Bio-based Functional Polymers from Plant Oils

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Abstract

Using biomass as starting material for chemicals and plastics contributes to global sustainability without depletion of scarce resources, because of their large potential to substitute petrochemical derivatives to bio-based ones in industries. Natural plant and animal oil sources are found in abundance in the world; and hence, are expected as an ideal alternative chemical feedstock. Inexpensive triglyceride natural oils have been utilized extensively for coatings, inks, plasticizers, lubricants, resins and agrochemicals in addition to their applications in food industry. Since most of oil-based polymeric materials do not show properties of rigidity and strength required for structural applications by themselves, these oils were used as a toughening agent to produce interpenetrating networks.

This study mainly deals with composites from epoxidized plant oils and cellulose fibers. A high-performance bio-based composite material, a cellulose nanofiber-reinforced oil polymer-based composite, was synthesized by impregnating microfibrillated cellulose (MFC) sheet with a mixture of epoxidized soybean oil (ESO) and a curing agent under reduced pressure, followed by thermal curing. The ESO / MFC composite exhibited the high storage modulus in the rubbery region of the ESO polymer, while the ESO polymer showed the enormous drop of storage modulus around its glass transition temperature, strongly suggesting the large reinforcement effect by the MFC nanofiber. The tensile modulus and strength at break of the composites were much superior to those of the ESO polymer or the MFC sheet. Furthermore, another bio-based composite was developed from epoxidized plant oil and kenaf fiber sheet by similar synthetic procedures.

Green nanocomposite coatings have also been developed by an acid-catalyzed curing of epoxidized plant oils with 3-glycidoxypropyltrimethoxysilane. The nanocomposite showed excellent film properties; the hardness and mechanical strength improved by incorporating the silica network into the organic polymer matrix and the good flexibility was observed. The dynamic viscoelasticity analysis clearly showed reinforcement effect by the inorganic network. In addition, the present nanocomposite exhibited good biodegradability.

The present lecture also demonstrates synthesis of branched bio-based polyesters from lactic acid and a plant oil and their applications to improve properties of bioplastics such as poly(L- lactic acid) (PLLA). Plant oils are expected as an ideal alternative chemical feedstock, since oils are found in abundance in the world. In this study, castor oil was used as initiator for synthesis of a branched bio-based polymer by ring-opening polymerization of L-lactide or polycondensation of L-lactic acid. The resulting polymer possessed a hydroxyl group at the terminal and the molecular weight was precisely controlled by the feed ratio of the monomer and castor oil. The addition of only a small amount of the branched polymer to PLLA improved the strain at break, showing good plasticization effect of the branched polymer for PLLA.1 This branched polymer was also used as monomer for bio-based polyurethane forms with good mechanical strength.

The terminal hydroxyl group in this branched polymer was modified by phthalic anhydride. The product with potassium salt form greatly induced the crystallization of PLLA to improve the thermal and mechanical properties of PLLA. The crystallization half time ($t_{1/2}$) of the PLLA/branched polymer blend decreased significantly. By the addition of the branched polymer, the spherulite size of PLLA became much smaller than that of neat PLLA. Izod impact strength and deflection temperature under load of the blend were 8 KJ/m^2 and 130 ºC, respectively, which were much superior to those of PLLA (2 KJ/m^2 and 55 ºC, respectively). The trimellitoyl-terminated branched polymer also showed good crystallization for PLLA. Interestingly, the branched polymer having the hydroxyl group at the terminal acted as a good crystal nucleating agent for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), an industrially important bacterial thermoplastic.

Keywords: Bio-based polymers; plant oils; bioplastics; composites