Effect of incorporation of zinc oxide on the properties of PHBV

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In this study, melt extrusion method was used to prepare biocomposites films of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and zinc oxide nanoparticles (ZnO). The effect of nano ZnO on PHBV was investigated by FTIR, DSC and TGA analysis. Oxygen permeation analyzer was used to examine the oxygen permeation properties of PHBV/ZnO composites. Mechanical properties of composites were examined by making DMA analysis. DMA analysis showed that adding ZnO to polymer increased the storage modulus of biocomposites. The increase in storage modulus is inversely proportional to the amount of ZnO added to the polymer. DMA analysis showed that the elasticity of the polymer increased with the addition of ZnO. In addition, the barrier properties of biocomposites have been improved.

Keywords: Biocomposite, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), zinc oxide, melt extrusion.

Introduction

Given the consumer demands and environmental impacts, the packaging industry is constantly trying to develop new products for food[1]. Environmental issues and food spoilage have been key issues to be addressed. Therefore, in recent years, the use of biodegradable materials and its active use in food packaging has been an important field of study[1]. The use of new biodegradable polymers such as polylactic acid (PLA), starch, cellulose, polyhydroxybutyrate (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) in the packaging industry has accelerated[2].

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is an important polyhydroxyalkanoate polymer due to its excellent biocompatibility and biodegradability[2]. PHBV is known to be of limited use due to its high crystallinity, low mechanical and thermal properties, and slow degradation rate[2,3]. Unless the properties of PHBV are improved, it is difficult to use in packaging industry[4]. It is known that the properties of polymeric materials improve by adding inorganic material to the polymeric material[4].

In terms of food quality, it is important for the packaging industry to extend the shelf life and remove contaminants while preserving food[5]. Since ZnO is a biocompatible material with strong antimicrobial properties, many attempts have been made on the production and investigation of bioactive biocomposites[3]. Zinc oxide (ZnO) in nano structure has a large volume/area ratio. High crystal structure, superior mechanical properties, low the thermal expansion coefficient and high thermal conductivity allow the use of zinc oxide as a filler in polymer materials[4]. It is known that zinc oxide is non-toxic and accepted by the FDA as safe "GRAS" substances[4]. ZnO reinforced materials have many applications in daily life, especially in the food industry[4].

In this study, biodegradable PHBV/ZnO nano composites were prepared via melt extrusion method. The melt extrusion method is of great interest due to its speed, simplicity of the process and compatibility with existing industrial applications. The melt extrusion method is a very useful method as it is more economical and more flexible for formulation. This method is also known as an environmentally friendly method since it does not contain solvents and contaminants[6]. The effect of nano ZnO on PHBV composites has been investigated. The mechanical and barrier properties of PHBV nanocomposites have been improved.

Experimental

The biopolymer PHBV used in the study has 8 mol% hydroxvalerate (HV) content. PHBV used is a pelletized poly-

mer suitable for melt extrusion under the trademark MAJ'ECO FN000HA by ADmajoris Company, France. Zinc oxide nanopowder (<100 particle size ZnO) were from Aldrich.

A twin screw extruder (Rondol Microlab, UK; L/D ratio is 20) was used for the preparation of PHBV/ZnO biocomposites by the melt method. Biocomposites were prepared by varying the weight percentage of ZnO (0.1, 0.5 and 1.0 wt%) in PHBV matrix. Screw speed of the extruder was 80 rpm. The operating temperatures were set at 90–135–160–160-155°C (from feed to death of extruder). Biocomposites were air-cooled before being formed into sheet samples. Sheet samples using a hot or cold pressing machine (Gülnar, Turkey) was prepared at about 0.8 mm thickness. Experimental conditions for biocomposites are given in Table 1.

Table 1. Experimental conditions for the biocomposites production

Sample code	Amount of ZnO (wt%)
Neat PHBV	–
PHBV/Z0.1	0.1
PHBV/Z0.5	0.5
PHBV/Z1.0	1.0

Results and discussion

Since the mechanical, barrier and thermal properties of PHBV are very low, the properties must first be improved in order to obtain useful products[8]. Improving the properties of the PHBV biopolymer in the presence of additives is of great importance for industrial applications and scientific studies.

Dynamic mechanical analysis of the samples was done using Perkin-Elmer DMA8000. Dynamic properties of samples was investigated in film extension mode in single cantilever mode at 1 Hz. DMA analyzes of the samples were carried out in the temperature range of –30°C to 150°C. The heating rate in the analysis was 2°C min^{-1}. For DMA analysis, the samples were cut into plates of 10.40 mm×10 mm and used. In the evaluation of the dynamic mechanical analysis of the samples, the change of the storage modulus E', loss modulus E'' and tan $\delta = E''/E'$ values with temperature was taken into consideration. The elastic and viscous nature of the polymeric material in a certain temperature range is determined by these parameters.

The change in the storage modulus of PHBV and PHBV/ZnO biocomposites with temperature is given in Fig. 1a. The storage modulus is related to the hardness (tensile modulus) of the polymer as well as determining the polymer's ability to absorb or store energy. As can be seen from Fig. 1a, the storage modulus of neat PHBV and biocomposites decreases with temperature. This reduction in storage modulus is due to the softening of the polymer matrix in the biocomposite.

With the introduction of ZnO, the storage modulus of the PHBV in both the glassy and rubbery region has increased. When the storage modulus is compared, it is seen that the biocomposites obtained except the addition of 1% (wt) ZnO are higher than PHBV in the whole temperature range (Fig. 1a). Max. storage modulus at all temperatures was achieved with the addition of 0.1% (wt) ZnO. As the amount of ZnO in the biocomposite increased, the storage module decreased. The increase in storage modulus shows that the addition of %0.1 (wt) and %0.5 (wt) ZnO to the biopolymer improve the composite below and above the glass transition temperature (T_g). These two biocomposites have a higher storage modulus than neat PHBV as a result of the natural hardness of the particle. The improvement of the storage modulus can be attributed to the good stress transfer between ZnO and the polymer matrix.

As can be seen from the storage modulus (Fig. 1a), at 0.1% (wt) ZnO loading, the elastic component of biocomposites increased by 26.1% at –15°C, and 87.3% in the rubbery stage at 145°C. The increase in storage modulus in the rubbery phase of the polymer matrix indicates that the fillers constitute a limitation to the free rotation of the molecular chains above the T_g.

Tan delta is a measure of energy expended, representing internal friction in viscoelastic material. Tan delta graphics of biocomposites were given in Fig. 1b. Glass transition temperature (T_g) can be defined as the peak of tan delta. The T_g value of neat PHBV was app. 26°C. As the amount of ZnO increased, the T_g value of biocomposites decreased. The minimum T_g value was obtained as 19.4°C at 0.1% ZnO loading. The T_g value was obtained as 20.8°C and 22.5°C at 0.5% and 1% ZnO loadings, respectively. The decrease in the T_g value indicates that the material has gained flexibility.

Perkin-Elmer Diamond DSC was used for DSC measurements. DSC analysis of biocomposites was carried out in
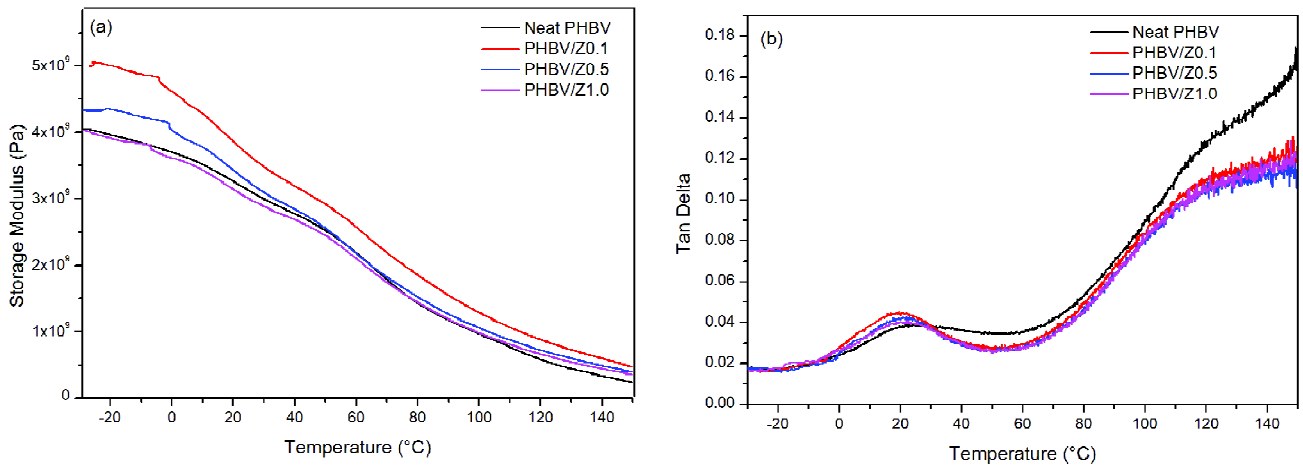
Fig. 1. DMA thermographs: (a) showing storage and (b) tan delta of neat PHBV and PHBV/ZnO composite.

three steps. About 5 mg samples taken in a standard aluminum crucible was analyzed under 50 mL/min nitrogen atmosphere with a heating and cooling rate of 10°C/min. DSC analysis took place in three stages. In the first stage of the analysis the biocomposites were heated from 0°C to 200°C, while in the second stage they were cooled back to 0°C. Biocomposites were re-heated from 0°C to 200°C in the last step. Melting temperature and enthalpy (T_m and ΔH_m), crystallization temperature and enthalpy (T_c and ΔH_c) of biocomposites were determined by DSC analysis. The crystallinity of samples was calculated using eq. (1)[9].

$$x_c\,(\%) = \left(\frac{\Delta H_m}{W_{PHBV} \times \Delta H_m^{ref}} \right) \times 100 \qquad (1)$$

where W_{PHBV} shows weight fraction of PHBV in the biocomposite, and ΔH_m^{ref} is melting enthalpy of sample. ΔH_m^{ref} is theoretical melting enthalpy for 100% crystallized PHBV (146 J/g^{-1})[10].

Fig. 2 shows DSC thermograms of first heating, cooling and second heating sequences for biocomposites. Table 2 shows the results obtained from DSC curves. The first melting temperature of biocomposites shifted to lower temperatures compared to neat PHBV. For biocomposites, the lowest melting temperature value was obtained at the least amount of ZnO addition. The value of ΔH_{m1} is 68.8 J/g for neat PHBV, while it ranges from 75–86.8 J/g for biocomposites. Crystallization temperature (T_{c1}) and crystallization enthalpy (ΔH_{c1}) values of the samples were determined from

the DSC cooling curves. Small decrease in crystallization temperatures of biocomposite samples was observed compared to neat PHBV. While the crystallization enthalpy of neat PHBV was 80.5 J/g, the crystallization enthalpy of the composites varied between 72.2–80.7 J/g.

According to the thermal properties based on the second heating scan of the composites, the melting enthalpy and crystallinity of the polymer decreased after the addition of zinc oxide to the polymer except for the PHBV/Z1.0 sample. A similar trend was observed in ΔH_{m2} enthalpy values. With the addition of 1.0 wt% ZnO to the biopolymer, the crystallinity of PHBV was 51.6%, and when the amount of ZnO was 0.1 wt%, the crystallinity of PHBV decreased to 48%. The decrease in crystallization enthalpy (ΔH_c) in ZnO added samples also indicates a decrease in the crystallinity of PHBV. Yu et al.[11] showed that the retarding effect of ZnO particles on the crystallization of PHBV nanofibers, while reducing the crystallinity, was ineffective on the T_m value. The decrease in crystallinity indicates that ZnO nanoparticles have a retarding effect on nucleation. High crystallinity causes a large increase in water vapor permeability. As the degree of crystallinity increases, the resistance of polymers against chemicals increases, while the paint holding feature decreases for the paint industry. Crystallinity generally provides hardness, thermal and mechanical strength in the polymer structure. On the other hand, it decreases the solubility, diffusion and permeability of the polymer. Therefore, the degree of crystallinity of the polymer varies according to the area where
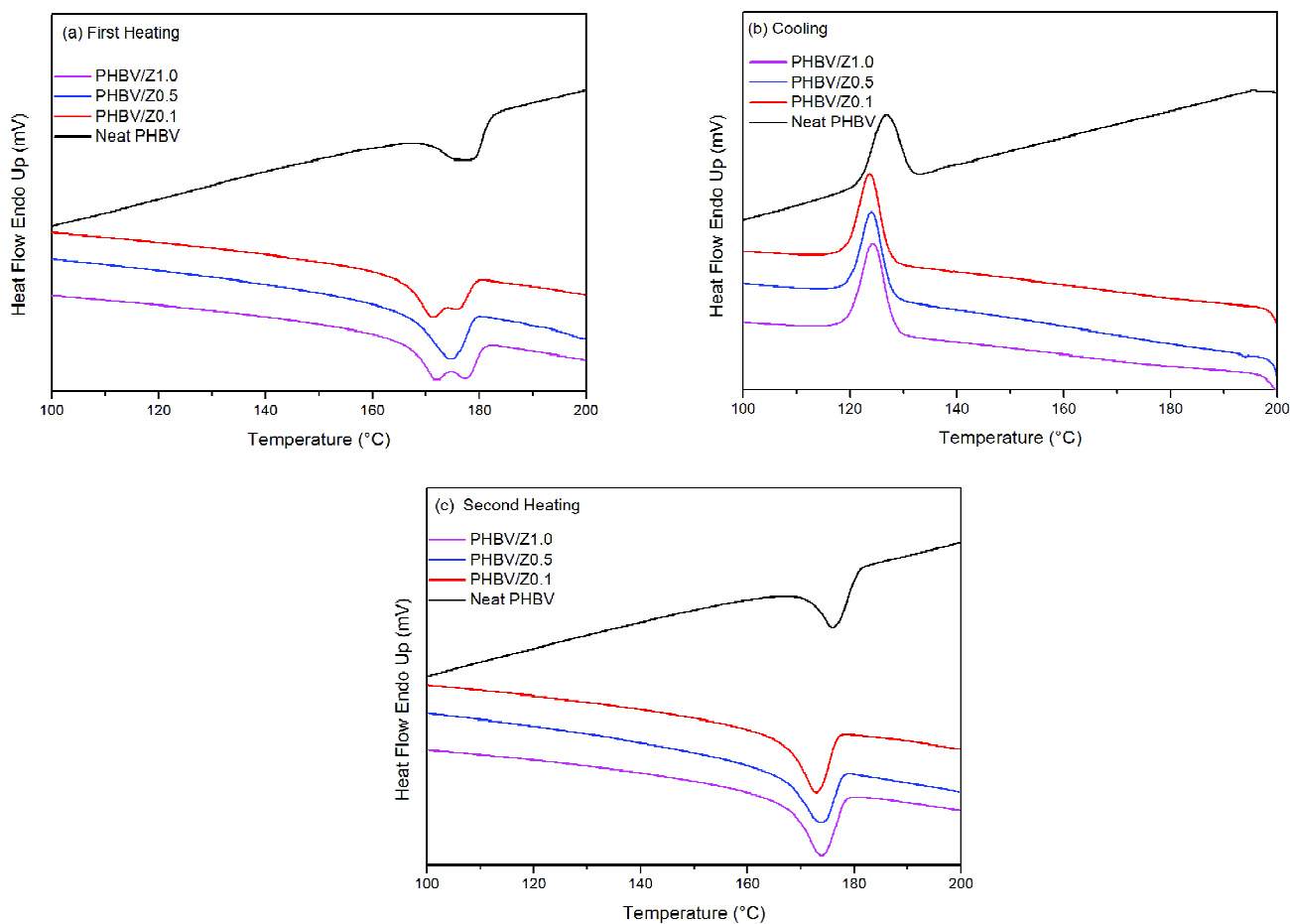
Fig. 2. DSC thermograms of biocomposite: (a) first heating cycle, (b) cooling cycle and (c) second heating cycle.

Table 2. The temperature and enthalpy values obtained from DSC curves for biopolymer composites

Sample	First heating		Cooling		Second heating		
	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{c1} (°C)	ΔH_c (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	X_C (%)
Neat PHBV	177.06	68.8	126.63	80.5	175.89	74.6	51.1
PHBV/Z0.1	172.88	75.1	123.80	72.2	171.37	70.0	48.0
PHBV/Z0.5	173.63	79.8	124.08	75.5	174.53	69.8	48.0
PHBV/Z1.0	173.88	86.8	124.31	80.7	172.06	74.6	51.6

the polymer is used.

We used Systech Model 8001, Oxygen transmission tester, to measure the oxygen permeability of biocomposites. ASTM D3985-05 was used for the measurements. Oxygen transmission rate (OTR) was performed at 23°C with a diameter of 10 cm, relative humidity (RH) at 0% and 1 atm pressure with oxygen (99.99%) and nitrogen (99.99%) gases. Oxygen permeability (OP) values were calculated by using

OTR and thickness of the samples.

By using the relationship between OTR and OP values of biocomposites, the barrier properties of PHBV/ZnO biocomposites were evaluated. Oxygen transmission rate (OTR) across a unit area of a flat material of unit thickness induced by the unit vapor pressure difference across the material is expressed as OP. Eq. (2) shows the relationship between OTR and oxygen permeability.

$$OP = OTR \times L/\Delta P \qquad (2)$$

where oxygen permeability coefficient (OP) is the (cc.mm. m^{-2}. day^{-1}), the oxygen transmission rate (OTR) is (cc. m^{-2}. day^{-1}), ΔP is the difference (bar) between oxygen partial pressure across the film and L is the film thickness (mm). It can be seen from Fig. 3, the change in OP values decreased with the increase of ZnO amount in biocomposite. The OP of neat PHBV has a value of 1.35 (cc.mm.m^{-2}.day^{-1}) at 23°C. The OP of PHBV/Z0.1, PHBV/Z0.5 and PHBV/Z1.0 shows 19.2%, 18.0% and 9.7% improvements, respectively compared to the neat PHBV. It can be said that ZnO creates a barrier for the passage of gas molecules. This improvement in the barrier property of the composite can be attributed to the fact that in the presence of ZnO the gas molecules follow a tortuous path for diffusion.
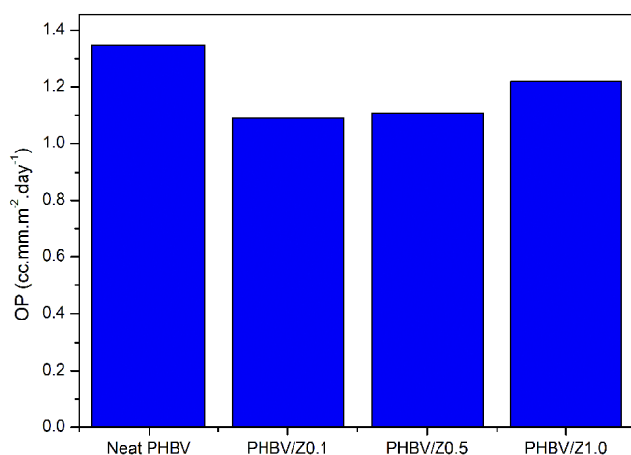

Fig. 3. Oxygen permeability (OP) of PHBV/ZnO biocomposites.

Conclusions

PHBV biocomposites were prepared with nano-sized zinc oxide particles and characterized for understanding the effect of ZnO on the mechanical and barrier properties of biocomposite. The mechanical and barrier properties were investigated by using DSC, OTR and DMA analysis. A decrease in crystallinity degree was observed with the addition of ZnO. Gas barrier properties of biocomposites increased with the addition of ZnO. DMA analysis showed that storage modulus of PHBV/ZnO biocomposites increased at temperatures below and above the T_g. In conclusion the barrier and mechanical properties of PHBV biocompoites were improved in the presence of ZnO nano-particle.

Acknowledgements

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