

Effect of Miscible Polymeric Diluent on Spherulites of Stereocomplexing Poly(L-Lactic Acid) and Poly(D-Lactic Acid)

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Stereocomplex PLA (sc-PLA) can form based on stereoselective van der Waals forces depending on the situation such as molecular weight, mixing ratio, annealing temperature, etc. Less attention has been paid to the influence of polymeric diluent as a third component on blends of sc-PLA system. Effects of PHB on thermal behavior, crystalline structures and morphology of miscible sc-PLA were studied using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), atomic-force and scanning electron microscopy (AFM/SEM), and polarizing optical microscopy (POM). Amorphous phase of PHB/sc-PLA blend is proven miscible as evidenced by single composition-dependent glass temperature (T_g) and the depression in the crystallization temperature of sc-PLA in blends with increasing PHB content. For neat sc-PLA, a single endotherm ($T_m \sim 220^\circ\text{C}$) was revealed during cooling or subsequent isothermal crystallization. However, the lower endotherm ($T_m \sim 190^\circ\text{C}$) was clearly observed in blends, indicating that the original sc-PLA endotherm was disrupted, leading to less perfect crystals with increasing PHB contents. When crystallized at high T_c (130°C or above), morphology transits from original Maltese-cross spherulites to highly dendritic form in PHB/sc-PLA blends of high PHB contents (50wt% or higher), where PHB acts as an amorphous species. Combination of DSC and POM results suggested that occurrence of dendritic spherulite was a result of the less perfect crystallites formed in sc-PLA. In-situ observation of evolving process of sc-PLA formation, morphology transformation from original Maltese-cross spherulites into a dendritic morphology by disintegrating the spherulites, which are restructured into two distinct crystal forms: edge-on feather-like dendrites (early growth) and flat-on wedge-like crystal plates (later growth). Regardless of spherulitic disintegration by PHB, the WAXD result shows that these two new morphologies still retain the original sc-PLA unit cells.