New Material Design of Polylactides by Controlled Stereocomplexation and Hybridization

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Abstract

Stereocomplexation of PLA has been studied in various ways for creating high-performance PLA materials. However, concomitant formation of hc and sc crystals reduces the performances of the final stereo mixture of PLLA and PDLA. Therefore, in this study, sc crystallization is manipulated on sub-micron or nano-meter level by using hybridization and composite techniques in order to obtain high-performance PLAs. In the first trial, the author used hydrolytic polycondensation of silyl-terminated PLA for hyper-conjugation and hybridization of PLA. Silane coupling reaction has been often used to provide a stable bond between organic and inorganic moieties and to convert the incorporated heterogeneous phase into a uniform composite structure. The general reaction of the silane coupling agents consists of two steps. The siloxyl groups are usually protected by alkoxyl, halo, or amino groups which are readily hydrolyzed in contact with water. Following their hydrolysis, reactive silanol groups are generated and

spontaneously, which can condense with each other to form siloxane bonds. These processes are repeated until a hyper-conjugated configuration is formed. Although the general hyper-conjugated polymers are formed through core-to-branch propagation, the author demonstrates a branch-to-core propagation mechanism for the hyper-conjugation in solution-cast films. The first approach for their trial is to modify PLA by using PDLA and PLLA prepolymers having a trimethoxysilyl terminal group (mSi-PLA) for which hydrolytic polycondensation affords hyper-conjugated PLLA (mH-PLLA) and PDLA (mH-PDLA). Here, both mSi-PLA and mH-PLA are bleneded with PLLA by solution casting method. The resultant films are then analyzed to reveal the properties and specific morphologies related to stereocomplex crystallization and hybridization. In the second trial, triethoxysilyl-terminated PDLA (eSi-PDLA) is synthesized and blended with PLLA to compare its effects on the morphology change with that of mSi-PDLA. Since the rate of hydrolytic polycondensation is changed with the alkoxyl chain groups, the competitive hydrolytic polycondesation and stereocomplexation gives profound difference in morphology. In the third trial, direct synthesis of trialkoxysilyl PDLA polymers is examined by one-step ROP of D-lactide in order to make them in larger scale. In this new method, it is important how to control the ROP without chain transfer reactions taking place between the propagation hydroxyls and terminal siloxane groups.

In the final trial, the author tries to fabricate sc-PLA fibers by using a mixture of two stereo di-block type PLAs (di-sb-PLA) having complementary PLLA/PDLA block ratios. The obtained sb-PLA fibers are allowed to form preferential sc crystallization with regularity of sc lamellae growth. These studies reveal that phase transition in PLA matrix is very important to control the properties and morphology of the sc-PLA materials in which modified PLAs play key role and effect.