IMPACT OF MIDDLE BLOCK COMPOSITION ON THE THERMAL BEHAVIOUR OF POLY(L-LACTIDE)-BASED TRIBLOCK COPOLYMERS

Ivan Ristić[1*], Marija Krstić[1], Suzana Cakić[2], Jelena Tanasić[1], Nina Jokić[1], Ljubiša Nikolić[2], Vladan Mićić[3]

[1]*University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, Novi Sad, Serbia, ivan.ristic@uns.ac.rs**

[2]*University of Niš, Faculty of Technology, Bulevar oslobođenja 126, Leskovac, Serbia*

[3]*University of East Sarajevo, Faculty of Technology Zvornik, Karakaj 34a, Zvornik, Bosnia and Herzegovina*

Abstract

Poly(L-lactide) (PLLA), a biodegradable polymer with properties comparable to conventional plastics, is limited by its inherent brittleness and thermal instability. This study explores the enhancement of PLLA properties through the synthesis of ABA-type block copolymers with distinct soft middle blocks—polyester poly(methylricinoleate) (PMR) and polyether poly(1,3-propane diol) (PPD). As a first two types of soft-middle blocks, poly(methylricinoleate) and poly(1,3-propane diol) with dihydroxyl end groups were synthesized. After that, two series of novel biodegradable triblock copolymers, PLLA-b-PMR-b-PLLA and PLLA-b-PPD-b-PLLA, were obtained. By systematically comparing these two systems using FTIR, DSC, and TG, this work investigates how the topology and structure of the middle block influence the thermal, and phase behavior of the resulting materials. FTIR spectroscopy analysis confirmed presumed structure of block copolymer. In addition, the block structure was confirmed by the existence of two separate glass transition temperatures for middle blocks and PLLA. The type of middle blocks influenced crystallization and melting of PLLA segments, which are completely hindered in PPD based block copolymers. PMR based triblock copolyester, due to the high degree of phase separation, shows a clear trend of increasing T_g value of PLLA segments with increasing its molar mass. Using TG analysis of the pure segments it was confirmed that the beginning of segment decomposition in triblock polymer significantly shifted to higher temperatures compared to pure blocks, as a consequence of phase separation of blocks, with PMR-based systems showing the most pronounced increase in decomposition onset temperatures. The topology of the copolymer components and the structure of the middle soft block were crucial for adjusting the thermal characteritics of synthetized block copolymers. The results reveal that the immiscibility between the hard PLLA and soft middle segments creates phase-separated structures, leading to a significant shift in thermal decomposition temperatures. These findings underscore the importance of middle block composition in tuning the thermal properties of biodegradable polymers and offer a pathway for designing high-performance, sustainable polymers for advanced applications.

Keywords: *biobased polymers, polylactide, segmented block copolymer, thermal properties.*