Combined Application of Extrusion and Irradiation Technologies: A Strategy Oriented for Green and Cost-Effective Chemistry

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Reactive extrusion is an attractive green route for cost-effective polymer processing, which has the potential to enhance the commercial viability of biomass-derived materials. In reactive extrusion, compatibilizers can be generated in the blend preparation through polymer-polymer grafting reactions using functionalized polymers. One very interesting new green strategy for processing is the use of intense UV-irradiation to create free radicals and controllable, ultra-fast reactions. It is reasonable to expect that the use of extrusion/irradiation green technology will be an important way to improve properties and compatibility of renewable biomass-derived polymers. We believe that in the future, many more cost-effective, sustainable extrusion/irradiation reaction processes will be developed to replace inefficient conventional biomass conversion procedures and stimulate the bioproduct-based industry.

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Reactive extrusion is an attractive route for cost-effective polymer processing. We propose that this approach can enhance the commercial viability of biomass materials in composite applications. The process can be applied in order to carry out melt blending simultaneously with various chemical reactions including polymerization, grafting, branching, and functionalization (Tzoganatis 1989). Therefore, production and processing can be integrated in a single stage that previously required extensive, discontinuous equipment with a high need for maintenance. In general, extrusion is being increasingly applied worldwide to manufacture an expanding list of products.

In the extrusion processes, product attributes are controlled not only by the feed composition but also by the manipulation of the specific mechanical or thermal energy inputs and the residence time of the product in the extruder, as adjusted by many variables, such as temperature, moisture, screw configuration, speed, and feed rate. The choice of the extruder type, screw profile, configuration, and operating conditions can be altered to modify the properties desired in the final product.

During the last two decades, the physico-chemical modification of biomass has become an important field of research that has great potential to produce materials with new properties. New technologies that allow for the efficient conversion of previously unstable materials and/or blending of immiscible/incompatible polymers offer attractive opportunities for developing new bio-based products with unique properties. Some of these technologies should find a good balance between the final properties desired and effective routes for processing to be successful. In addition to the academic interest of

these kinds of systems, there exists additional industrial interest due to environmental and economic concerns in recent years.

New biomass-based materials from blends of two biopolymers often suffer from segregation of phases. They are also responsible for high interfacial tension and poor adhesion between the phases, giving rise to poor mechanical properties and unstable morphologies. In many cases, expensive compatibilizers using hazardous materials in the preparation are utilized to improve blends. A proactive solution is to generate compatibility in the blend preparation through polymer-polymer grafting reactions using functionalized polymers.

Moreover, there is a clear attraction to replace existing synthetic procedures with environmentally friendly and sustainable processing strategies. This will open the door not only to better designed reactors, but also to the use of alternative energy sources. One very interesting new strategy for processing is the intense illumination provided by UV-irradiation, which can create free radicals and more selective reactions. Feeding an extruder with different polymers having free radicals in one continuous and homogeneous process will become an increasingly important pool of technology to overcome the above mentioned shortcomings in blends and to achieve the goals of green chemistry.

Recently, Ayoub *et al.* (2012) used UV-irradiation extrusion to compatibilize different synthetic recycled polymers. Improved mechanical properties were achieved in the processed materials. Qu *et al.* (1995) reported a successful and promising process converting the polyethylene thermoplastic material to a thermosetting material by applying UV-irradiation in the production line of an extruder in a specially designed apparatus, in order to combine its low cost, easy processing, and good properties with product dimensional stability.

It is reasonable to expect that the same type of technology will be an important way to improve properties and compatibility with biomass-derived polymers. Some examples of applications for biomass-based composites are for filtration devices, membranes, non-woven and paper type products, foams, structural composites, nanocomposites, coatings, fibers, films, and electrical devices. For example, the extrusion of starch-based foam materials (Patel *et al.* 2009) or hemicellulose-based foam materials (Salam *et al.* 2010) blended with other functional additives could produce a host of new materials with unique properties. The extrusion method can potentially replace exotic foaming processes such as solvent exchange (Patel *et al.* 2009) or freeze drying (Salam *et al.* 2010). The expectation is that by using UV-irradiation extrusion technology, the process efficiency can be improved, the range of blends can be expanded, and the product functionality can be enhanced.

Radiation chemistry has formed the basis for a number of environmentally friendly or "green" industrial process technologies. Decker (2012) reported in his keynote speech entitled "High performance UV-cured protective coatings" in the 8th Coatings Science International Conference, COSI 2012, that the photoinitiated polymerization of multifunctional monomers remains one of the fastest and more efficient methods presently available to generate three-dimensional polymer networks. Commercial success has been found in the elimination of volatile organic compounds in industrial large-scale applications. The process has been recognized for its environmental benefits by organizations such as the International Atomic Energy Agency, The United States Environmental Protection Agency, and the National Science Foundation. In addition to

state and regional utility related organizations, the Electric Power Research Institute also has been supportive of the UV processing.

In some instances, there has been a tolerant conjunction of public support, mainly through state-based programs, for industrial implementation of environmentally friendly irradiation processing technologies, combined with public desires for pollution prevention and energy conservation. More such programs to assist industry with capital conversion to irradiation processing are needed. Radiation chemistry combined with extrusion technology will only prosper when there is greater public understanding of the benefits of this environmentally friendly, "green" process. Radiation is, after all, as natural as sunlight itself.

We believe that in the future, many more extrusion/irradiation reactions will be developed, and that such reactions will simplify time- and resource-consuming conventional procedures. Extrusion/irradiation processes offer potential for transformations of biomass to clean products in an intriguing, effective way not reported before. The future for the application of this combined technology looks bright on an industrial scale.

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