REACTIVE BLOCK COPOLYMERS OF LACTIDE AND THEIR APPLICATION IN PLA PROCESSING

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ABSTRACT

Polylactide (PLA) is a synthetic biodegradable polymer which may be obtained from renewable resources. This material is tough, usually semi-crystalline but brittle and non-resilient. The techniques of extrusion, injection molding, 3D printing or vacuum thermoforming (in case of amorphous material) can be applied for the processing of PLA. Melt processing, carried out often at 180-210°C causes some defects in PLA chain structure, due to radical and hydrolytic side reactions of degradation. Therefore, chain extenders are sometimes used as plastic components in order to compensate these flaws. Commercially available epoxy-functionalized chain extenders (e.g. Joncryl ADR 4368, CESA-extend) are dedicated generally for PET, however, they can be applied to other polyesters, polyamides and polycarbonates. The aim of this work was the synthesis of PLA-dedicated epoxy chain extender comprising a PLA segment.

Block copolymers consisting of PLA block and epoxy-rich segments were prepared using controlled polymerization techniques. The topology of diblock (AB), triblock (ABA) and three arm star block (AB_3) copolymers was achieved. First, linear or star PLA homopolymers defined by M_n in the range of 9 - 14 kg/mol were obtained *via* ROP of L-Lactide initiated with isopropanol, ethylene glycol and trimethylolpropane and carried out in bulk at 190°C for 3 hours. After that, terminal hydroxyl groups were reacted with 2-bromoisobutyric bromide in order to transform end groups into ATRP initiating species. It was found that after purification of ω-bromo-PLA, their molar masses increased significantly. Glycidyl and butyl methacrylates were used as comonomers in ATRP initiated with refunctionalized PLA segments and star. Block copolymers of PLA containing epoxy-rich (outer) segments were formed. Molar masses were found to be in the range of 33 - 38 kg/mol, whereas the content of PLA varied from 30 to 55%. These copolymers were characterized with various epoxy equivalent weight (EEW 574 - 5500). The copolymers obtained were used for stabilization of PLA during processing (30 minutes of mixing) in MiniLab II laboratory twin screw extruder (compounder) equipped with integrated backflow channel which allows to measure relative viscosity (RV) of melt due to two pressure sensors. It was found that RV of pure PLA decreased dramatically during measurement due to degradation processes, whereas the introduction of 1% of linear diblock (EEW = 574) or 2% of triblock (EEW = 3000) PLA-epoxy copolymers fully compensated the effect of PLA matrix chain destruction. GPC analysis of the mixtures confirmed the reaction between PLA chains and epoxy additive which led to high molar mass branched fraction. Star block copolymer was not efficient even at load of 9 % because of too high EEW (5500). All materials after mixing were formed in extrusion process into thin strings and were submitted for tensile strength test. The linear additives improved the elongation at break and slightly the tensile strength, whereas the star copolymer did not affect or marginally worsened these features of composites.

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