ABSTRACT

Currently, biobased polymers from renewable feedstocks have been the pursuit of sustainable development to reduce our dependence on petroleum-based products. The field of sustainable polymers has grown in the past three decades from a few obscure examples to one of the most vibrant domains of modern polymer science and technology. In this background, the present thesis work reports the polymerization of wide family of acyclic terpenes, particularly the β -myrcene (MY), β -ocimene, alloocimene and β -farnesene from renewable feedstocks (classical chemistry similar to isoprene, unsaturated hydrocarbon from crude oil) via solvent-free redox emulsion pathway. The chemistry of polymerization towards reactivity of these biobased synthons based on the molecular architecture has been established. The synthesized polymyrcene displayed molecular weight of 168,250 Da and a sub-ambient glass transition temperature of -70 °C. The polymyrcene polymer predominantly contains 1,4-microstructure (mixture of 1,4-cis and 1,4-trans). The effect of ingredients and kinetic study on redox emulsion polymerization of β -myrcene was also delineated in this research work. The probable polymerization sites in β -myrcene were predicted from theoretical calculations. The use of acyclic terpene, β -myrcene, was further extended by synthesizing its copolymers with different methacrylates, like glycidyl methacrylate (GMA) and furfuryl methacrylate (FMA), for some basic and novel applications. The copolymers having different weight ratio of MY/GMA displayed molecular weight in the range of 71,500 to 105,870 Da and a sub-ambient glass transition temperature between -48 to -8 °C depending on the acrylate content. The synthesized copolymers from MY and FMA showed molecular weights between 59,080 to 84,210 Da and glass transition temperature between -25 to -40 °C, implying rubbery properties. The microstructures of all of these polymers were analyzed from spectroscopic measurements. Finally, to demonstrate the application, the surface and adhesion property of the synthesized polymers were measured. Then, β -myrcene based sustainable copolymers were compounded and vulcanized using conventional recipe and rubber processing method. 20 phr silica filled 80/20 MY/GMA and 80/20 MY/FMA elastomer vulcanizate offered good mechanical and dynamic mechanical properties (higher tan δ value at 0 °C as well as at -10 °C and -20 °C). Finally, the self-healing and thermo-reversible behaviour of MY/FMA elastomer was achieved via a Diels-Alder (DA) coupling reaction with bismaleimide as a cross linker. The reversible nature of the MY/FMA polymer network was evident from FT-IR, NMR spectroscopy, DSC analysis and by optical microscopy and atomic force microscopy (AFM). Mechanically adaptive nanocomposites were prepared, which were able to respond to exposure to a specific stimuli such as water, as reflected from the values of tensile storage modulus. In order to find alternative to petroleum-based polymers, preparation, characterization and properties of these terpene based polymers reported here would widen the future applications of sustainable polymers.

Keywords: Sustainable polymer, Terpenes, β -myrcene, Emulsion polymerization, Silica nanocomposite, Self-healing elastomers