ANNOTATION

of the dissertation thesis for the degree of Doctor of Philosophy (PhD) in the educational program “8D07502 – Standardization and Certification (by industry)” by

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STANDARDIZATION OF RECYCLED PLASTIC MATERIALS FOR ADDITIVE MANUFACTURING

General description of the work

The thesis presents results on quality enhancement and standardization of recycled polylactide acid for additive manufacturing.

Relevance of the topic

Today, the accumulation of plastic waste is a huge threat of environmental pollution. To deal with plastic waste, i.e. slow-degrading petroleum-based polymers, in addition to the generally accepted methods of processing plastic waste, alternative biodegradable polymers are being developed. One of the most popular biodegradable polymers is polylactic acid $(C_3H_4O_2)_n$ or PLA. Its tensile strength is comparable to that of polyethylene terephthalate, and also PLA has a relatively low melting point. Because of its properties, this polymer is widely used in the field of food packaging and in the production of surgical sutures and pins. In addition, PLA is one of the most popular polymers for additive manufacturing (or 3D printing) based on material extrusion.

Additive manufacturing, in the industrial revolution Industry 4.0, is a perspective direction in product manufacturing due to the speed of production changeover, which is problematic in the traditional plastic industry. Also, the ability to locate additive manufacturing closer to the consumer is an important advantage of this technology in the rapidly developing modern world. Due to the ease of use and relatively inexpensive price of 3D printers, additive manufacturing based on the extrusion of materials is suitable for small-scale production and domestic use.

However, despite the positive qualities of additive manufacturing, one must consider that 3D printing and prototyping generate polymer waste, including polylactide acid. To prevent the accumulation of polylactide acid waste in the environment from 3D printing, this waste must be placed in compost plants, as rapid biodegradation of polylactide can only be achieved under certain composting conditions. The construction of composts is economically justified only for industrial waste in large volumes and is unprofitable for small-scale production. To date, the market price of polylactide is higher than the price of petroleum-based polymers.

Thus, to prevent the accumulation of polylactide waste in the environment and save resources, various methods of recycling polylactide waste from 3D printing are being explored.

Life cycle assessment studies of PLA have shown that mechanical recycling is the most environmentally friendly way to recycle PLA. However, during the mechanical processing of polylactide waste, the tensile strength of the received products becomes lower than that of the primary polymer. Taking into account the fact that when 3D printing products from recycled polylactide there are problems with interlayer adhesion of layers of products and clogging of the nozzle of a 3D printer, it is necessary to improve quality indicators and ensure the printability of recycled polymer, i.e. create a material with improved properties based on recycled polylactide.

Based on world practice, for sustainable development and ensuring competitiveness, quality and safety of the material, standardization is used, through which uniform requirements are set for the standardized object. Thus, improving a polymer based on recycled polylactide waste for additive manufacturing and standardizing its quality indicators is an urgent task.

Based on the above, the thesis work aims to improve and standardize the quality indicators of polylactide waste for its use in material extrusion-based additive manufacturing.

Connection of the thesis topic with the plan of scientific projects

The thesis work was conducted within the framework of the project "Improvement in resource efficiency and sustainability through the implementation of additive manufacturing methodologies for maintenance of facilities in the chemical industry". Funding: Fundación Campus Tecnológico. Participating entities: Universidad de Cádiz and Indorama Ventures Química SLU. Period from 1 January 2020 to 31 June 2021. Granted ammount: 6058,48€. Coordinator: Sales Lérida, David

The thesis aims is to enhance and standardize the thermal and mechanical properties of plastic waste for 3D printing applications by adding virgin polymer and nanoparticles.

To achieve these goals, it was necessary to solve the following tasks:

- to investigate the degradation process of 3D-printed polylactide samples under temperature and humidity conditions for subsequent recycling;
- to check the quality of polylactide filaments processed from real 3D printing waste with the addition of pure polylactide;
- to improve the quality of granules for 3D printing made from recycled polylactide by adding pure polylactide and titanium dioxide nanoparticles;

- to develop an organization standard for nanocomposites based on pure and recycled polylactide with nano-TiO_2 for additive manufacturing based on material extrusion.

The object of study is polylactide waste from 3D printing.

The subject of study is the standardization of recycled polylactide with improved thermal and mechanical properties.

Research methods

The following methods were used to solve the tasks and achieve the goals:

To study the dynamics of thermal and hydrothermal ageing of 3D printed polylactide samples, the method of controlled accelerated laboratory ageing was used.

Polylactide waste was shredded, screened and extruded in a single screw extruder to manufacture filaments for FFF printed samples.

A twin-screw extruder was used to manufacture nanocomposites, from which samples were FGF printed.

The properties of the obtained samples were characterized by scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis and mechanical testing.

The methods of unification and advanced standardization, as well as the ordering of standardized objects were applied to standardize the recycled polylactide acid.

The scientific novelty of the work is that for the first time:

1. Accelerated laboratory ageing was used to experimentally determine the changes in the thermo-mechanical quality indicators of 3D-printed polylactide samples.

2. The quality of samples made from polylactide waste and mixtures of polylactide waste and primary polylactide in ratios of 25-75, 50-50, and 75-25 was checked.

3. Nanocomposites based on primary and secondary polylactide with the addition of titanium dioxide nanoparticles were made and their quality was checked.

4. The percentage and quality indicators of improved material based on recycled polylactide were standardized and documented in the organization's standard.

Statements for defense

1. Standardized process of accelerated hydrothermal aging in standard of organization St JSC 002-2023 “Polylactide for additive manufacturing. Accelerated hydrothermal aging test” of 3D printed polylactide samples at 50 °C and 70 % humidity for 1344 hours results in a 33 % reduction in tensile strength;

2. Increasing the proportion of secondary polylactide from 0 to 75 % in a mixture with pure polylactide increases the tensile strength of FFF printed samples from 44.20 ± 2.18 MPa to 52.61 ± 2.28 MPa;

3. Adding 18 % of pure polymer and 7 % of titanium dioxide nanoparticles to secondary polylactide increases the tensile strength and fluidity of FGF samples to match those of a standard sample during 3D printing;

4. Standard of organization St JSC 001-2023 “Nanocomposites based on polylactide and its waste with titanium dioxide nanoparticles for additive manufacturing. Technical specifications” establishes the percentage of pure and recycled polylactide and titanium dioxide nanoparticles in proportions 25/75/0, 22/75/3, 18/75/7 for subsequent certification.

Theoretical and practical significance of the work

Accelerated thermal and hydrothermal ageing reveal the changes in the dimensional, thermal, and mechanical properties of polylactide samples over time. This theoretical knowledge is necessary to understand the period during which 3D-printed polylactide products maintain optimal quality.

The nanocomposite based on recycled polylactide with a primary polymer and titanium dioxide nanoparticles demonstrates the feasibility of mechanically recycling polylactide waste for additive manufacturing based on material extrusion with quality indicators matching a standard sample.

Two organizational standards were developed. The first standard St JSC 002-2023 “Polylactide for additive manufacturing. Accelerated hydrothermal aging test" regulates the process of accelerated hydrothermal aging of polylactide to identify the dynamics of its aging. The thermal and mechanical quality indicators of nanocomposites based on recycled polylactide with the addition of virgin polymer and titanium dioxide nanoparticles is written in the second standard “Nanocomposites based on polylactide and its waste with titanium dioxide nanoparticles for additive manufacturing. Technical specifications”. If the requirements of the second standard are met, the quality of products obtained from this nanocomposite through additive manufacturing based on the extrusion of materials can be guaranteed. These two standards were approved by the director of JSC Ust-Kamenogorsk Machine-Building Plant of Industrial Fittings. In the future, JSC Ust-Kamenogosk Machine-Building Plant of Industrial Fittings plans to use the second standard of organization to certify nanocomposites based on pure and processed polylactide with the addition of titanium dioxide nanoparticles, which will increase its competitiveness.

Publications in international peer-reviewed journals and participation in regular international conferences confirm the practical significance of the results obtained.

The author's contribution consists of conducting the entire thesis work, choosing the research method, solving problems, conducting research on the thermomechanical properties of polylactide samples for additive technologies,and developing regulatory and technical documentation independently. The author collaborated with the supervisors in setting tasks and discussing results.

Reliability and validity of the obtained results

The reliability and validity of the results obtained are confirmed by publications in high-ranking journals far abroad with a high impact factor and in publications recommended by the Committee for Quality Assurance in Education of the Ministry of Education of the Republic of Kazakhstan for the publication of the main results of scientific activity, and in the proceedings of international scientific conferences of the near and far abroad.

Approbation and publication of thesis work

Eight scientific publications, including three articles in journals indexed by Web of Science (Clarivate Analytics, USA) and Scopus (Elsevier, the Netherlands), one article in a journal recommended by the Committee for Quality Assurance in Education of the Ministry of Education of the Republic of Kazakhstan for obtaining a PhD degree, and four papers in abstracts of international conferences, published the main results of the thesis work.

The structure of the dissertation

The thesis consists of an introduction, seven sections, a conclusion, a list of references and four appendices. The work consists of 115 pages of typewritten text, illustrated by 36 figures, 17 tables, and a list of 162 bibliography references.