Abstract

The aim of the study was to modify polylactide (PLA) by introducing a group containing a covalent bond susceptible to thermal dissociation into the PLA structure. The group selected was tetraphenylethane (TPE), which, upon heating, dissociates to form radicals. Introducing TPE groups into the PLA structure opened up pathways for modifying PLA in various ways.

The first research objective was the introduction of the TPE group into the PLA chain. For this purpose, preliminary research was conducted to analyze the reactivity of tetraphenylethane-1,2-diol (TPED) as a compound allowing the introduction of TPE groups into the PLA structure. The studies showed insufficient reactivity of TPED's tertiary -OH groups in both lactide polymerization initiation and reactions with diisocyanates to couple with PLA diol. Alternative methods for introducing the TPE group were developed, including the synthesis of benzophenone (BP) derivatives with reactive -OH groups, which serve as precursors to TPE groups. Using the obtained derivatives, two methods were developed to introduce TPE groups into the PLA macromolecule. The first method was cationic polymerization of lactide (LA) initiated by the obtained BP_ET derivative, followed by chains coupling which resulted in PLA with single embedded TPE group in the middle of the chain. The second method involved coupling the TPE-diET derivative with PLA oligodiol using diisocyanate, yielding a polyester-urethane containing multiple TPE groups in the chain. The introduction of TPE groups into the polylactide-based polymer chain paved the way for PLA block copolymers with vinyl monomers, which formed the first direction of the research. The obtained polylactides with TPE groups in the center were used as macroinitiators to initiate the polymerization of vinyl monomers. In this way, for the first time using the iniferter method, PLA/poly(vinyl monomer) block copolymers were obtained.

The second focus of the research was the use of TPE groups for the synthesis of reversible/dynamic covalent polylactide networks. Two methods for synthesizing networks with TPE groups at the network nodes were developed. In the first method, the epoxy ring containing derivative (BP_EP) was used as a comonomer in the copolymerization reaction with LA. The resulting (LA-co-BP_EP) copolymer was then cross-linked through UV-induced coupling of the BP side groups. The reversible nature of the resulting network was demonstrated through rheological studies. The presence of TPE groups at the network nodes, capable of initiating vinyl monomer polymerization, was also used to introduce AN units into the network structure. It was shown that the introduction of PAN blocks into the network structure improved

thermal resistance and mechanical properties. The second method for producing networks containing TPE groups in their structure involved coupling star-shaped PLA containing TPE groups in the core, using diisocyanate. Rheological studies demonstrated the dynamic nature of the networks. The networks' ability to self-repair after damage was also demonstrated.