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THE EFFECTS OF ZINC OXIDE AND CLAY NANOPARTICLES ON THERMAL, BARRIER, AND MECHANICAL PROPERTIES OF POLYPROPYLENE AND HIGH DENSITY POLYETHYLENE

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ABSTRACT

Rod-shaped ZnO crystals were synthesized by chemical precipitation method and added into polypropylene and high density polyethylene together with montmorillonite particles by melt extrusion method. Surface modification with stearic acid was applied to the ZnO particles. Decreased oxygen permeability and increased elastic modulus were observed for both polypropylene and polyethylene when ZnO and clay particles were added together. Thermal properties of the polymers were preserved with the addition of the particles.
Keywords: Polyolefins, barrier property, mechanical properties, ZnO.

ÇİNKO OKSİT VE KİL NANOPARÇACIKLARININ POLİPROPİLEN VE YÜKSEK YOĞUNLUKLU POLİETİLENİN TERMAL, BARİYER VE MEKANİK ÖZELLİKLERİNE ETKİLERİ

ÖZET

Kimyasal çöktürme yöntemiyle çubuk şekilli ZnO kristalleri sentezlenmiş ve polipropilen ve yüksek yoğunluklu polietilen matrisleri içerisine montmorillonit parçacıkları ile birlikte eriyik harmanlama yöntemiyle eklenmiştir. ZnO parçacıklarına stearik asit ile yüzey modifikasyonu uygulanmıştır. ZnO ve kil parçacıkları birlikte ilave edildiğinde, hem polipropilen hem de polietilen için, oksijen geçirgenliği değerlerinde azalma ve elastik modül değerlerinde artış elde edilmiştir. Parçacıkların ilavesiyle, polimerlerin termal özelliklerinde önemli bir değişiklik gözlenmemiştir.
Anahtar Sözcükler: Poliolefinler, bariyer özellik, mekanik özellikler, ZnO.

1. INTRODUCTION

ZnO is a versatile material exhibiting various properties and can be synthesized by various methods[1]. Improvements in the thermal and mechanical properties were reported in the literature for both polypropylene [2-7] (PP) and high density polyethylene [8-10] (HDPE) for the incorporation of ZnO particles into polymer matrices. However, addition of ZnO particles or any other inorganic particles together with nanoclay into polymer matrices has not been studied. In a previous study carried out by our group [11], enhancement of the oxygen barrier property of PP was achieved by the incorporation of ZnO rod-shaped crystals together with nanoclay particles.

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In this study, the effect of ZnO crystals together with/without nanoclay particles on the thermal, oxygen barrier and mechanical properties of HDPE was studied. Also, the effects of the particles on the mechanical properties of PP were investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of the Nanocomposites

PP with a density of 0.91 g/cm^3 and a melt flow index of 3 g/10min was supplied from Rompetrol Company (PP F401). HDPE with a density of 0.955 g/m^3 and melt flow index of 0.35 g/10min was supplied from Sidpec Company (HD 5403EA). Rod-shaped ZnO crystals were synthesized in our lab and the synthesis method is described elsewhere in detail [12]. ZnO particles had the mean width of 199±69 nm and the mean length of 1812±467 nm. Surface modification was applied using stearic acid [11]. Commercial montmorillonite was supplied from Nanocor Company (Nanomax P-802).

In our previous study [11] , various concentrations of ZnO and nanoclay were studied for PP and the best results in terms of oxygen barrier property were obtained for 5% nanoclay in case of nanoclay addition and 1% ZnO in case of ZnO addition. PP/ZnO(1%)/nanoclay(5%) and PP/ZnO(1%) nanocomposites were the samples with the lowest oxygen permeability results, respectively. Same compositions of PP and HDPE nanocomposites were also used in this study for comparison purposes. Sample compositions and coding are given in Table 1.

Table 1. Compositions of the PP and HDPE nanocomposites prepared

Sample	Polymer content, wt.%	ZnO content, wt.%	Nanoclay content, wt.%
PP	100	-	-
PP1Z	99	1	-
PP5N	95	-	5
PP1Z5N	94	1	5
PE	100	-	-
PE1Z	99	1	-
PE5N	95	-	5
PE1Z5N	94	1	5

A twin-screw extruder (Microlab, Rondol) with L/D ratio of 20 was used for the preparation of polymer nanocomposites. The extrusion temperatures used were 90, 130, 160, 180, and 210 °C from feed to die for both polymers and the screw speed was 85 rpm. After extrusion, polymer nanocomposites were cooled and cut into pellets, then they were compression molded into sheets of about 1 mm thickness.

2.2. Characterization Methods

Crystallinity and thermal properties of the HDPE samples were measured with Perkin Elmer DSC 4000 differential scanning calorimeter. Samples were heated from 30 to 300 °C with a heating rate of 20 °C/min under nitrogen atmosphere and kept at 300 °C for 1 min. Then they were cooled to 30 °C with 20 °C/min cooling rate. Crystallization temperature (T_c) was obtained. A second scan was performed with the same parameters in order to obtain melting temperature (T_m) and melting enthalpy (ΔH_m). The degree of crystallinity (X_c, %) was calculated using $X_c, \% = (\Delta H_m)/(\Delta H_m^0) * 100$, where $\Delta H_m{}^0$ is the enthalpy of fusion of an ideally fully crystalline HDPE (taken as 279 J/g).

Morphological characterization of the samples was carried out using scanning electron microscopy (SEM, JEOL JSM6335F).

Oxygen permeability (OP) values of the HDPE were measured using Systech 8001 Oxygen Permeability Analyzer according to ASTM D3985 standard. Measurements were conducted under dry conditions and at 25 °C.

Mechanical properties of the PP and HDPE samples were measured using Mares Mechanical Analyzer with 20 kN load capacity according to ASTM D638 standard. PP and HDPE specimens with about 10 mm width and 60 to 80 mm length were prepared. The thicknesses of the specimens were around 1 mm.

The thermal, OP and mechanical properties were determined from at least three separate experiments and only the average values were reported.

3. RESULTS AND DISCUSSION

Measured thermal properties of the HDPE samples are given in Table 2. T_m and T_c values did not change significantly. ΔH_m and X_c values were slightly increased for 1 % ZnO addition. Thermal properties of HDPE polymer were preserved by addition of the nanoparticles.

Table 2. Thermal properties of the HDPE samples

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	X_c, %
PE	138	159	118	57
PE1Z	135.1	169.5	118.1	60
PE5N	135.1	158.3	117.3	56.7
PE1Z5N	136.3	163.1	118.8	58

OP values of the HDPE samples are given in Table 3 together with PP samples from our previous study[11] for comparison purposes. Addition of ZnO into HDPE matrix decreased the OP value by 7%, and addition of nanoclay decreased the OP by 20%. When ZnO and nanoclay were added together, the decrease in OP value was 23%.

Table 3. Oxygen permeability values of PP and HDPE samples

Sample	OP (cc.mm/m^2.day.bar)	Decrease in OP value, %	Source
PP	54.7	-	[11]
PP1Z	45.3	17	[11]
PP5N	49.6	9	[11]
PP1Z5N	42.4	23	[11]
PE	52.3	-	This study
PE1Z	48.7	7	This study
PE5N	41.8	20	This study
PE1Z5N	40.5	23	This study

Contradictory results were given previously in the literature for the effect of nanoclay on OP value of HDPE such as 24% decrease [13] and 146% increase [14]. The 146% increase was obtained by twin-screw extrusion method and was attributed to the shear forces occurring inside the extruder that break the HDPE chains and lead to an increase in the free volume [14]. Li et al. [10] suggested 16% decrease in OP value for the addition of 1% silane-treated ZnO, despite severe particle agglomeration. SEM micrographs of PE5N and PE1Z5N samples are given in Fig. 1a and b, respectively. Exfoliation of nanoclay particles can be observed while ZnO particles were partially agglomerated.

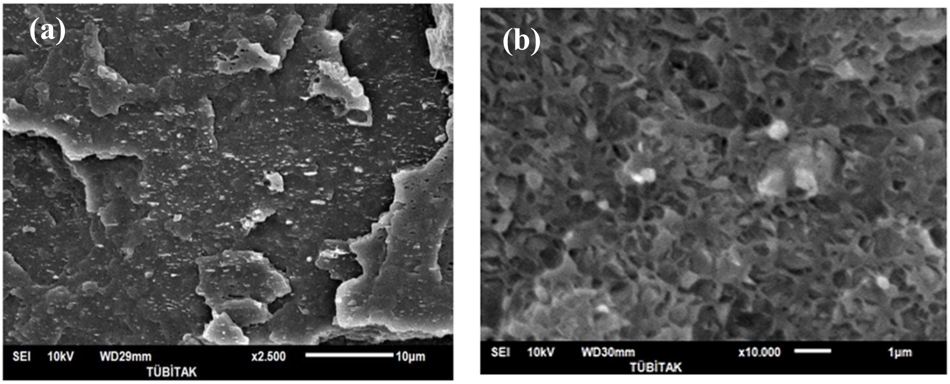

Figure 1. SEM micrographs showing the dispersion of the nanoparticles inside the samples (a) PP1Z5N and (b) PE1Z5N

Considering the mechanical properties of PP nanocomposites, Zaman et al. [5] and Lepot et al. [6] reported increase in the tensile strength and elastic modulus values with incorporation of ZnO particles. Tensile properties of the PP and HDPE specimens measured in this study are given in Table 4. Tensile strength and elastic modulus values were increased for all samples which could be due to the stiffness of the nanoparticles. Highest modulus value was obtained for PP1Z5N sample (6.5% increase). Elongation at yield remained almost the same for all samples.

Table 4. Tensile properties of the PP and HDPE samples

Sample	Tensile Yield Strength, MPa	Elongation at Yield, %	Elastic Modulus, MPa
PP	30.9	7	886.3
PP1Z	32.3	8	902.7
PP5N	37.9	9	911.2
PP1Z5N	37.1	8	943.6
PE	25.4	13	604.2
PE1Z	22.4	13	655.4
PE5N	24.1	12	665.6
PE1Z5N	24.5	14	665.8

Carrera et al. [15] reported decrease in elastic modulus with the incorporation of polyvinyl alcohol modified montmorillonite particles into HDPE in 0.6% and 2% ratio; but increase in tensile strength and yield elongation for 2% montmorillonite addition. In this study, tensile strength and elongation at yield values of the HDPE samples did not change significantly. Elastic modulus increased for all samples and the highest modulus values were obtained for PE5N and PE1Z5N samples (10% increase for both samples).

The properties of polycaprolactone containing zinc oxide (ZnO) nanocomposites were investigated by Elen et al.[16]. It was found that the ZnO nanoparticles reduces the gas permeability of the nanocomposites via two mechanisms: by the creation of a tortuous path and by gas adsorption.

4. CONCLUSION

The effects of rod-shaped ZnO crystals with/without nanoclay particles on the thermal, barrier, and mechanical properties of PP and HDPE matrices were investigated. Thermal properties of PP and HDPE were preserved with the addition of ZnO and clay nanoparticles. Incorporation of ZnO crystals inside PP and HDPE helped enhancing oxygen barrier properties of the polymers. Usage of ZnO and nanoclay particles together resulted in lower OP values. Highest tensile property values were also obtained for the incorporation of both particles together, for both polymers.

ZnO nanorods are promising fillers for polyolefins and their usage together with nanoclay particles helps enhancing polymer properties in a greater extent.

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REFERENCES / KAYNAKLAR

[1] Wang Z.L., "Nanostructures of zinc oxide", Mater. Today 7, 26–33, 2004.
[2] Chandramouleeswaran S., Mhaske S.T., Kathe A.A. et al., "Functional behaviour of polypropylene/ZnO–soluble starch nanocomposites", Nanotechnology 18, 385702, 2007.
[3] Merijs M.R., Bochkov I., Grigalovca A. et al., "Nanocomposites based on ZnO modified polymer blends", Macromol. Symp. 322,130–134, 2012.
[4] Cui Y., Wang X., Li Z. et al., "Fabrication and Properties of Nano-ZnO / Glass-Fiber-reinforced polypropylene composites", J. Vinyl Addit. Technol. 16,189-194, 2010.
[5] Zaman H.U., Hun P.D., Khan R.A. et al., "Morphology, mechanical, and crystallization behaviors of micro- and nano-ZnO filled polypropylene composites", J. Reinf. Plast. Compos. 31, 323–329, 2012.
[6] Lepot N., Van Bael M.K., Van Den Rul H. et al., "Influence of incorporation of zno nanoparticles and biaxial orientation on mechanical and oxygen barrier properties of polypropylene films for food packaging applications", J. Appl. Polym. Sci. 120,1616-1623, 2011.
[7] Altan M., Yildirim H., "Effects of compatibilizers on mechanical and antibacterial properties of injection molded nano-ZnO filled polypropylene", J. Compos. Mater. 46,3189–3199, 2012.
[8] Li S., Li Y., "Mechanical and antibacterial properties of modified nano-ZnO/high-density polyethylene composite films with a low doped content of nano-ZnO", J. Appl. Polym. Sci. 116, 2965–2969, 2010.
[9] Kijkobchai P., Wacharawichanant S., "Effect of surface-treated ZnO on mechanical and morphological properties of high density polyethylene/ZnO nanocomposites", TIChe International Conference, Thailand (2011), Paper code pp011.
[10] Li Y.N., Cha K.H., He Q.H., "Preparation and properties research of modified nano-ZnO/HDPE composite films", Adv. Mater. Res.174,450–453, 2011.
[11] Atayev P., Oner M., "Effect of incorporation of clay and zinc oxide nanoparticles on oxygen barrier properties of polypropylene sheet", J. Plast. Film Sheeting 30,248–265, 2013.
[12] Akin B., Oner M., "Aqueous pathways for formation of zinc oxide particles in the presence of carboxymethyl inulin", Res. Chem. Intermed. 38,1511–1525, 2012.
[13] Ercan N., Durmus A., Soyubol G. et al., "Rheological and barrier properties of HDPE/clay nanocomposites compatibilized by an OX-PE blend", Acad. J. Mat. Eng. 8,55–60, 2010.

[14] Monsiváis-Barrón J., Bonilla-Rios J., Ramos de Valle F. et al., "Oxygen permeation properties of HDPE-layered silicate nanocomposites", Polym. Bull. 70,939–951, 2013.

[15] Carrera M.C., Erdmann E., Destéfanis H., "Barrier properties and structural study of nanocomposite of HDPE/montmorillonite modified with polyvinylalcohol", J. Chem. 2013,1–7, 2013.

[16] Elen K., Murariu M., Peeters R. et al., "Towards high-performance biopackaging: barrier and mechanical properties of dual-action polycaprolactone/zinc oxide nanocomposites", Polym. Adv. Technol. 23,1422–1428, 2012.