalently functionalizing the graphene basal plane; this “pristine” graphene may be stabilized, dispersed, and processed for use in a range of high-performance materials. In particular, our group has shown that both polyvinylpyrrolidone as well as pyrene derivatives can naturally adsorb to the graphene surface, create repulsive (steric and electrostatic) forces, and prevent aggregation. This allows for graphene dispersion in a range of solvents and composite precursors without compromising graphene structure. Such dispersions are stable against aggregation even when subjected to extreme temperature changes, pH changes, and lyophilization. The graphene/stabilizer ratio obtained using pyrene-based stabilizers is exceptionally high relative to conventional surfactants. The mechanism of stabilization by pyrene derivatives were investigated as a function of the type and number of functional groups, counterions, and the electronic interaction between the functional groups and the basal plane.

Polymer nanocomposites formed from these dispersions include graphene-loaded epoxy and graphene-loaded polyvinyl alcohol films and nanofibers; these composites consistently show enhanced modulus, strength, and electrical conductivity. We also demonstrate novel results in the use of graphene as physical crosslinks and percolating network components in polymer hydrogels and cryogels. The functional groups associated with these stabilizers hold promise for the creation of application-specific “Designer Stabilizers” for graphene.