IMPROVING THE PROPERTIES OF BIODEGRADABLE PLASTICS

PhD THESES

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1. INTRODUCTION AND OBJECTIVES

One of the main challenges of our time is the protection of our environment, which is also included in the sustainability goals set. One of the basic pillars of environmental protection is the reduction of the amount of accumulated plastic waste and the elimination of its formation, as well as the reduction of global CO_2 emissions. In practice, two methods can lead to the achievement of the goals, either the recycling of the generated waste (chemically or thermally, or regranulation followed by mechanical recycling), which can significantly reduce the amount of waste, or the introduction of biodegradable plastics and composites onto the market. It also contributes to the prevention of waste material and the reduction of CO_2 emissions with an almost neutral carbon cycle. There is a lot of potential in the application of biodegradable plastics that can be introduced as an alternative to traditional plastics and, with the development of appropriate technical properties, can serve as an alternative to mass plastics or plastic utensils from non-renewable sources used in specific application areas. The above motivated me to develop a biodegradable polymer composite that, in addition to its basic components being derived from renewable sources, meets the technical requirements for bulk plastics and, in terms of rheology, meets the parameters expected in the shear rate ranges of the devices used in the plastics processing industry. In addition, I determined that preserving the biodegradability characteristic of the basic components was an important criterion. In order to achieve my goal, I created composites from polylactic acid and native corn starch with a 10-50% corn starch content. Due to the unfavorable miscibility between the two polymers, the technical properties proved to be inadequate. Eliminating the antagonistic effects, I wanted to increase the interfacial adhesion with additives that are able to extend and stabilize the miscibility limit. For the synthesis of the additives, I chose vegetable oils with several reactive/functional groups and significantly different fatty acid compositions. In order to promote favorable reactions, I placed significant emphasis on optimizing the reaction parameters of the additive synthesis and on determining the necessity of the solvent used as the reaction medium through syntheses due to its significant cost and carcinogenic effect.

2. EXPERIMENTS AND MEASUREMENT METHODS

2.1. Additive synthesis

The additive synthesis was carried out in a round-bottomed flask equipped with electric heating and a stirrer. The reactions were examined at temperatures between 120-200 °C, the stirring speed was 120 1/min. The experiment was performed with different types of vegetable oil: castor, rapeseed and sunflower oil, the molar ratio of vegetable oil to maleic anhydride was 1:1. Xylene was used as solvent and di-tert-butyl peroxide as an initiator for the radical reactions. Since I also studied additive production without an organic solvent, an additive synthesis was also carried out, in which I omitted the solvent while preparing the reaction medium. After the reaction time, the volatile substances and the solvent were removed from the reaction medium using a vacuum evaporator.

2.2. Follow-up of additive synthesis and test methods of additives

The additive synthesis process was followed by classical analytical and large-scale instrumental qualification methods. The classical analytical measurements determined the progress of the additive synthesis and the quality of the reaction products. The acid number, the iodobromine number and the unreacted maleic anhydride content remaining in the reaction products were determined using classical titration techniques. Using Fourier transform infrared spectroscopy, I examined the rotational-vibrational vibrations in the mid-infrared range (i.e. between 400-4000 cm^{-1}) on a germanium crystal, and based on the absorbance plotted as a function of the wavenumber, I could conclude that the reaction had occurred. The rheological behavior of the additives was characterized using a dynamic shear rheometer in the shear rate range of 0.01-1000 1/s. Furthermore, I supplemented the qualification of the additives by examining the thermogravimetric properties of the prepared samples (at a heating rate of 10 °C/min, in a nitrogen atmosphere (20 ml/min)).

2.3. Qualification of composites, additive effect testing

For the additive effect study, I used the additives in the form of a masterbatch - a PLA mixture with a high active ingredient content - which enabled simpler and more accurate measurement. The qualification of the composites was carried out in each case by Fourier transform infrared spectroscopy (on zinc selenide crystal) and thermogravimetric properties determination, supplemented by the knowledge and determination of the crystallization characteristics of the composites, which I studied by differential scanning calorimetric analysis in a nitrogen atmosphere, with a heating/cooling rate of 10 °C/min. Differential scanning calorimetric analysis was performed in four stages: in the first heating stage, the temperature increased from 20 °C to 200 °C, then in the second stage, the sample was tempered at 200 °C for three minutes, in the third stage, it was cooled to 20 °C, and then in the fourth stage, the second heating phase to 200 °C took place. The second heating stage was taken into account when evaluating the results. The rheological characterization of the composites was followed by a capillary rheometer in the shear rate range of 5-10000 1/s. The mechanical properties were determined with a universal tensile tester with a crosshead displacement speed of 75 mm/min for tensile tests and 5 mm/min for bending tests. The Charpy impact strength was determined using a 1J hammer on specimens with an “A” type notch. The morphological structure was examined by studying scanning electron microscopy images (HV: 5–10 kV, mag: 80–20,000×).

2.4. Preparation of specimens

I determined the technical properties of test specimens produced by three different techniques: pressing technique, calendering and injection molding, all during the implementation of my experimental work. During the pressing technique, I kept the composite regrind at a temperature of 170 °C for 10 minutes under a load of 11 tons, as a result of which I formed composite sheets measuring 170 mm × 170 mm × 2 mm. Then, I cut test specimens 10 mm wide and 50 mm long from the sheets. During the calendering processing, I used a temperature profile of 160-180 °C and an extrusion screw speed of 125 1/min to produce a foil sample, from which I formed foil test specimens measuring 100 mm x 20 mm x 0.06 mm. Regarding injection molding, the corn starch content influenced the temperature profile: while for the sample containing the highest proportion of corn starch (50/50 polylactic acid/corn starch), the profile starting from a temperature of 160 °C was favorable for production. For the blend with the lowest corn starch content (90/10 polylactic acid/corn starch), an injection molding temperature of 180 °C was necessary. I injection molded test specimens measuring 5 mm x 75 mm x 2 mm.

2.5. Composting experiments of test specimens and their monitoring

The biodegradability of the test specimens was examined by placing them in different compost material (compost according to MSZ EN ISO 20200:2016 standard, compost containing α-amylase and lipase enzymes), determining the ratio changes of the amorphous and crystalline phases (differential scanning calorimetry) and morphological examinations (optical microscopy and scanning electron microscopy)..

3. THESIS POINTS

3.1 Investigation and optimization of additive synthesis conditions through temperature as a parameter, solvent and vegetable oil type

3.1.1 Based on titrimetric studies (acid number values and unreacted maleic anhydride content), it was determined that the optimal temperature for the reaction between sunflower, rapeseed, and castor oil and maleic anhydride in the case of solvent-based additive synthesis was 120 °C in the tested temperature range of 120-200 °C [4.1].

3.1.2 It was found that in the case of castor oil, maleic anhydride and castor oil triglyceride react at 140 °C without the solvent [4.1]. The presence of the product resulting from the reaction was confirmed by Fourier transform infrared spectroscopy and titrimetric studies (acid number and unreacted maleic anhydride content). This finding provides flexibility for additive synthesis from environmental, food safety and health perspectives.

3.1.3 Based on the acid number values and unreacted maleic anhydride content, it was determined that during the reaction between sunflower, rapeseed, castor oil and maleic anhydride, the incorporation of maleic anhydride was the highest when using castor oil, while the lowest incorporation was observed when using sunflower oil. [4.1].

3.2 Investigation of the effects of synthesized additives on the structural and technical properties of polylactic acid/corn starch composites

3.2.1 It was found that in the case of pressed PLA/corn starch specimens, compared to the effect of the reference polylactic acid grafted maleic anhydride (PLA-g-MA) additive, the additives synthesized at 140 °C in the presence of xylene significantly increased the Charpy impact strength value, regardless of the vegetable oil type (castor, rapeseed and sunflower oil) and conditioning [4.2].

Based on the tensile tests, it was found that in the case of the pressed specimens, neither PLA-g-MA nor the vegetable oil-based additives synthesized by me at 140 °C in the presence of xylene increased the tensile strength value [4.2]. It was confirmed with measurements that the increase in elongation at break could always be achieved in the case of composites made by pressing with rapeseed or castor oil-based additives synthesized at 140 °C in the presence of xylene [4.2]. Furthermore, it was found that the use of the reference PLA-g-MA at the same concentration was more effective in increasing the flexural modulus of the pressed specimens than the additives synthesized by me at 140 °C in the presence of xylene [4.2].

3.2.2 Based on differential scanning calorimetry studies performed on foils produced by calendering technique, it was determined that corn starch had an effect on the crystallization of polylactic acid in the matrices of the prepared mixtures. The degree of crystallinity increased with increasing the blending ratio of corn starch [4.3]. Furthermore, it was found that the castor oil-based additives synthesized at 140 °C in the presence and absence of xylene did not affect the chain mobility of the polylactic acid, as there was no significant difference between the glass transition temperatures (58.1-60.2 °C) [4.3].

Based on tensile tests of the foil samples, it was determined that both tensile strength and elongation at break decreased with the addition of castor oil-based additives synthesized at 140 °C in the presence and absence of xylene [4.3].

3.2.3 It was found that the mechanical properties (tensile and impact tests) of injection-molded specimens containing 50% corn starch could not be enhanced by the addition of castor oil-based additives synthesized without or in the presence of xylene at 140 °C. However, it was found that by adding these additives, both the tensile strength and the impact resistance of injection-molded specimens containing 10% corn starch could be significantly increased. In addition, the elongation at break of the specimens was also enhanced regardless of whether the additive synthesis was carried out with or without solvent [4.1].

3.3 Investigation of changes in biodegradability due to corn starch content, castor oil-based additive and enzymes

3.3.1 Based on differential scanning calorimetry studies of injection-molded specimens, it was found that, regardless of the addition, both 10% and 50% corn starch content influenced the polylactic acid chain mobility and, consequently, the rate of biodegradation: the addition of corn starch at a low concentration increased the degradation of the lactic acid polymer chains, as the crystalline fraction increased during composting compared to the reference virgin polylactic acid. This is evidenced by the fact that the PLA/corn starch specimens, after the biodegradation test in standard compost, showed a higher degree of crystallinity compared to the reference PLA specimen.

3.3.2 Examining the 50/50 polylactic acid/corn starch injection molded specimens, based on the higher degree of crystallinity observed after composting (compared to the reference sample), it was concluded that the castor oil-based additive enabled a faster biodegradation process, as the degree of crystallinity increased in the presence of xylene solvent and without the addition of castor oil-based additives compared to the reference PLA/corn starch specimen. This finding is not true in the case of the 90/10 polylactic acid/corn starch specimens containing additive, based on the lower degree of crystallinity of the specimens compared to the reference PLA specimen.

Following the biodegradability tests, the mechanical properties were not determined due to degradation of the specimens.

3.3.3 Based on the crystallinity degrees and electron microscopy images observed during the composting experiments with α-amylase enzyme, it was determined that the addition of the α-amylase mixture had a positive effect on the biodegradability of the injection-molded specimens containing 10% corn starch and the solvent-free synthesized castor oil-based additive. Compared to the reference, additive-free 90/10 PLA/corn starch specimen, a higher value was measured in the case of the 90/10 PLA/corn starch specimen containing the solvent-free synthesized castor oil-based additive after the biodegradability test.

3.3.4 Comparing the structures and crystallinity degrees observed during composting of the reference (standard compost), the α-amylase and the lipase containing composts, it was found that in the case of the composites/blends with higher corn starch content tested, the crystallinity degree could not be increased by mixing the enzyme under the tested conditions. Namely, after the biodegradability test in the enzyme-free standard compost, higher crystallinity degrees were measured in both the castor oil-based additive synthesized in the presence of xylene and the 50/50 PLA/corn starch test specimen containing the additive synthesized without xylene than in the composts containing the enzyme.

4. PUBLICATIONS FORMING THE BASIS OF THE PhD THESIS

Published papers

4.1 B. Nagy, F. Török, Sz. Tomasek, N. Miskolczi: Vegetable oil based additives to enhance the properties of PLA/Starch composites: The effect of reaction parameters, Industrial Crops & Products 191 (2023) 116025. DOI: 10.1016/j.indcrop.2022.116025. (IF = 5,363, based on JCR)

4.2 B. Nagy, N. Miskolczi, Z. Eller: Improving Mechanical Properties of PLA/Starch Blends Using Masterbatch Containing Vegetable Oil Based Active Ingredients, Polymers 2021, 13, 2981.DOI: 10.3390/polym13172981. (IF = 4,967, based on JCR)

4.3 B. Nagy, N. Miskolczi, Z. Eller: Evaluation of the Effect of Castor Oil-Based Experimental Additives on Pla/Starch Foils, Hungarian Journal of Industry and Chemistry 2023, 51 (2). DOI: 10.33927/hjic-2023-16. (IF: -)

Conference presentations without full text

4.4 Bianka Nagy, Norbert Miskolczi: Investigation of films made of biodegradable components int he presence of vegetable oil-based additives, Ph.D. Workshop of 2022 Silk Road International Symposium ont he Cooperation and Integration of Industry, Education, Research and Applications of Energy & Chemicals

4.5 Nagy Bianka, Miskolczi Norbert: Kukoricakeményítőből és politejsavból előállított kompozitok összeférhetőségének javítása növényi olaj alapú ágenssel, 50. Műszaki Kémiai Napok, 2022.04.26-28.

4.6 Bianka Nagy, Norbert Miskolczi: Vegetable oils for the modification of polylactic acid: opportunities and challenges, 10th IconSWM-CE 2020, 2-5 December 2020, Jadavpur University, Kolkata, West Bengal, India

5. Publications related to the topic of the PhD thesis

Published papers

5.1 B. Nagy, Cs. Varga, L. Simon-Stőger, K.Kontos: Remarkable Role of Experimental Olefin-Maleic-Anhydride Copolymer Based Compatibilizing Additives in Blends of Waste PET Bottles and Polyamide, Waste and Biomass Valorization, 2020, 12, 3035-3047. DOI: 10.1007/s12649-020-01253-5.

5.2 L. Simon-Stőger, Cs, Varga, E. Greczula, B. Nagy: A journey into recycling of waste elastomers via a novel type of compatibilizing additives, Express Polymer Letters, 13, 443-445, 2019. DOI: 10.3144/expresspolymlett.2019.37.

5.3 Nagy Roland, Hartyányi Máté, Nagy Bianka, Varga Csilla: Szabad dietanolamin tartalom meghatározása, Műszaki Tudományos Közlemények, 13, 2020. DOI: 10.33895/mtk-2020.13.32; 10.33894/mtk-2020.13.32.

Conference presentations without full text

5.4 Nagy B., Varga Cs.: PET/PA blendek mechanikai tulajdonságainak vizsgálata olefin-maleinsav-anhidrid kopolimer alapú adalékok jelenlétében, Műszaki Kémiai Napok 2019. 04. 16-18.

5.5 B. Nagy, Cs. Varga: Remarkable role of experimental olefin-maleic-anhydride copolymer based compatibilizing additives in PET bottle recycling, 16th International Conference on Environmental Science and Technology CEST2019, 4-7 September 2019

6. SCIENTOMETRIC DATA

Total number of publications: 6 pcs

Number of publications forming the basis of the PhD thesis: 3 pcs

cumulative impact factor: 10,33

Number of independent references: 34 pcs

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