ABSTRACT

The doctoral dissertation entitled "Eco-polyols based on PLA waste as alternative raw materials for obtaining rigid polyurethane–polyisocyanurate foams" concerns the development of a method for utilizing waste polylactide (PLA) originating from 3D printing through chemical recycling and the application of the resulting eco-polyols in the synthesis of rigid polyurethane – polyisocyanurate foams (PUR/PIR). The research is consistent with the principles of the circular economy, as it combines the reduction of petrochemical raw material consumption with the extension of the life cycle of waste biodegradable polymer.

The aim of the research was to carry out the chemical recycling of PLA, obtain polyhydroxyl compounds with properties suitable for use in polyurethane formulations, and determine the effect of the type and content of eco-polyol on the properties of the resulting foams. Two transesterification agents were used: diethylene glycol (DEG) and glycerol (GL). The resulting series of eco-polyols were designated ODE and OGL, respectively. The effect of the PLA to transesterification agent ratio on the physicochemical properties and structure of the products was investigated.

The eco-polyols were comprehensively characterized, including determination of hydroxyl and acid values, density, viscosity, water content, average molecular weight, dispersity and functionality. Their chemical structure was confirmed using FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy, while thermal properties were determined by differential scanning calorimetry (DSC). The results demonstrated that both the type and amount of transesterification agent significantly affected the structure and properties of the eco-polyols. A decrease in the amount of DEG or GL resulted in longer oligomer chains and, consequently, higher molecular weight and viscosity. The highest hydroxyl values were obtained for ODE 500 (329.49 mg KOH/g) and OGL 500 (543.93 mg KOH/g). All analyzed eco-polyols demonstrated high susceptibility to biodegradation in a soil environment.

In the next stage, PUR/PIR formulations were developed in which the eco-polyols partially replaced the commercial petrochemical polyol Rokopol RF – 551. The resulting foams were subjected to a comprehensive assessment including technological times, apparent density, cellular structure by scanning electron microscopy (SEM), compressive strength, brittleness, dimensional stability during accelerated aging, thermal conductivity, closed-cell content, water absorption and water uptake. Their fire performance was evaluated using the Butler combustion test, limiting oxygen index (LOI) and cone calorimetry. The biodegradation susceptibility of selected foams was also investigated.

The results demonstrated a pronounced effect of the transesterification agent on the structure and properties of the PUR/PIR foams. ODE-based foams maintained a high closed-cell content of 89.56 % – 91.23 %, while exhibiting low density, high compressive strength and favorable thermal insulation properties. Particularly favorable properties were obtained for the ODE 500 formulation at 0.5 R, which exhibited a density of 31.43 kg/m^3, compressive strength of 303.16 kPa, brittleness of 0.60 %, approximately 91 % closed cells and a thermal conductivity coefficient of 0.033 W/(m·K). OGL-based foams exhibited considerably stronger cell opening; at 0.5 R, the closed-cell content decreased to approximately 2.74 % – 6.54 %. This was accompanied by increased water absorption and thermal conductivity and a decrease in mechanical strength.

The incorporation of eco-polyols in the presence of TCPP had a favorable effect on the combustion behavior of the foams. An increase in the residue after combustion and a reduction in the intensity of combustion development were observed, as confirmed by cone calorimetry. At the same time, the limiting oxygen index remained relatively stable at approximately 24 vol.% O_2. An important result was also the increased biodegradation susceptibility of the obtained materials. For ODE-based foams, the degree of biodegradation (D_t) ranged from 47.49 % to 74.25 % whereas for OGL-based foams it ranged from 10.49 % to 46.21 % the value obtained for the reference foam was 8.03 %.

The obtained results confirmed that the chemical recycling of waste PLA can constitute an effective route for producing valuable polyol raw materials for the synthesis of PUR/PIR foams. The type of transesterification agent enables the cellular structure and functional properties of the foams to be controlled. The results indicate that maximum replacement of the petrochemical polyol is not necessarily advantageous; rather, its content should be selected according to the required properties of the final material. The developed approach makes it possible to utilize waste PLA, reduce the contribution of petrochemical raw materials and obtain materials with controlled functional and fire properties as well as increased biodegradation susceptibility.