

The Effect of Nanoboron Nitride on Some Properties of Biopolymer Nanocomposites with Cellulose Nanofibrils and Nanoclays

Učinak nanočestica boron-nitrida na neka svojstva biopolimernih nanokompozita s celuloznim nanovlaknima i nanočesticama gline

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ABSTRACT • The aim of this study was to investigate the effect of nanoboron nitride (BN) as nano-fire retardant on some properties of polylactic acid (PLA) and polyhydroxybutyrate (PHB) biopolymer nanocomposites reinforced with cellulose nanofibrils (CNFs) and nanoclays (NC). BN particles, as nano-fire retardant, were added to enhance the thermal stability of the obtained biopolymer nanocomposites. PLA and PHB nanocomposites were prepared with a twin screw extruder and characterized with mechanical tests, TGA, and DSC. Densities of the PLA and PHB nanocomposites were found to decrease with the addition of NBN loading. The mechanical properties of biopolymer nanocomposites decreased, except for tensile modulus. According to TGA results, NBN loadings generally improved the thermal stability of the PLA and PHB nanocomposites. The degradation temperature for weight loss at 10 %, 50 % and 85 % ($T_{10\%}$, $T_{50\%}$ and $T_{85\%}$) increased with NBN loadings; the value of DTGmax was determined to improve with the loading of BN. DSC results showed that melt temperature (T_m) and crystallization temperature (T_c) generally increased with BN loadings, whereas crystallinity (X_c) decreased with BN loadings in PLA nanocomposites.

Keywords: nanoboron nitride, polymer nanocomposites, cellulose nanofibrils, nanoclays, biopolymers

SAŽETAK • Cilj ove studije bio je ispitati učinak nanočestica boron-nitrida (BN) kao usporivača gorenja na neka svojstva biopolimernih nanokompozita proizvedenih od polilaktične kiseline (PLA) i polihidroksibutirata (PHB) ojačanih celuloznim nanovlaknima (CNFs) i nanočesticama gline (NC). Nanočestice boron-nitrida (NBN), koji je usporivač gorenja, dodane su kako bi se povećala toplinska stabilnost proizvedenih biopolimernih nanokompoziti-

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ta. Nanokompoziti PLA i PHB pripremljeni su uz pomoć dvostrukoga vijčanog ekstrudera i ispitani mehaničkim testovima te TGA i DSC analizom. Utvrđeno je da se gustoća PLA i PHB nanokompozita smanjuje dodatkom NBN čestica. Dodavanjem NBN čestica sva su se mehanička svojstva biopolimernih nanokompozita, osim modula vlačne čvrstoće, smanjila. Prema rezultatima TGA analize, dodane NBN čestice općenito poboljšavaju toplinsku stabilnost PLA i PHB nanokompozita. Dodavanjem NBN čestica povećana je temperatura degradacije za gubitak mase od 10, 50 i 85 % ($T_{10\%}$, $T_{50\%}$ i $T_{85\%}$), a poboljšala se i vrijednost DTG_{max} . Rezultati DSC analize pokazali su da se temperatura taljenja (T_m) i temperatura kristalizacije (T_c) povećavaju s povećanjem udjela NBN čestica, dok se kristaliničnost (X_c) smanjuje s povećanjem količine NBN čestica u PLA nanokompozitu.

Ključne riječi: nanočestice boron-nitrida, polimerni nanokompoziti, celulozna nanovlakna, nanočestice gline, biopolimeri

1 INTRODUCTION

1. UVOD

Nanocomposite is a two-phase material, where one of the phases has at least one dimension in nanometer range (1-100 nm) and generally nanoscale materials result in composites with superior thermal, barrier and mechanical properties (Oksman *et al.*, 2006; Yao *et al.*, 2002; Zanetti *et al.*, 2001). Due to growing environmental awareness, new standards try to develop environmental friendly and biodegradable systems (Gorrasi *et al.*, 2003; Lee *et al.*, 2002; Oksman *et al.*, 2006; Pluta *et al.*, 2002; Ray *et al.*, 2003). Polylactic acid (PLA) is one of the renewable biopolymer produced from lactic acid derived from sugar cane, potato and corn fermentation process (Aldana *et al.*, 2014; Vink *et al.*, 2003). PLA has high mechanical properties, low hydrophobicity, low cost and good process ability compared to other alternatives. For all this properties, PLA is the biopolymer with the greatest potential for plastic industries (Aldana *et al.*, 2014; Molinaro *et al.*, 2013; Svagan *et al.*, 2012).

Polyhydroxybutyrate (PHB) is another biopolymer produced by fermentation of renewable resources (Steinbuechel, 2003; El-Hadi, 2014). PHB is a thermoplastic, biodegradable, renewable and environmentally friendly polymer. PHB also has a high crystallinity and low glass transition temperature (T_g) (El-Hadi, 2013; Fernandes *et al.*, 2004). Initial bio-sourced polymers were used in short term applications but today environmental concerns and oil shortage issues expand their areas of usage. They are used for construction, transportation and electronics, where fire risk requires the use of fire retardant materials (Bocchini *et al.*, 2012; Bourbigot, 2010; Wei *et al.*, 2013). Some studies have been conducted with various fire retardants, which are an effective and convenient way to increase thermal properties of polymers (Lee *et al.*, 2006; Yu *et al.*, 2002; Zhang *et al.*, 2011). However, the studies about the effect of boron nitride on thermal behavior of biopolymers are not enough. There are a few studies on biopolymer/BN composites. In a previous study, Pradhan *et al.* (2014) studied the effects of boron nitride on the thermal properties and tensile strength of starch biocomposites. The obtained results showed that thermal stability of the starch was increased with rising concentrations of boron nitride due to the addition of rigid nano BN with starch matrix, and the tensile strength of starch/BN bionanocomposites was found to increase with BN loading. In another study, Dash and Swain (2013) studied nanoboron nitride-soy protein

composites. According to the obtained results, the degradation temperature of pure soy protein is lower than that of corresponding soy/BN nanocomposites. Hence, the thermal stability of soy/BN nanocomposite was found to be higher than that of virgin matrix due to the addition of thermally stable nanoboron nitride. Öner *et al.* (2016) used nano boron nitride to improve the thermal properties of polyhydroxybutyrate biocomposites. The barrier properties of the composites decreased with BN addition and it was found that the thermal stability of the composites with BN was higher than that of neat biopolymers. The differential scanning calorimetry results indicated that the addition of BN nanoparticles to the composites increased their crystallinity.

In this study, BN was used to improve the thermal properties of polylactic acid (PLA) and polyhydroxybutyrate (PHB) biopolymer nanocomposites prepared with twin screw extruder. The mechanical and morphological properties of biopolymer composites were also investigated.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Materials

2.1. Materijali

Polyhydroxybutyrate (PHB) and polylactic acid (PLA) were supplied by Good Fellow, England. Density of PHB and PLA was 1.25 g/cm³ and 1.24 g/cm³, respectively. Cellulose nanofibrils (CNF) and Nanoclays (NC), used as a reinforcing filler, were obtained from J. Rettenmaier & Sohne (JRS) (Germany) and Nanocor (Canada). Hexagonal nano boron nitride (BN), used as fire retardant, was supplied by Boron Product Tech. San. Tic. A.Ş (BORTEK) (Eskisehir, Turkey). All reinforcing fillers and fire-retardant were dried for 24 hours at 80 °C, and all materials were stored in sealed containers.

2.2 Preparation of Biopolymer Nanocomposites (BNCs)

2.2. Izrada biopolimernih nanokompozita (BNCs)

Polymers and fillers were mixed with speed mixer and then composites were compounded using a twin screw extruder (Aysa Instruments, Turkey). Rotor speed was 5 rpm and process temperature was set at 160 °C – 180 °C. The extruded strand passed across a water bath so that this was pelletized.

The extruded nanocomposites were grounded with a lab-grinder and then the pellets dried for 3-4

Table 1 Formulations and codes for nanocomposites

Tablica 1. Sastav i oznake nanokompozita

Formulations <i>Sastav</i>	Codes <i>Oznaka</i>	Formulations (weight %) <i>Sastav</i>	Codes <i>Oznaka</i>
PLA+4%CNFs	LF	PHB+4%CNFs	HF
PLA+4%CNFs+1%BN	LF1	PHB+4%CNFs+1%BN	HF1
PLA+4%CNFs+5%BN	LF5	PHB+4%CNFs+5%BN	HF5
PLA+4%CNFs+10%BN	LF10	PHB+4%CNFs+10%BN	HF10
PLA+4%NCs	LC	PHB+4%NCs	HC
PLA+4%NCs+1%BN	LC1	PHB+4%NCs+1%BN	HC1
PLA+4%NCs+5%BN	LC5	PHB+4%NCs+5%BN	HC5
PLA+4%NCs+10%BN	LC10	PHB+4%NCs+10%BN	HC10

hours before compression molding. The compression molding temperature was 175 °C, barrel temperature 170 °C and compression pressure 25 bar. The formulations of the composites are shown in Tab.1.

2.3 Methods

2.3. Metode

The properties of the PLA and PHB nanocomposites were analyzed with the standard tests such as density, flexure strength (*FMOR*) and modulus (*FMOE*), tensile strength (*TMOR*) and tensile modulus (*TMOE*), Izod impact strength (*Izod-IS*), thermal properties (TG-DTA, DSC), and morphological characterization (SEM). The tension tests were conducted according to the American Society of Testing and Materials (ASTM) standard D 638-03 Type I. All tension tests were conducted at a rate of 0.2 in./min. The flexure tests were conducted according to ASTM D 790-03, Test Method 1, Procedure A, i.e. three-point loading system. The support span was 50.8 mm, resulting in a span-to-depth ratio of 16 (±1). The tests were run at a test speed of 1.27 mm/min. The impact tests were conducted according to ASTM D 256-06. The notches were added using a NotchVIS machine manufactured by Ceast. The specimens were tested on a Resil 50 B impact test machine, manufactured by Ceast. At least eight specimens for all tests were tested for each composition, and the results are presented as an average for tested samples.

TG-DTA was tested using Hitachi STA 7300 analyzer with a heating rate of 10 °C/min from 25 °C to 600 °C, under nitrogen with a flow rate of 20 ml/min to avoid sample oxidation. DTA peaks, such as melting point (T_m) and decomposition point (T_d), were also measured during the thermogravimetric analysis; DSC analysis of the samples was performed using a Perkin Elmer analyzer on samples of about 5 mg. For all specimens, testing was performed by heat/cool methods. All samples were heated to 25 °C to 300 °C at a ramp rate of 10 °C/min and cooled at the same ramp rate. Melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), crystallization enthalpy (ΔH_c), crystallinity (X_c) of materials was determined from thermograms. The value of theoretical melting enthalpies of 100 % crystalline PLA and PHB was 93.1 J/g and 146 J/g, respectively. The samples were observed with an environmental scanning electron micro-

scope (ESEM), the Tescan MAIA3 XMU-SEM at an acceleration voltage of 5 kV. The surface of all samples was sputter-coated with gold using a Denton sputter coater for enhanced conductivity.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

The effects of BN on some properties of biopolymer nanocomposites (BNCs) were investigated in this study. Tab. 2 shows the density and mechanical properties of BNCs.

As seen in Tab. 2, the density for all BNCs generally decreased with BN loading. The decrease in the density was found to be higher as the loading of BN increased. The effects of boron nitride on the mechanical properties were generally found to be negative. It was determined that the effects of BN on the mechanical properties of PHB nanocomposites were higher than on PLA nanocomposites. For all that, in a study on BN, the densities of PP composites were generally found to increase with BN loadings (Ayrimis *et al.*, 2013). It was determined that the decrease in the density of biopolymers was caused by gaps and porous structure generated by interactions between biopolymer and BN, as shown in Fig. 1. The morphological properties of the BNCs obtained with the help of SEM are presented in Fig. 1.

According to Fig. 1, the BN particles dispersed inside the matrix, and generally showed uniform dispersion in the matrixes. However, some BN aggregates were found in Fig. 1. SEM pictures show that the loading of BN caused the gaps of different diameters, and the porous structure was determined in both matrixes after BN loading. It can be said that this porous structure has a negative effect on the mechanical properties according to Tab.1. TGA analysis of biopolymer nanocomposites is given in Tab.3.

The thermal stability of all nanocomposites was affected by BN loading. The thermal stability at $T_{10\%}$ improved with the addition of BN except for the PLA biopolymer nanocomposites (LF) with 1, 5, and 10 % BN. This showed that the BN loading increased the thermal stability of BNCs at initial response ($T_{10\%}$). The thermal stability at $T_{10\%}$ was found to be better for HF and HC biopolymer nanocomposites with BN compared to PLA biopolymer nanocomposites with BN. As

Table 2 Mechanical properties of polymer nanocomposites with nanoboron nitride**Tablica 2.** Mehanička svojstva polimernih nanokompozita s nanočesticama boron-nitrida

Composite formulations (BNCs) <i>Sastav kompozita</i>	Density <i>Gustoća</i> g/cm ³	TMOR MPa	TMOE MPa	FMOR MPa	FMOE MPa	Izod IS kJ/m ²
LF	1.18	50	2983.7	90.9	2983.7	4.8
LF1	1.14	48.2	4699.1	31.27	1547.1	2.3
LF5	1.08	37.5	4122.5	21.7	1069.1	2.7
LF10	1.07	32.1	3980.1	25.4	1174.2	2.4
LC	1.18	55	3324.5	100.5	3324.5	3.9
LC1	1.17	20	2562.3	20.2	998.4	2.2
LC5	1.09	31.4	3858.3	30.1	1075.7	2.1
LC10	1.12	40.2	4682.4	31.5	1249.5	2.5
HF	1.15	16	1436.7	27.4	1711.8	2.1
HF1	1.16	10.1	1418	7.9	515.3	1.9
HF5	1.11	9.1	1321	7.3	462.4	1.3
HF10	1.09	6.2	925	7.1	400.9	1.1
HC	1.19	12.2	1233.5	21.9	2136.5	1.9
HC1	1.07	2.7	296	9.8	1009.2	1.6
HC5	1.18	2.1	325	9.4	885.4	1.4
HC10	1.16	5.1	755.8	8.7	739.2	1.7

TMOR - tensile strength / *vlačna čvrstoća*; TMOE - tensile modulus / *vlačni modul elastičnosti*; FMOR - flexure strength / *čvrstoća pri savijanju*; FMOE - flexure modulus of elasticity / *modul elastičnosti pri savijanju*; Izod-IS - Izod impact strength / *Izod udarna čvrstoća*. See Table 1 for composite formulations. / *Za sastav kompozita vidjeti tablicu 1.*

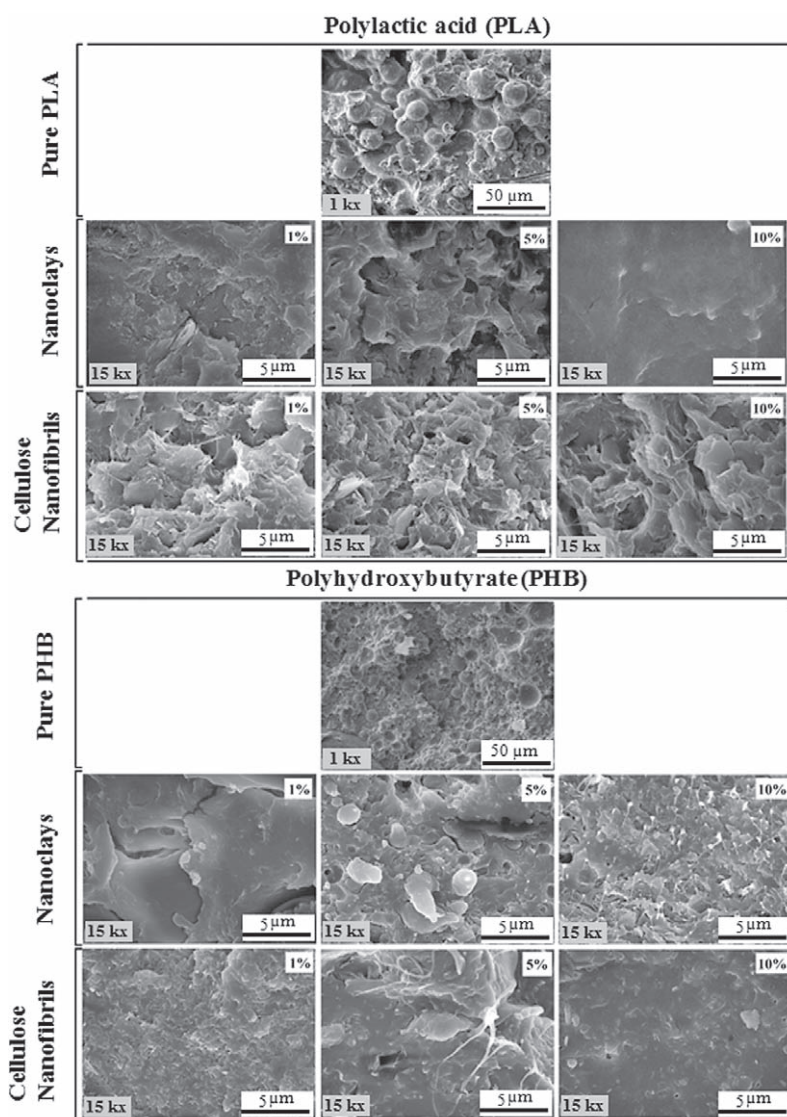
**Figure 1** Biopolymer nanocomposites with BN**Slika 1.** Biopolimerni nanokompoziti s nanočesticama boron-nitrida

Table 3 Review of thermal properties of polymer nanocomposites

Tablica 3. Sažeti prikaz toplinskih svojstava polimernih nanokompozita

Formulations	TGA, °C			DTG, °C	DTA, °C	
	$T_{10\%}$ °C	$T_{50\%}$ °C	$T_{85\%}$ °C	DTG_{max} °C	T_m °C	T_d °C
HF	267.2	284.8	300.5	288.2	156.7	286.2
HF1	277.6	287.1	377.5	287.3	175.7	288.0
HF5	267.5	282.0	352.5	286.0	173.7	284.5
HF10	248.8	263.2	314.2	266.0	168.0	264.1
HC	275.3	289.4	310.9	293.3	159.1	290.5
HC1	285.1	296.2	353.5	304.4	161.8	305.1
HC5	274.7	295.1	357.0	285.9	173.8	281.0
HC10	276.3	286.2	354.8	287.9	173.7	287.5
LF	340.9	356.9	444.1	361.6	152.2	360.1
LF1	337.2	352.4	363.5	354.6	154.5	352.9
LF5	334.6	345.1	356.5	347.6	147.7	353.6
LF10	334.0	345.4	361.0	347.3	148.2	350.1
LC	322.8	356.3	443.4	357.2	148.9	354.9
LC1	342.7	356.3	372.4	358.8	146.8	356.4
LC5	344.7	360.8	379.1	363.6	149.5	362.2
LC10	341.1	357.4	372.2	362.8	150.1	360.8

the temperature was increased, the degradation temperature at $T_{50\%}$ was found to be generally better for HC and LC biopolymer nanocomposites than for neat polymers. At $T_{85\%}$ the thermal stability of HF and HC biopolymer nanocomposites increased as compared to neat biopolymer, whereas the thermal stability of LF an LC biopolymer nanocomposite was determined to decrease with the addition of BN. The best temperature in DTG_{max} was found to be 304.4 °C in HC with 1 % BN, and 363.6 °C in LC with 5 % BN. The maximum T_m and T_d of BNCs were determined to be 175.7 °C in HF with 1 % BN, and 305.1 °C in HC with 1 % BN, and 154.5 °C in LF with 1 % BN and 362.2 °C in LC with 5 % BN, respectively. The other thermal properties of biopolymer nanocomposites with BN were determined by differential scanning calorimetry. Tab. 4 shows the summary of DSC results of all biopolymer nanocomposites.

DSC analysis was conducted by cooling and heating of neat polymers and all biopolymer nanocomposites. The crystallization temperature (T_c) and melting temperature (T_m) changed with the loading of fillers. The highest value of T_c was found to be 109.5 °C for HC without BN in PHB nanocomposites, and 116.6 °C for LF with 10 % BN. The highest T_m was found to be 169.7 °C for HC with 10 % BN for PHB nanocomposites, and 164.8 °C for LF without BN for PLA nanocomposites. Seen as X_c values, the crystallinity was found to decrease with the addition of BN except for HC1 and HC5.

4 CONCLUSION 4. ZAKLJUČAK

The addition of BN to biopolymer matrixes decreased the density of nanocomposites and mechanical properties except for TMOE of PLA nanocomposites.

Table 4 Review of DSC isotherms of nanocomposites

Tablica 4. Sažeti prikaz DSC izoterma nanokompozita

Formulations Sastav nanokompozita	Cooling Hlađenje		Heating Zagrijavanje		X_c %
	T_c °C	ΔH_c J/g	T_m °C	ΔH_m J/g	
HF	107.7	48.6	166.5	55.1	37.7
HF1	109.3	52.9	168.6	63.6	43.6
HF5	109.0	50.8	166.4	60	41.1
HF10	109.2	48.9	168.5	54.5	37.3
HC	109.8	45.8	165.7	63.1	42.2
HC1	109.5	41.8	153.4	42.8	29.3
HC5	108.2	40.4	169.6	49.7	34
HC10	108.2	54.8	169.7	58.9	40.3
LF	110.0	12.8	164.8	48.4	52.0
LF1	115.6	27.1	152.2	21.2	14.5
LF5	115.1	20.3	151.8	22.2	15.2
LF10	116.6	21.3	153.4	24.5	16.8
LC	108.8	20.8	155.5	38.3	41.1
LC1	115.3	18.7	154.6	19.9	13.6
LC5	115.2	22.1	153.6	21.4	14.6
LC10	113.7	22.4	153.3	22.8	15.6

It was found that the effects of BN were higher on the mechanical properties of PHB nanocomposites than on PLA nanocomposites. The SEM result showed that BN particles dispersed inside the matrix, and generally showed uniform dispersion in the matrixes. However, some BN aggregates were found in the SEM images. Thermal stability of biopolymer nanocomposites was found to improve with the addition of BN. The addition of BN showed improvement of $T_{10\%}$, $T_{50\%}$, and $T_{85\%}$. In DSC analysis, T_m and T_c generally increased with the addition of fillers, and X_c was also raised with the increase of ΔH_c and ΔH_m .

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