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Influence of glass microspheres on selected properties of polylactide composites

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ABSTRACT

Comparison of some changes occurring in polylactide (PLA) due to its modification by glass filler being in the form of microspheres (GM) was the objective of the present study. Mechanical and thermal properties, density, mass flow rate, and were determined. In addition, there were examined surface free energy and changes in the surface geometrical structure of sample fractures. It was found that PLA as modified with GM exhibited the enhanced longitudinal modulus of elasticity, flexural modulus, and mass flow rate. The impact strength and flexural strength did not change. The tensile strength and tensile strain at break decreased. The used glass filler did not affect essentially the thermal properties of PLA. The prepared composites exhibited uniform distribution of the dispersed phase in the polymer matrix and adequate adhesion at the interface between the two components. Substantial changes in the properties of the surface layer were observed, mainly in surface free energy.

1. Introduction

Polymeric materials constitute a fast-growing area of the global economy, which has been confirmed by continuous and dynamic production of plastics [1]. However, this results in greater and greater load to the natural environment by waste originating from used polymeric products and, indirectly, from production and processing of mineral raw materials, meant for manufacture of polymers and other products or semi-finished products. It is a source of many problems experienced by contemporary civilization. Because of limited mineral raw materials and environmental protection, activity has been undertaken to search for and utilize other sources of raw materials that can be used to produce polymers. One of them is represented by renewable resources (mainly of plant origin), from which conventional polymers can also be obtained [2–5].

Biodegradable polymers produced from the renewable resources are a group of plastics that may contribute to enhancement of the natural environment protection [6–9]. Among them, polylactide attracts the greatest interest since it is being used not only in medicine and tissue engineering, but also in manufacture of everyday items, e.g., food packaging products [10–12]. PLA shows adequate functional properties and can be processed by using known machines, devices, and techniques. Nevertheless, it has to be modified for many applications, especially in the packaging production, because poor heat stability, unfavorable permeability towards several gases and mechanical properties limit its some applications. Some properties of this polymer can be modified by formation of blends, composites, or nanocomposites with such admixtures as fillers, nucleants, nanocompounds, so-called chain elongators, oligomers, or polymers, in which PLA would play a role of a matrix [13–22]. In addition, polylactide may be subjected to the processes of copolymerization, grafting, or crosslinking [23–26].

Better understanding of influence of some glass fillers applied in the form of microspheres on selected properties of PLA may be interesting from the cognitive and utilitarian viewpoints. Available scientific publications on this issue concern mainly non-biodegradable polymers [27–31]. It is known from the literature that microspheres favorably affect mechanical properties of polymers, like modulus of elasticity, tensile strength, hardness, or abrasion resistance. They also improve processing and rheological properties, causing easier flow of a polymeric material through channels of the processing machines and reducing its processing shrinkage.

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It is also worth to mention that a small number of literature reports and research works, which concern biodegradable polymeric composites containing glass microspheres, may result from possible hindrances to recycling of these materials, especially from troubles dealing with biodegradation of the polymers. Such composites may undergo biodegradation to a limited extent and the inorganic fraction may accumulate in compost. In such a case, it is more beneficial to subject the composites to other kinds of recycling, e.g., mechanical one [32,33]. In this regard, these materials could be reused many times, which is especially important in terms of their valuable and unique functional properties. The mechanical recycling of composites of that kind may fully be profitable due to lower and lower costs of biodegradable materials and considerable amount of occurring industrial waste. This, in turn, should stimulate undertaking research works in the field of investigation of such composites.

The above-mentioned issues inspired authors to undertake research works aimed at comparison of changes in: (a) mass flow rate, (b) tensile strength, (c) tensile strain at break, (d) flexural strength, (e) longitudinal modulus of elasticity and flexural modulus, (f) impact strength, (g) thermal properties, (h) surface geometrical structure of sample fractures, and (i) surface free energy. The comparison concerns the mentioned quantities determined for pristine PLA and for PLA composites of various contents of glass microspheres. The results are presented in the present paper.

2. Experimental

2.1. Materials

The following materials were used in the investigations:

- Polylactide (PLA), type 2003D (NatureWorks®, USA). Its melt flow rate was 2.9 g/10 min (2.16 kg, 190 °C), density, 1.24 g/cm^3, and the number-average molecular mass, 155,500 Da. The polymer contained 3.5% of D monomer units.
- Glass microspheres (GM), type MinTron 7™ (RockTron International Limited, UK). Their density was 2.2–2.4 g/cm^3, hardness on the Mohs scale, 5–6, and moisture content, below 0.5%. The microspheres of various diameters were used as the PLA filler (Fig. 1).

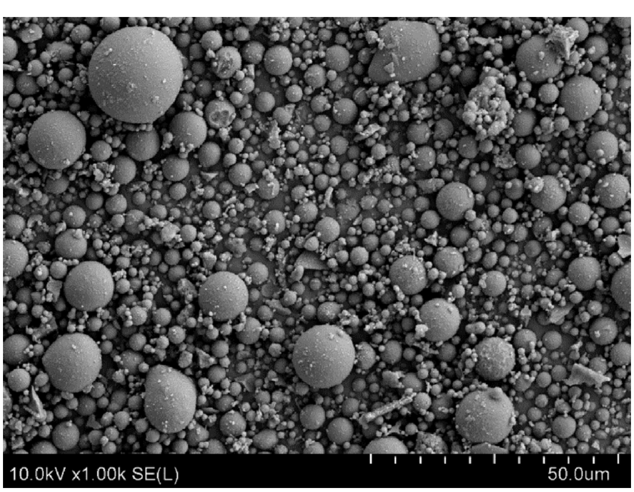

Fig. 1. Glass microsphere structure.

2.2. Apparatus

The following devices were utilized to prepare and investigate the PLA samples:

- Co-rotating twin screw extruder, type BTSK 20/40D (Bühler, Germany), equipped with screws of 20 mm diameter and L/D ratio of 40, intended to produce granulated PLA composites.
- Screw injection molding machine, type Battenfeld Plus 35/75 (Battenfeld GmbH, Germany), equipped with a screw of 22 mm diameter and L/D ratio of 17, designed to produce standard dumbbell- and bar-shaped specimens.
- Helium pycnometer, type Ultrapycnometer 1000 (Quantachrome Instruments, USA), meant to determine the specific density.
- Capillary plastometer, type LMI 4003 (Dynisco, USA), intended for determination of the melt flow rate.
- Tensile testing machine, type TIRAtest 27025 (TIRA Maschinenbau GmbH, Germany), designed to examine mechanical properties under static tension and static three-point bending.
- Pendulum Impact Tester, type IMPats-15 (ATS FAAR, Italy), intended for determination of Charpy impact strength.
- Goniometer, type G10 (Krüss GmbH, Germany), meant for contact angle measurements being used to determine surface free energy.
- Differential scanning calorimeter, type DSC 1 STARe System (Mettler Toledo, Swiss), designed for determination of thermal properties and crystallinity.
- Scanning electron microscope, type Hitachi SU8010 (Hitachi, Japan), meant to examine surface geometrical structure of sample fractures.

2.3. Methods

- Extrusion of the pristine PLA and granulated PLA composites was performed at the following temperatures of particular cylinder zones of the co-rotating twin screw extruder: 190, 195, 200, and 205 °C. The temperature of the extrusion head was 200 °C and screw rotational speed, 250 min^{-1} (constant). The screws were of a special design that facilitated adequate dispersion and distribution of admixtures in the polylactide matrix (Fig. 2).

PLA and GM were poured into the extruder from volume feeders in such proportions that polylactide composites of the GM contents equal to 5, 10, 15, 20, and 25 wt% were obtained. The prepared samples of the granulated composites were denoted as LG5, LG10, LG15, LG20, and LG25, were L means polylactide, G, glass microspheres, and the numbers, microsphere percentages. A reference sample, made of the pristine PLA, was also prepared and denoted as L.

- The dumbbell- and bar-shaped specimens were prepared according to a relevant standard (PN-EN ISO 527-2:1998) by using a screw injection molding machine (Battenfeld Plus 35/75). The temperatures of the plasticizing zones I and II of the barrel were 190 and 200 °C, respectively, and the temperature of the injection molding head, 200 °C. The temperature of the injection mold was 30 °C and the injection pressure, 116–128 MPa, depending on the composite kind.
- PLA dried at 75 °C for 4 h in a PIOVAN dryer (Piovan, Italy) was used in the processes of extrusion and injection molding. The dryer was equipped with molecular sieves.
- Sample density was determined according to the PN-EN ISO 1183-3:2003 standard.