Physical Modification of Polylactide

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Light weight and durability, valuable feature of plastics, become serious flaws when they turn to waste: post-consumer polymer packaging degrade slowly and they occupy large space in plastics waste disposal. One of the solutions are biodegradable polymers that are transformed quickly by enzymes into water and carbon dioxide. Most interesting is polylactide (PLA) that can be produced from renewable resources: agricultural products and side products of food production. Potential applications of PLA are: foil packaging, foil fibers, injection mouldings and extruded profiles.

Due to a broad range of applications PLA must be subjected to serious modifications in order to accomplish the best performance. Chemical modification is achieved by introducing a fraction of lactide of opposite chirality or by copolymerization with selected biodegradable co-monomers. Simpler and easier way is by physical modification. In our research we explored various means of physical modifications: by thermal treatment, plastification, filling with natural fibrous fillers and particulate mineral fillers, compounding with various organo-modified nanoclays and by molecular orientation resulting from cavity-free plastic deformation [1-10]. The driving force of the investigation was an expected improvement of mechanical and physical properties of PLA and PLA based systems.

Plastic deformation in cavity-free manner (channel die) of amorphous copolymer P(L/DL)LA, 70/30 (i.e. unable to crystallize thermally), was studied at the temperature from 60 to 90 ^{o}C. Evolution of structure and modification of mechanical properties were investigated as a function of compression ratio. Transformation of amorphous P(L/DL)LA to crystalline texture oriented in the direction of plastic flow without a trace of lamellar structure was clearly detected. Formed crystalites (α crystallographic form) were small up to 9 nm in the transverse direction to the flow, while the crystallinity was not exceeding 9% at highest compression ratios. Significant increase of T_g and few fold increase of tensile strength of 120 MPa as compared to 33 MPa for unoriented PLA.

Improvement of deformability of PLA both amorphous and crystalline was achieved by elaborating of a new plasticizer – poly(propylene glycol) (PPG). PPG is soluble in PLA and is not exuded by a crystallizing front of spherulites and remains dissolved in the amorphous phase of PLA. Improvement of deformability depends on the amount of plasticizer and is very effective for amorphous PLA. However, in the case of crystalline PLA PPG is concentrated in the amorphous phase between crystalline lamellae and plasticizes PLA very efficiently: by a decrease of yield stress, an increase of strain at fracture up to 100%, and an increase of tensile impact strength from 36 to 60 kJ/m^2 for 10wt.% of plasticizer. Improvement of mechanical properties of crystalline PLA by plastification demonstrated the use of crystalline PLA at temperature higher than its T_g, up to the melting point of crystals (+160-170^{o}C), i.e. cups for hot drinks, plates for hot food, micro-oven heating etc.

Filling PLA with natural fibrous fillers such as hemp fibers, grinded cacao shells, grinded apple pomace, oat chaff and other leads to the increase of tensile modulus. Plasticizing such systems with PPG or poly(ethylene glycol) allows the recovery of drawability.

Studies of nanocomposites of PLA with organo-modified nanoclay showed that the dispersion of nanoclay depends on the nature of organo-modification and it is best with Cloisite 30B. Exfoliation of nanoclay can be increased by increasing the mixing time with fixed other compounding parameters. It indicates that the main mechanism of exfoliation is stripping clay platelets one by one. Nanocomposites were characterized by thermal, rheological, structural and mechanical studies. It was found that the molar mass of PLA decreases during mixing, nevertheless the main parameter influencing the performance of PLA nanocomposites is their phase structure. The best exfoliated PLA nanocomposite showed the best barrier properties for gas diffusion. The barrier properties of PLA nanocomposites are especially important because of possible application of PLA for food and drink packaging. The presented results illustrate a broad range of physical modifications including plastification, molecular orientation, filling with fibrous and particulate natural fillers as well as nanofillers. The role of those factors is extending beyond to interaction during mechanical loading to modification of supermolecular structure and all physical properties of PLA based systems.

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