

## Abstract

Current environmental concerns and environmental regulations have led to the necessity to synthesize monomers and polymers from renewable resources through environmentally friendly processes. In this work, photoinduced polymerization and aqueous emulsion polymerization were selected as polymerization techniques. Natural phenols have not been widely researched and employed in the synthesis of monomers to be polymerized through the aforementioned polymerization methods. Thus, eugenol, isoeugenol and dihydroeugenol, natural phenols coming from clove oil and lignin depolymerization, were chosen as building blocks.

The synthesis of nine monomers (eight novel molecules) derived from eugenol bearing polymerizable functional groups such as (meth)acrylate, epoxy and carbonate was achieved. Successful radical polymerization in solution was achieved with the (meth)acrylated eugenol-derivatives. The polymerization rate was affected by secondary reactions involving the allylic and propenyl groups in the eugenol and isoeugenol derivatives (degradative chain transfer and cross-propagation). However, most of the allylic and propenyl groups were preserved for post-polymerization reactions.

Photoinduced polymerization was executed with the methacrylate eugenol-derived monomers. The polymerization was monitored in the absence and presence of a photoinitiator and under air or protected from air, using Real-Time Fourier Transform Infrared Spectroscopy. The polymerization rate was again affected by the presence and reactivity of the allyl and propenyl groups in the eugenol- and isoeugenol-derived methacrylates, respectively. These groups are involved in radical addition, degradative chain transfer, and termination reactions, yielding crosslinked polymers. Without photoinitiator and in the presence of air, the formation of hydroperoxides for eugenol and isoeugenol derivatives led to a second polymerization regime. The materials, in the form of films, were characterized by differential scanning calorimetry, thermogravimetric analysis, and contact angle.

Eugenol-derived methacrylates were then homopolymerized through aqueous emulsion polymerization using three different initiation systems. Latexes of poly(ethoxy dihydroeugenyl methacrylate), poly(ethoxy eugenyl methacrylate) and poly(ethoxy isoeugenyl methacrylate) with particle diameter in the 45–71 nm range were successfully obtained. Glass transition temperatures of the resulting polymers ranged between 20°C and 72°C. This study opens the way to the use of these new biobased monomers into latexes formulation for adhesives and coatings applications. Subsequently, eugenol-derived methacrylates were copolymerized by emulsion polymerization to produce latexes for adhesive applications. Latexes containing ethoxy dihydroeugenyl methacrylate and ethoxy eugenyl methacrylate with high total solids content of 50 wt% were obtained and characterized. Latexes synthesis was carried out using a semibatch process, and latexes with particle diameters in the 159–178 nm range were successfully obtained. Glass transition temperature values of the resulting polymers ranged between –32°C and –28°C. Furthermore, tack and peel measurements confirmed the possibility to use these latexes in adhesive applications.