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Comparison of Antibacterial Properties of Nano TiO_2 and ZnO Particle Filled Polymers

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Antibacterial property for the plastic products is very important due to their wide spread usage in many areas close to human health such as a child toy or a food package. There are some methods to make polymers antibacterial such as ionizing radiation but they can be still infected by micro organisms during usage of them. The best and easy way to obtain antibacterial polymers is melt mixing of polymers with antibacterial agents. In this study, nano TiO_2 and ZnO particles were mixed with polypropylene and high density polyethylene with a twin screw extruder. Silane was applied to the particles prior melt mixing in order to prevent agglomeration and FT-IR analysis was done to characterize the particles. After melt mixing, particle filled rectangular plates were obtained by plastic injection molding and antibacterial tests were done on the plates according to a standard method, JIS Z 2801. According to the results, satisfactory antibacterial properties were obtained for both polymers and it has been seen that particles without silane could not provide antibacterial effect.

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1. Introduction

Nano sized titanium dioxide and zinc oxide, the most popular metal oxides, are used in the demand of antibacterial property in many areas. It is possible to use them with polymer products that are close to human health such as child toy, food packing, or medical appliances. There are several methods to make polymers antibacterial such as sterilizing them with ethylene oxide or ionizing radiation but they can still be contaminated or infected by microorganisms when they are exposed to air. Therefore, some other methods have been investigated to make polymers antibacterial and melt mixing of polymers with antibacterial agents is known to be the most preferred method [1]. In the early of 1950s, scientists had already started to research ZnO as an antibacterial material and then researchers continued the studies related to the antibacterial activities of the metal oxides like TiO_2 and MgO [2–6]. Antibacterial agents like TiO_2 and ZnO have photocatalytic activity under UV light so daylight or UV light is needed to make them active in killing bacteria [7, 8]. In this study, two different polymers, high density polyethylene and polypropylene were used and they were mixed with nano TiO_2 and ZnO particles in different ratios. The antibacterial properties of each polymer and nanoparticle were investigated.

2. Experimental study

2.1. Materials

Polymers used in this study were polypropylene copolymer (56 M10, Sabic Company) with melt flow index of 6.2 g/10 min, density of 0.902 g/cm^3 and high density polyethylene (Lanufene, HDI-6507UV) with melt flow index of 7.5 g/10 min and density of 0.965 g/cm^3. Nanomaterials were TiO_2 (Nabond Company, China) and ZnO (20 nm, Nabond Company, China) with the average grain size of 20 nm. Vinyltrimethoxysilane (VTMS, Aldrich) was used for the surface modification of the nanoparticles.

2.2. Surface modification of the particles with silane

Silane was used by preparing a solution of 96% absolute alcohol and 4% distilled water with 1% silane. Pure nanoparticles were added slowly into this solution and mixed for 3 h with a mechanical mixer (IKA RW 20 digital). The mixture was pulverized after drying the mixture at 50 °C for 8 h. Pulverization was done under control to keep the particles in nanoscale.

2.3. Compounding and injection molding

The dried powders and the polymer were loaded into a twin screw extruder (Rondol MicroLab, England) with L/D ratio of 20. The die temperature was 220 °C and the speed of the screw was 60 rpm. The extrudate strands were granulized and dried at 80 °C under vacuum for 2 h. The loading of the particles was as follows: 1%, 3%, and 5%. The coding of the compoundings were done as: PP/TiO_2/SILANE 1, PP/ZnO/SILANE 1, HDPE/TiO_2/SILANE 1 and HDPE/ZnO/SILANE 1. SILANE 1 changes as SILANE 3 or SILANE 5 according to the amount of the nanoparticle content. Then, the dried composite granules were injection molded with a 40 tone injection molding machine (Yelkenciler, Turkey) and antibacterial test specimens were obtained.

2.4. Characterization

The Fourier transform infrared (FT-IR) spectra of particles were obtained between 650 and 1800 cm^{-1} by using of Perkin Elmer Spectrum 100. Morphology of the fracture surface of the each specimen was analyzed by scanning electron microscope (XL-306 ESEM FEG, Philips). All the specimens were coated with gold prior SEM analysis.

2.5. Antibacterial test

Bacterial activity of the injection molded composite specimens (30×30 mm^2 plaques) was evaluated by examining their killing capability of Escheria coli using viable cell counting technique, a standard method, JIS Z 2801 as the authors used in their previous studies [9, 10].

3. Results and discussions

3.1. Characterization of the particles

Silane coating was applied on the particles prior melt mixing in order to reduce the surface energy between the particles and polymer. The characterization of the coated particles were investigated by FTIR as given in Fig. 1.

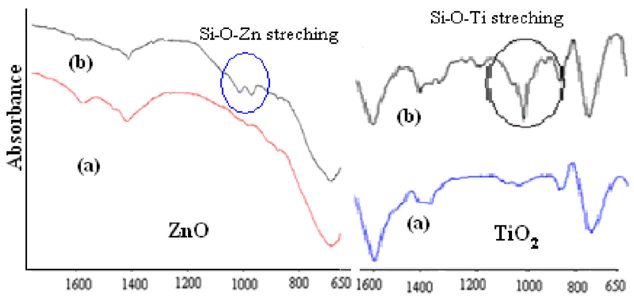

Fig. 1. FT-IR spectra of the nanoparticles: (a) pure particles, (b) silane coated particles.

The band of 1050 cm^{-1} is attributed to the stretching of Si–O bonds and the band around the region of 940 cm^{-1} corresponds to the Si–O–Ti and Si–O–Zn stretching [11–13]. These bands verify the surface modification.

3.2. Antibacterial efficiency

After the particles were coated with silane, polymers and nanoparticles were mixed on twin screw extruder under particle loading of 1%, 3%, and 5%. Then, the extrudate strands were granulized and injection molded, and antibacterial test was done on the molded plaques. The results were given in Table. Some photographs of survival bacteria colonies in diluted solutions are given in Table in three categories such as for pure polymers, for no bacterial growth and for bacterial growth in acceptable limits.

According to the JIS standard, the log reduction must be equal to 2 or higher than 2 to accept a material antibacterial [14]. Here, pure materials give increment in bacteria colonies normally due to the absence of the antibacterial agent. On the other hand, the polymers including nanoparticles without silane gave log reduction but this reduction is lower than 2. Polymers with silane coated particles gave better antibacterial property and this is due to better distribution of the silane coated particles in the matrix. The SEM images given in Fig. 2 verify this result. The circles given on the images show the regional agglomerations of particles without silane in polymer matrix.

TABLE

Antibacterial results of the polymer composites.

No	Material	*E.coli* (initial) [cfu/ml]	Reduction in *E.coli* after 24 h [cfu/ml]	Log reduction [cfu/ml]
1	PP	1.6×10^5	15.8 increase	−1.2 increase
2	HDPE	4×10^5	15.1 increase	−1.18 increase
3	PP/TiO_2 (without silane)	4×10^5	27.23	1.38
4	PP/ZnO (without silane)	1.6×10^5	36.35	1.56
5	HDPE/TiO_2 (without silane)	2.76×10^5	79.30	1.90
6	PP/ZnO (without silane)	1.6×10^5	36.35	1.56
7	PP/TiO_2/SILANE 1	2.6×10^5	no bacterial growth	no bacterial growth
8	PP/TiO_2/SILANE 3	2.76×10^5	no bacterial growth	no bacterial growth
9	PP/TiO_2/SILANE 5	2.76×10^5	178.5	2.25
10	PP/ZnO/SILANE 1	4×10^5	727	2.86
11	PP/ZnO/SILANE 3	4×10^5	no bacterial growth	no bacterial growth
12	PP/ZnO/SILANE 5	4×10^5	363.5	2.56
13	HDPE/TiO_2/SILANE 1	2.76×10^5	no bacterial growth	no bacterial growth
14	HDPE/TiO_2/SILANE 3	2.76×10^5	714	2.85
15	HDPE/TiO_2/SILANE 5	2.6×10^5	238	2.38
16	HDPE/ZnO/SILANE 1	2.6×10^5	517.5	2.71
17	HDPE/ZnO/SILANE 3	2.76×10^5	714	2.85
18	HDPE/ZnO/SILANE 5	2.6×10^5	207	2.31

(cfu: colony forming unit per millimeter)

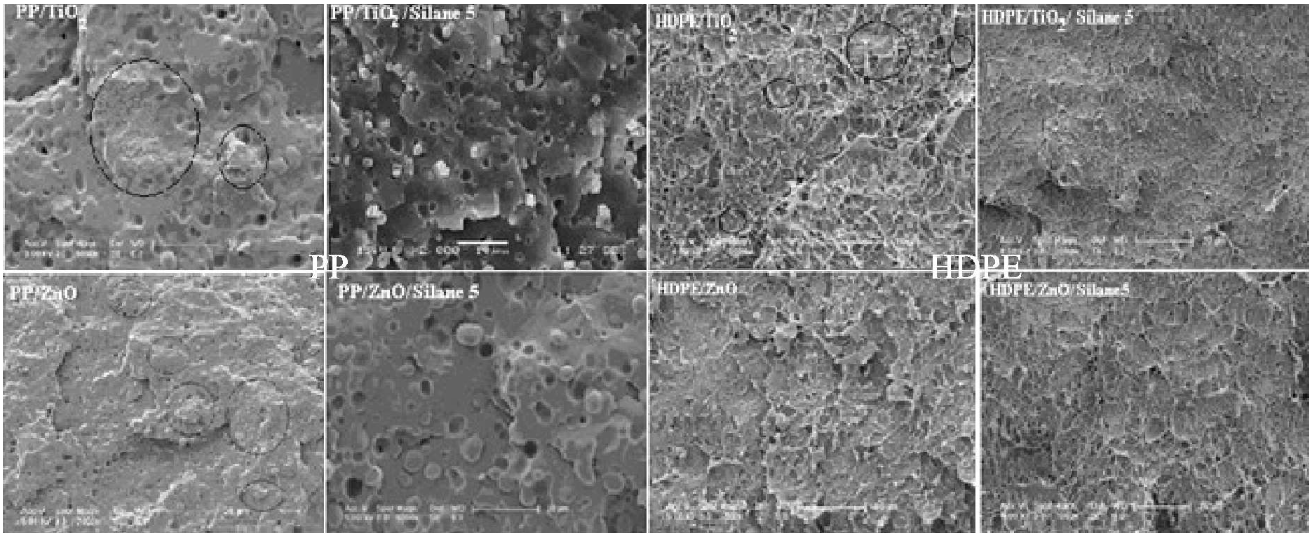

Fig. 2. SEM images of nanoparticle filled PP (left) and HDPE (right) with silane and without silane.

It is known that when the content of the inorganic particle increases, light can be masked and photocatalyst is not activated which is very important for killing the bacteria [10–12]. The mechanism of ZnO or TiO_2 in killing bacteria is about photocatalytic activity of the particles. During photocatalytic reactions, the active oxygen species which act as oxidizing agent causes the death of the bacteria by contacting the bacterial membrane. In this study, plaques were kept under UV light (200–300 nm) cabinet about 2 h prior antibacterial test. When the antibacterial results are compared, it could be seen that polymers gave similar antibacterial character but TiO_2 was a better antibacterial agent due to its improved surface adhesion gained between polymer and particle by means of silane.

The amount of the particle content was also important factor in antibacterial property. In Table, it could be seen that the lowest log reduction is seen in the 5% content of the particles with silane. This shows that there should be possible agglomeration and not well dispersed particles induced antibacterial property that reduces the photocatalytic performance of the particles [12, 15].

4. Conclusion

Nanosized titanium dioxide and zinc oxide were used as antibacterial agent for polypropylene and high density polyethylene. Silane coating was applied prior melt mixing to distribute the particles well in the matrix. The results showed that higher amounts of the nanoparticles reduce antibacterial efficiency due to agglomeration and less dispersion which could reduce the photocatalytic activity. Both polymers showed same behavior in gaining antibacterial property, but titanium dioxide showed slightly better antibacterial efficiency, because silane gave a better compatibility with titanium dioxide rather than with zinc oxide.

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