ABSTRACT

The formation of functional hybrid polymeric materials by attaching graft polymer chains with desirable and advantageous tailored properties to the surface of a base polymer with desirable bulk character is an attractive application of graft polymerization. The grafting process allows us to modify, tune and alter the characteristics of base polymers and to control their wettability, biocompatibility, adsorption capacity and behavior, conductivity, antimicrobial property, and reactivity. The resulting graft copolymer creates significant opportunities to develop new hybrid platforms for a number of applications.

In this work, graft copolymers were prepared from natural and synthetic base polymers through the radiation-induced graft polymerization in solution and emulsion phases. We report the synthesis of adsorbents based from lignocellulosic polymers (water hyacinth fibers and abaca-based nonwoven fabric) and the development of method for imparting hydrophobic property to microcrystalline cellulose. The radiation-induced method that we employed results in the synthesis of base polymers with covalently bonded poly(glycidyl methacrylate) graft polymers that serve as anchors for the ligand which is responsible for the enhanced adsorption character. The synthesized grafted adsorbents exhibited improved adsorption capacity and kinetics than the base polymers and in some cases even better than commercially available ion exchange resins. The “grafting from” approach that stemmed from radiation-induced initiation offers the possibility to functionalize the surface of these base materials with graft polymer chains that possess contrasting properties (hydrophobic/hydrophilic). The developed modification platform enables the fabrication of radiation grafted cellulose that is compatible with hydrophobic matrices.

We also investigated the graft polymerization of a polymer through a technique that combines the merits of radiation-induced synthesis and reversible addition-fragmentation chain transfer (RAFT) process in emulsion phase. We demonstrated the facile combination of these techniques in simple reaction that ultimately results in the fabrication of copolymer with immobilized epoxide groups on the surface. The preparation of graft copolymers through a method that combines the advantages and merits of radiation-induced grafting in water-based emulsion, an environment friendly green method, and
controlled radical polymerization via RAFT-mediation is described, for the first time, in the second major part of this thesis. Both electron beam- and γ-radiation initiation processes were used in the synthesis. While conventional graft polymerization in emulsion phase yielded graft copolymers with low degree of grafting values (< 7.5% at 10% (wt/wt) glycidyl methacrylate concentration), addition of RAFT agent to the graft polymerization system allowed the synthesis of polyethylene/polypropylene-g-poly(glycidyl methacrylate) (PE/PP-g-PGMA) with more tunable degree of grafting (8% ≤ \( D_g \leq 94\% \)) by controlling the grafting parameters. Relatively good control (PDI ~ 1.2 for selected grafting conditions) during polymerization was attained. The number average molecular weight of free homopolymers increased as a function of monomer conversion. NMR analyses of the free homopolymers indicate the presence of dithiobenzoate group from 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid RAFT agent on the polymer chain. These evidences have been considered as a proof of RAFT mechanism.

Furthermore, the reactivity and adsorption behavior of the graft copolymer produced from the combination of radiation-induced grafting in emulsion phase and RAFT-mediation was evaluated. The PGMA graft chains from the PE/PP-g-PGMA that was prepared in emulsion phase through radiation-induced RAFT-mediated graft polymerization showed higher reactivity towards amination reaction at 40 °C compared to the conventionally prepared graft copolymer. Similar to the previously prepared adsorbent, the epoxide rings of PGMA served as a precursor group that were eventually converted to diglycol amic acid ligands. The diglycol amic acid modified PE/PP-g-PGMA prepared with RAFT mediation exhibited better Eu and Sm adsorption performance than the diglycol amic acid adsorbent prepared using conventional grafting. The diglycol amic acid modified PE/PP-g-PGMA exhibited selectivity for Eu over Cu and Fe in acidic solutions. The introduction of RAFT polymerization in the DA-modified adsorbent preparation process enhanced the reactivity and performance in terms of Eu and Sm adsorption.