THE MECHANICAL PROPERTIES OF BIO(NANO)COMPOSITES BASED ON PBS WITH THE ADDITION OF CNTs

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Abstract
Nanocomposites are a new class of composites that are particle-filled composites in which at least one dimension of the dispersed particles is in the nanometer range. One of the interesting aspects of the use of nanofillers in nanocomposite is the low concentration of that filler that needs to be added to the polymer system to obtain desired property improvements. However, owing to concerns over environmental pollution and the depletion of fossil oils, intensive research is being conducted for developing biodegradable polymers and plastic materials. This paper presents the results of research from selected mechanical properties of bio(nano)composites with poly(butylene succinate) (PBS) matrix. Bio(nano)composites based on PBS, containing 0.5wt% of carbon nanotubes (CNTs), were prepared for experiments. The specimens for testing were prepared by extrusion and their selected mechanical properties were tested by static tensile test and Shore hardness test.

Key words: biocomposites, poly (butylene succinate), carbon nanotubes, tensile test, Shore hardness test.

INTRODUCTION

At present, polymers and composites based on polymers are among the most widespread materials in all spheres of human activity [1]. The processes of manufacturing of polymeric products are characterized by the availability of raw materials, low power intensity and labour input, and simplicity of the technologies. At the same time, polymeric materials are rarely used repeatedly because secondary polymeric raw materials have numerous significant disadvantages: incompatibility with each other, high degrees of contamination of the secondary raw materials, noticeable degradation of the operating and technological characteristics after repeated processing, wide range of colours, etc.
Therefore, polymers and polymer-based materials exert an increasingly harmful influence on the ambient medium. This is why the application of biodegradable polymers capable of regulated decomposition in the environment under the action of external factors (humidity, heat, microorganisms, ultraviolet radiation, etc.) realized with the possibility of recovery of their initial raw materials is currently regarded as the most acceptable and generally recognized direction in the development of the chemistry and technology of polymeric materials [2].

BIOPOLYMERS

Rising energy concerns, rapid infrastructure development, and greater environmental awareness have fuelled the demand for sustainable materials. In this direction, sustainable bio-based polymer generated from different resources through several operations can meet most of the annual synthetic plastics demand at least in Europe. The advancement of sustainable technologies for the effective utilization of sustainable materials for bioplastic and biomaterials production can afford a novel bio renewable source of sustainable products and biofuel as well as address the rising environmental concerns. [3]. Global production of bioplastics represents approximately 0.5% of all plastics [4]. The production of bioplastics in the years 2017-2023 is shown in Figure 1.

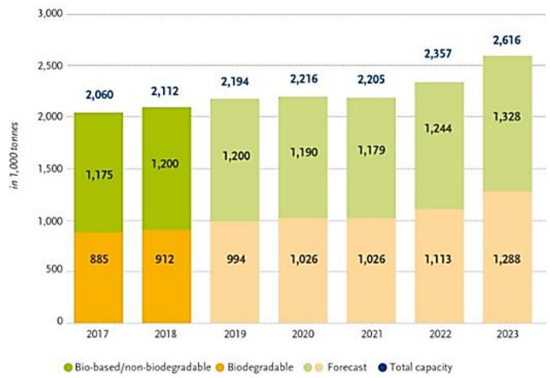

Fig.1 Global production of bioplastics [4]

Global production capacities of bioplastics by region in 2018 and 2023 is shown in Figure 2 [5].

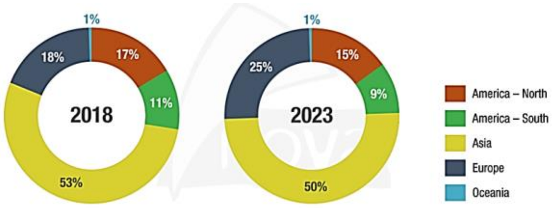

Fig. 2 Production capacities of bioplastics by region in 2018 and 2023 [5]

Most synthetic polymers are resistant to microbial organisms possessing chemical structures that cannot be biodegraded in soil or marine environments. Unfortunately, lack of consumer and producer responsibility with poor waste management policies has led to the pollution that affects all ecosystems [6,7]. New and existing legislations are targeted to ban non-degradable plastics for fields like packaging, food containers and agricultural films [2,8]. Therefore, replacements require the ability to biodegrade in the environment.

Structure determines the polymer's ability to interact with microorganisms and degrade. Such properties can be inherited from naturally occurring structures like proteins, polysaccharides, and lipids. To further contribute to lowering environmental impact, these polyesters are produced wholly or partly using renewable resources. Commercially available biodegradable polyesters include polyhydroxyalkanoates (PHA), polyhydroxy valerate (PHV), polyhydroxybutyrate (PHB), polylactic acid (PLA), polycaprolactone (PCL), poly(butylene succinate) (PBS), polybutylene succinate adipate (PBSA), polybutylene adipate/terephthalate (PBAT) [3,8]. The production of bioplastics (biodegradable) by types in 2018 and 2023 is shown in Figure 3 [4].

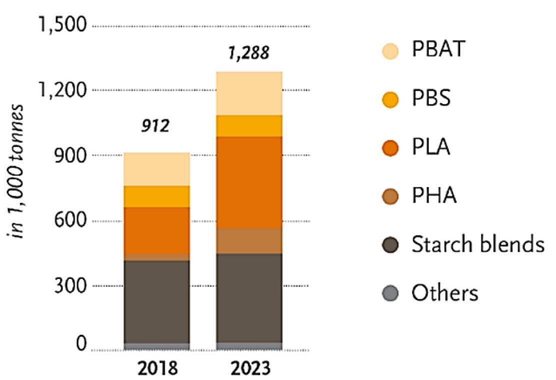

Fig. 3 Production of bioplastics by types [4]

Biodegradable polymers can be either natural or synthetic and can be derived from either renewable or non-renewable resources. There have been many research achievements in biodegradable and biobased polymers, including naturally occurring biodegradable polymers, biodegradable polymers derived from renewable resources, and biodegradable polymers based on petroleum, although several biobased polymers may not be biodegradable. Classification of biopolymers is shown in Figure 4 [8].

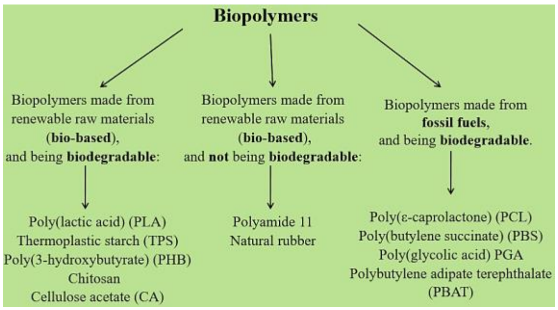

Fig.4 Classification of biopolymers [8]

POLYMER COMPOSITE MATERIALS

Polymer composite materials (PCM) to a large extent satisfy high demands of consumers and compete successfully with various materials of structural and heat engineering purposes. At present, thermoplastic polymers with fillers of various natures, in particular silicates are widely used for their production, since on their basis it is possible to create materials with a complex of new and necessary properties with a small expense [9]. The physico-mechanical, thermophysical and rheological properties of PCM containing fillers are largely determined both by the nature of the filler itself and its technological compatibility with the polymer matrix [10].

The filled polymer can be considered as a three-phase system, which consists of filler, a polymer matrix, and a boundary layer, whose properties are different from the properties of the first two components of PCM. The filler particles may also form a grid in the polymer matrix due to the interaction between themselves or through the association of the adsorption layers of the polymer. At the same time, the probability of formation of such a grid increases with increasing content and anisotropy of the filler particles in the polymer matrix [11].

At present, nanotechnology is a rapidly growing interdisciplinary field of knowledge, spanning many areas of research. There are always critical needs for lighter, stronger, less expensive, and more versatile materials to meet the demands of industrial consumers. Nanocomposites are materials that comprise a dispersion of nanometer-size particles in a matrix. The matrix may be single or multi-component. It may contain additional materials that add other functionalities to the system (e.g., reinforcement, conductivity, toughness, etc.).

Optimizing polymeric materials by the addition of a small filler content with nanometer-scale dimensions has been the focus of many industrial and academic studies. The introduction of filler contents to polymeric materials has been found to significantly increase the mechanical, barrier, thermal, and electrical properties, and in general, the better the dispersion of nanoparticles (NPs) and the more effective the polymer particle interface, the greater the obtained reinforcing effect. Among the NPs studied, the most prominent are the lamellar clays, such as montmorillonite (MMT) and carbon nanotubes (CNTs) [12].

In this study, PBS/CNTs bio(nano)composites were prepared. Basic mechanical properties namely elastic modulus, tensile strength, and hardness of the bio(nano)composites filled with 0.5wt% CNTs were investigated.

MATERIALS AND METHODS

The components to obtain the bio(nano)composite for experiment were used:

- PBS as a polymer matrix, which is a completely biodegradable polymer in the open environment and similar in properties to polyethylene,
- CNTs as a nanofiller, which are extremely promising natural nanofillers for polymers capable of significantly improving the main characteristics of polymers (electrical conductivity, strength and durability, thermal insulation, and sorption properties, etc.) at a low content in the composite.

PBS is one biopolymer that has enormous potential to be used in a wide range of applications, such as packaging, agriculture, fishery, forestry, construction, and electronics as demonstrated by Figure 5 [13].

Fig. 5 Some applications of PBS [14]

Multi Walled CNTs have a variety of potential applications in different fields. These applications include medicine, mechanics, electric-electronics, chemicals, energy and others.

BioPBS™ FZ91PM (Fig. 6), purchased from PTT MCC Biochem Company Limited (Bangkok, Thailand), with density of 1260 kg/m^3, MFR (190°C, 2.16 kg) of 5 g/10min, melting point of 115 °C, puncture impact of 4 kJ/m was used.

Fig. 6 Material BioPBS™ FZ91PM for experiment

Industrial Grade Multi Walled Carbon Nanotubes (MWCNT, hereafter CNT), purchased from Nanografi NanoTechnology (NG01IM0101), Ankara, Turkey, with the following technical properties were used: colour black, purity > 92 %, outside diameter 8-28 nm, inside diameter 5-10 nm, length 10-35 μm, tap density 150 kg/m^3, true density 2200 kg/m^3, SSA 220 m^2/g,Ash 9 wt%, electrical conductivity 98 S/cm, manufacturing method - CVD.

The bio(nano)composite was produced using a granulation line based on a twin-screw extruder type BTSK 20/40D (Bühler, Germany) with a CNTs content of 0.5 wt% in the form of pellets.

The standardized samples for studies mechanical (tensile strength and strain, tensile modulus (Fig. 7), hardness (Fig. 8)), properties of PBS/CNT nanocomposite were obtained from the film (Fig. 9), which was produced by the cast film extrusion method.

Fig. 7 Sample for tensile strength, strain and tensile modulus testing

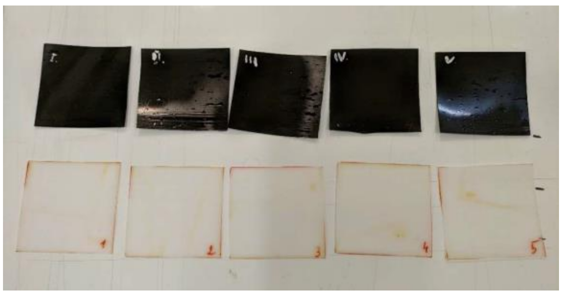

Fig. 8 Samples for hardness testing

Fig. 9 PBS (white) and PBS/CNT_0.5 (black) flat films

Hardness tests were performed by Shore method according to the ISO EN 868:2003 using samples of films of square shape in size of 50×50 mm and a thickness of 350 μm (Fig. 8). Film samples were stacked on top of each other until the required thickness of 4 mm was reached. Shore A and D hand-held hardness testers and a special test stand with load weight (Zwick Roell Group, Germany) were used.
Mechanical properties tests under static tension were carried out using a TIRAtest 2300 testing machine (TIRA Maschinenbau GmbH, Germany) testing range of tension force from 0 to 10 kN. Maximum stress (Rm) and stress at break (Rb), tensile modulus (Et) and strain at maximum stress (δm) and the break (δb) were determined in accordance with STN ISO EN 527-3:2019-01.
The experiment was based on investigation of basic mechanical properties of the bio(nano)composite PBS/CNT_0.5 and original PBS.

RESULTS AND DISCUSSION

Measured hardness values of PBS and PBS/CNT_0.5 samples are presented in the Table 1. The results of tensile tests for PBS and PBS/CNT_0.5 samples are presented in the Table 2.

Table 1 Hardness values of PBS and PBS/CNT_0.5

Sample	Shore A	Shore D
PBS	90 ±1	57 ±1
PBS/CNT_0.5	90 ±1	58 ±1

From the measured hardness results of the tested materials, we can conclude: the addition of CNTs to PBS in the amount of 0.5 wt.% has almost no effect on the hardness.

The tests were carried out in the machine direction (MD) and transverse direction (TD). The addition of CNTs to PBS in the amount of 0.5 wt% increases the mechanical tensile strength and stiffness of the material (the tensile modulus increases), but simultaneously, it significantly reduces its elasticity (the relative elongation decreases by 1.5-2 times). Insignificant values of the standard deviations of the measurement results testify to the high homogeneity of the bio(nano)composite.

CONCLUSION

In this paper, a comparative analysis of the basic mechanical properties of the bio(nano)composite PBS/CNT_0.5 and the original PBS was performed. It is shown that CNTs have a slight effect on the hardness of PBS. It was also established that the addition of CNTs in the amount of 0.5% wt. increases strength properties of prepared and tested bio(nano)composite.
Reinforcing thermoplastic polymers with nanotubes to form nanocomposites is a way to increase the usage of polymeric materials in engineering applications by improving their mechanical properties.

ACKNOWLEDGMENTS

This research was funded by the European Union's programme for research and innovation Horizon Europe under the Marie Skłodowska-Curie Action grant agreement No 101129698–PROMATAI–Horizon–MSCA–2022–SE–01. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or European Research Executive Agency. Neither the European Union nor the granting authority can be held responsible for them.

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Table 2 The results of tensile tests for PBS and PBS/CNT_0.5

Sample	Rm, MPa		δm, %		Rb, MPa		δb, %		Et, MPa	
	MD	TD	MD	TD	MD	TD	MD	TD	MD	TD
PBS	34 ±0.6	32 ±0.9	22 ±1.1	12 ±1.0	29 ±0.9	26 ±2.0	330 ±23	274 ±35	480 ±13	557 ±31
PBS/CNT_0.5	36 ±0.7	34 ±0.7	17 ±1.7	13 ±0.5	32 ±1.0	30 ±2.0	208 ±28	125 ±24	620 ±22	575 ±9

where: Rm, Rb – maximum stress and stress at break, respectively, MPa (MD – machine direction, TD – transverse direction); δm, δb – strain at maximum stress and the break, respectively, %;Et – tensile modulus, MPa.