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ScienceDirect

Energy Procedia 56 (2014) 102 – 111

Energy Procedia

11th Eco-Energy and Materials Science and Engineering (11th EMSES)

Effect of TiO_2 and ZnO on Thin Film Properties of PET/PBS Blend for Food Packaging Applications

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Abstract

This research was aimed to investigate the effect of TiO_2 and ZnO along with its ratio on physical, thermal, mechanical and antibacterial properties of PET-poly(ethylene terephthalate) and PBS-poly(butylene succinate) blend thin film. The content of TiO_2 and ZnO was added at 1% and 2%wt on PET/PBS (ratio of 90:10) blend thin film because the ratio of PET and PBS of 90:10 was found to be the best in clarity. The melting temperature of PET/PBS blends were completely separated due to immiscibility of polymer blend. The addition of ZnO made film more transparency than TiO_2 because ZnO particles were physically bigger than TiO_2 particles. In addition, TiO_2 increased thermal stability of PET/PBS blends. The addition of TiO_2 and ZnO would not significantly increase tensile strength, young's modulus and percentage elongation at break. In term of antibacterial activity, PET/PBS blend thin film with TiO_2 was more active against both E.coli and S.aureus than the one with ZnO.

Peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)

Keywords: Films; Packaging; Polyethylene terepthalate; Polybutylene succinate

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Peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)
doi:10.1016/j.egypro.2014.07.137

1. Introduction

In recent years, plastic parts and products play many important roles in everyday life. The appealing properties are durability, light weight, seal-ability, and cost effectiveness. Furthermore, some types of plastics can withstand the penetration of gas, vapor, and oil. Majority of plastics are being used for food packaging purposes. The more we use plastics, the more waste by product we accumulated, especially those from synthetic polymers could lead to negative impacts on the environment. Therefore, the development of biodegradable and recyclable alternatives to conventional plastic is a matter of urgency [1, 2].

Most of degradable plastic are obtained from naturally derivative products, for example, protein, starch and natural fiber. Susceptibility and sensitivity to moisture and water absorption are the major drawback, which restricts the usage of these natural derivatives [3]. High cost of technology compared to typical plastics production is of another significant factor to be considered. Recently, the increasing awareness of the negative environmental impacts generates green technological demands and subsequently reduces the cost of production. Thus, encourage the usage of degradable plastics.

Poly(ethylene terephthalate) (PET or PETE) is a thermoplastic and among one of the most widely used, due to its high mechanical properties. They are optically clear with high melting point and most importantly, their high resistant to gas absorption. Poly(butylene succinate) (PBS) is synthesized from succinic acid and butanediol by polycondensation reactions [2, 4], which can be degraded in the nature by microorganism activities. PBS, in general, is expensive and poor in mechanical properties, thus not attractive to use in several applications. Since PET is non-degradable by microorganism, blending PET with PBS could improve degradable property. The studies of microbiocidal effects of TiO_2 and ZnO photocatalytic reaction were carried out with *E.coli* and *S.aureus* [5-12]. PET/PBS blends are then improved mechanical and antibacterial properties by the addition of either TiO_2 or ZnO. For this study, we compare mechanical, thermal, and antibacterial properties of PET/PBS thin film for food packaging obtained between TiO_2 and ZnO.

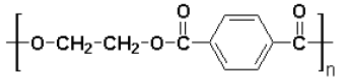
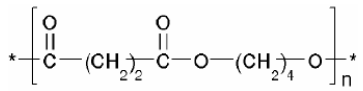
Furthermore, in term of compatibility, series of mixtures of PET and PBS must be considered in this study. The reaction blending of block PET/PBS copolyesters had the best process temperature at 290°C [6]. The increase of PBS content would decrease the glass transition temperature (T_g), melting temperature (T_m), elastic modulus, and tensile strength of copolymers. In contrast, the elongation at break would be increased. The block copolymers were prepared by solution blending or melt blending, however only in the batch-sized capacity. Therefore, these methods had some limitations on the small quantity of copolymer output. In this work, we wish to produce PET/PBS thin film that will make possible by the process employed in the industry. After mixing the polymer blend in twin screw extruder, the flat film extrusion process would then be used to produce PET/PBS thin film.

Moreover, not only the polymer-blended thin films would be our interests of study for production as food packaging purposes; it also has antibacterial and biodegradable material factors. Therefore, the effect of ratio of PET/PBS on various properties, as well as, the impact of TiO_2 and ZnO would be investigated on the properties of thin film.

2. Experimental

2.1 Materials

Table 1 Chemical structure of PET and PBS

Materials	Chemical structure
PET	
PBS	

Poly (butylene succinate) (PBS, AZ91TN) used in this study (standard extrusion for film grade) was purchased from BC Polymers Marketing (Thailand) Co., Ltd. Poly(ethylene terephthalate) (PET) of commercial grade was purchased from Pacific Color Co., Ltd. Structures of PET and PBS are shown in Table 1. TiO_2 and ZnO were purchased from N.P. Science Co., Ltd.

2.2 Blend preparation

Both resins were oven-dried for 12 hrs at 100 ^oC for PET and at 70 ^oC for PBS before blending. PET and PBS blends were prepared in twin screw extruder (diameter 16 mm, L/D 40) with model LWD-40 from Labtech Engineering. PET/PBS blends were prepared at different ratios of 100:0, 90:10, 80:20, 70:30 and 0:100. Furthermore, the content of TiO_2 and ZnO was added at 1% and 2%wt on PET/PBS (ratio of 90:10) blend thin film. Temperature ranges of feed zone to die are 140^oC, 230- 265 ^oC and screw speed of 300 rpm. With the exception of either TiO_2 or ZnO added PBS, temperature range of feed zone to die were 120^oC, 135-140^oC at the same screw speed of 300 rpm. Then samples were prepared in flat film extruder with chill roll (Model LCR-300-HD: Labtech Engineering) with the temperature range of feed zone to die 140^oC, 270-280 ^oC at the screw speed of 35 rpm. Only PBS thin film and either TiO_2 or ZnO added PBS thin films, temperature range of feed zone to die were 120 ^oC, 130- 140 ^oC with screw speed of 35 rpm. Film thickness was set at 70 ±10 μm.

2.3 Characterization

2.3.1 Differential Scanning Calorimeter (DSC)

Melting temperature (T_m), enthalpy (ΔH) and degree of the crystallization (X_c) were measured using Perkin Elmer DSC under nitrogen atmosphere. It was pre-melted at the temperature of 50-280^oC with the heating rate of 10^oC/min and then cooled to 50^oC with the cooling rate of 10^oC/min. The sample was subsequently reheated to 280^oC with the heating rate of 10^oC/min. Degree of the crystallization, X_c was calculated according to the equation (1).

$$X_c = \frac{\Delta H}{w\Delta H^*} \times 100 \tag{1}$$

where ΔH is enthalpy of the sample, ΔH^* is enthalpy of crystallization pure PET and PBS are 140.1 J/g and 210 J/g respectively, w is weight fraction of PET and PBS.

2.3.2 Thermogravimetric Analyzer (TGA)

The thermogravimetric analyses were carried out under nitrogen atmosphere at the heating rate of 10^oC/min in Perkin Elmer TGA-7. The samples were heated from 50 to 600 ^oC with the heating rate of 10 ^oC/min. The temperature at the rate of maximum mass loss was referred as the decomposition temperature (T_d).

2.3.3 Mechanical properties

The tensile test was carried out by an Instron Universal Testing Machine according to ASTM D882 at loading of 10 kN with cross head speed of 5 mm/min. These tests provided the tensile strength, elongation at break and Young's modulus values of PET/PBS blends thin film.

2.3.4 Morphological studies

Samples were prepared in compression molding machine from Lab tech engineering. Sample size is 1.3×6.4×3 mm^3.Morphology of the distribution of TiO_2 and ZnO in polymer blends was carried out by using scanning electron microscope (SEM).

2.3.5 Antibacterial activity against E.coli and S.aureus

Samples were performed in dynamic shake flask method according to ASTM E2149-10. Bacteria was transferred from stock culture to slant culture medium and then transferred into 5 ml NB tube. The tube was incubated at 37^{o}C for 16-24 hrs and then pipette 1 ml into 50 ml NB flasks. The thin films were irradiated with ultraviolet light at room temperature for 2 hrs and then 0.3 g thin films were added into flasks and incubated at 37 ^{o}C for 20-24 hrs. The 10-fold serial dilutions was made by using phosphate-buffered saline 9 ml/tube and pipette 1 ml of each flask into dilution tube and dilute continuously to 9 tube.Then 0.1 ml of bacteria suspension in dilution factor 10^{6}-10^{8} was taken into sterilized plates containing 10 ml NB by pipette and then plates were incubated at 37 ^{o}C for 20 hr. All experiments were conducted in triplicate. The colony forming units (CFU) of bacteria were taken count, and the antibacterial rate (R) was calculated via the following equation (2) and (3), respectively.

$$CFU/ml = \frac{content \cdot of \cdot colony \times Dilution \cdot factor}{volume \cdot of \cdot dilution \cdot (0.1 \cdot ml)} \tag{2}$$

$$Antibacterial \cdot ratio \cdot (\%) = \frac{(A-B)}{A} \times 100 \tag{3}$$

where A is the CFU of blank sample and B is the CFU of antibacterial samples.

3. Results and discussion

3.1 Effect of ratio between PET and PBS on thin film properties of PET/ PBS blends

3.1.1 Clarity of PET/PBS thin films

A set of films showing the clarity at different ratios of PET/PBS was illustrated in Fig. 1. Pure PET thin film seemed to exhibit more clarity than pure PBS thin film due to the different size of its crystal. Moreover, the increment of PBS content led to the gradual haziness of PET/PBS thin films. For instances, the sample which was labeled (Fig. 1d) with the PET/PBS thin film of ratio 70:30 covered would thus show less clarity when compared with its counterpart of PET/PBS flat film 90:10 (Fig. 1b).

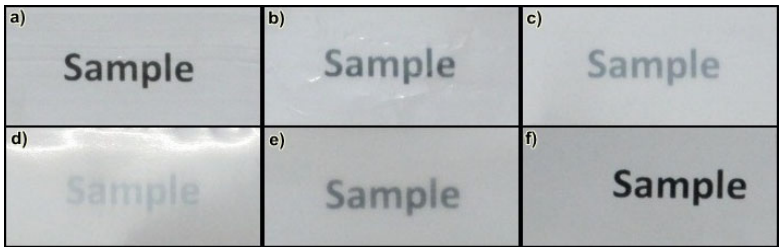


Fig. 1. Clarity of PET/PBS thin films in different ratio a) 100:0 b) 90:10 c) 80:20 d) 70:30 e) 0:100 compare with f) sample without thin film.

3.1.2 Differential Scanning Calorimetry (DSC)

Table 2 showed melting temperature (T_m) and % crystallinity (X_c) of PET/PBS blends (100:0, 90:10, 80:20, 70:30, 0:100). Percentages of PET crystallinity for PET/PBS blends at 90:10, 80:20 and 70:30 were in the proximity of percentage of pure PET crystallinity. On the other hand, percentages of PBS crystallinity for PET/PBS blends at 90:10, 80:20 and 70:30 showed significantly drop in term of crystallinity values when compared with pure PBS. The effect of PET could highly likely interrupt the rearrangement of PBS that cause the low percentage of crystallinity of PET/PBS blends. In this study, melting temperature of pure PET and pure PBS were at 251 ^{o}C and 111 ^{o}C,

respectively. Due to the immiscible blends as a consequence of physical mixing, the melt temperatures of PET/PBS blends were displayed at two different spots in the range of melting temperatures for both pure polymers as shown in Table 2.

Table 2 Effect of ratio between PET and PBS on melting temperature and % crystallinity of PET/PBS blends

PET:PBS	T_m (℃)		Δ H (J/g)		X_c (%)	
	PET	PBS	PET	PBS	PET	PBS
100:0	251	-	14.24	-	10.16	-
90:10	250	110	9.36	0.88	7.42	4.19
80:20	247	106	6.92	2.93	6.17	6.98
70:30	249	107	8.53	3.62	8.69	5.75
0:100	-	111	-	70.48	-	33.56

3.1.3 Thermogravimetric Analyzer (TGA)

Thermal stability of polymer blend was investigated by Thermogravimetric Analyzer. Fig. 2 showed onset temperature (T_{onset}) of PET and PBS at 416 ^{o}C and 357 ^{o}C, respectively. While the degradation temperatures (T_d) of PET and PBS were at 429 ^{o}C and 385 ^{o}C, respectively. It was found that T_{onset} and T_d of PET/PBS blends were between those of pure PET and pure PBS. Thermal stability of PET/PBS blends is decreased with increasing PBS content because PBS had lower heat stability than PET.

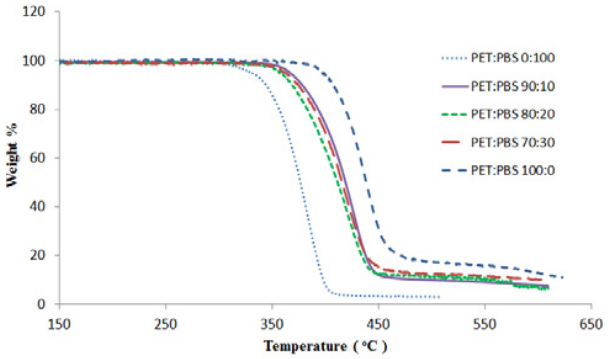


Fig. 2. TGA curves of PET/PBS blends in different ratio of PET and PBS

3.1.4 Tensile Testing

Tensile test was used to measure behavior of materials under tension. Table 3 showed Young's modulus (YM) and tensile strength (TS) of PET/PBS thin films. The Young's modulus and tensile strength of pure PBS thin film had the lowest value whereas the Young's modulus and tensile strength of pure PET thin film exhibited the highest value. The degree of crystallization of PET and PBS are 10.16% and 33.56% respectively (Table 2). The degree of crystallization of PBS does not influence the Young's modulus and the tensile strength of polymer blends. In addition, Young's modulus and tensile strength values of PET/PBS thin films for ratios of 90:10, 80:20 and 70:30 were between pure PET and pure PBS thin films. The Young's modulus and tensile strength values of PET/PBS thin film with ratio of 70:30 was therefore higher than the ones with ratio of 90:10 because of its higher amount of degree of crystallization of PET.

Table 3 showed percentage of elongation at break (EB) of PET/PBS thin films in the different ratio. It was observed that pure PBS thin film performed the most elongated behavior. The percentage of elongation at break value of pure PET thin film was the lowest value due to its benzene ring in main structure that caused the restriction

of polymer chains. The polymer blend in the ratio of our study displayed the correlative to the DSC result of incompatibility of the two polymers. Therefore, the low percentage elongation at break would be noticeable.

Table 3 Tensile properties of PET/PBS films

PET:PBS	YM (*MPa*)	TS (*MPa*)	EB (*%*)
100:0	2245 ± 105	47.1 ± 2.5	1.80 ± 0.15
90:10	1820 ± 61	27.7 ± 1.6	1.82 ± 0.24
80:20	1700 ± 55	23.9 ± 0.4	1.90 ± 0.26
70:30	2000 ± 98	28.0 ± 0.8	2.40 ± 0.28
0:100	372 ± 45	17.0 ± 1.1	15.21±2.11

3.2 Effect of TiO_2 and ZnO on thin film properties of PET/PBS blends

3.2.1 Clarity of PET/PBS films with TiO_2 and ZnO

In this section, thin film of PET/PBS blend at the ratio of 90:10 was chosen to study of influence of TiO_2 and ZnO on thin film properties of PET: PBS blends by consideration of film clarity.

The clarity of PET/PBS films with TiO_2 and ZnO content (each would be added with 1% and 2%wt) were shown in Fig. 3. PET/PBS films with TiO_2 and ZnO (Fig. 3b-e) illustrated more opacity than PET/PBS films (Fig. 3a) due to the naturally white powder of TiO_2 and ZnO. The addition of TiO_2 made film less transparency than ZnO because TiO_2 particles were physically smaller than ZnO particles as shown in Fig. 4. The more content of the white powder at 2%, the more opacity of the films would be obtained.

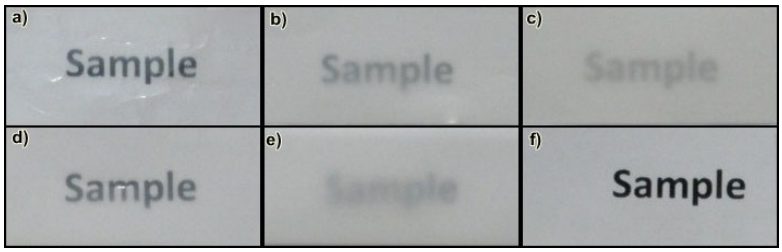


Fig. 3. Clarity of a) PET/PBS films with b) TiO_2 1%wt, c) TiO_2 2%wt, d) ZnO 1%wt and e) ZnO 2%wt compare with f) sample without film

3.2.2 Differential Scanning Calorimetry

Melting temperature (T_m) and % crystallinity (X_c) of PET/PBS blends at the ratio of 90:10 with TiO_2 and ZnO at 1 and 2% wt were shown in Table 4.

Table 4 Effect of TiO_2 and ZnO on melting temperature and % crystallinity of PET and PBS blends

Filler	T_m (℃)		Δ H (*J/g*)		X_c (*%*)	
Content	PET	PBS	PET	PBS	PET	PBS
0	250	110	9.36	0.88	7.42	4.19
TiO_2 1%	247	107	14.24	1.10	11.29	5.24
TiO_2 2%	248	107	4.77	0.12	3.78	0.57
ZnO 1%	248	106	13.43	0.52	10.65	2.48
ZnO 2%	247	107	9.42	0.42	7.47	2.00

At 1%wt of the thin film added with TiO_2 or ZnO, the percentage of crystallinity for PET and PBS on PET/PBS thin film with TiO_2 is higher than the film with ZnO. This might be the fact that TiO_2 particles are smaller than ZnO

particles as seen in Fig. 4. This could lead to a better dispersion and more effectiveness as the nucleating site. However, both of % crystallinity of PET and PBS significantly dropped when the addition of 2% wt of either TiO_2 or ZnO was taken place in PET/PBS blends. Because the higher amount (at 2%wt) of TiO_2 and ZnO tended to be easily aggregate. Particularly for TiO_2, the percentage of PET and PBS crystallinity drastically decreased at higher content of 2%. The aggregated TiO_2 is not only a factor to poor dispersion as evidenced by SEM in Fig. 5 but also

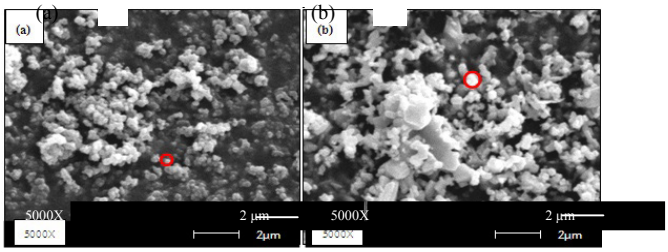


Fig. 4 SEM images of a) TiO_2 and b) ZnO particles

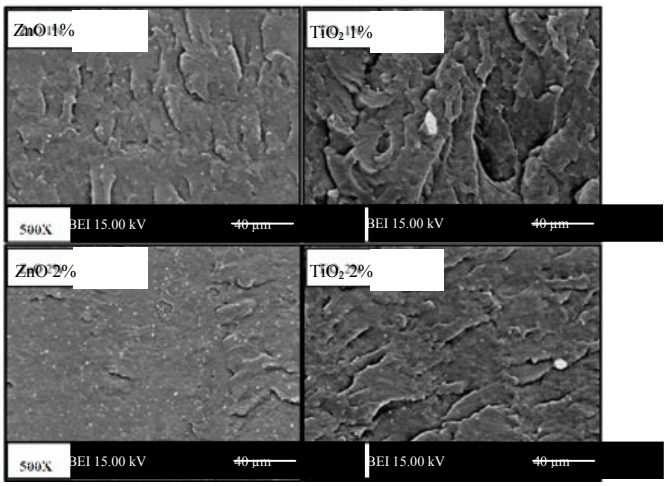


Fig. 5 SEM images of PET/PBS blends with TiO_2 and ZnO at 1% and 2% wt

make itself less effective as the nucleating agent. Moreover, it was found that addition of either TiO_2 or ZnO had no influence on melting temperature of PET/PBS thin films.

3.2.3 Thermogravimetric Analyzer

The influence of TiO_2 and ZnO on thermal stability of PET/PBS blends were graphically shown in Fig. 6. The single stage in the thermal degradation occurred for the case of PET/PBS blends with TiO_2 at around 370-450 ^oC. The decomposition temperature of PET/PBS blend is 425 ^oC, and that of PET/PBS blends with TiO_2 1% and 2% are 425^oC and 429 ^oC, respectively. This indicated that the addition of TiO_2 2% wt could increase heat stability for polymer blends due to high thermal stability of TiO_2. It could absorb heat that make polymer blends withstand heat up to higher temperature. However, addition of TiO_2 at 1% wt could not improve heat stability of PET/PBS blends.

Considering the effect of ZnO in Fig. 6, thermogravimetric diagram was performed for the PET/PBS blends with ZnO 1% and 2% wt which resulted in two stages decomposition. The first stage from 340-360°C was due to the degradation of 10% of PBS. The second stage was related to the degradation of PET at the range of 360-440 ^oC. PET/PBS blends with higher amount of 2% ZnO showed the onset temperature for thermal degradation at lower temperature. ZnO would be able to form free oxygen and oxygen vacancies in the lattice induced by thermal energy and took place in the PBS degradation process.

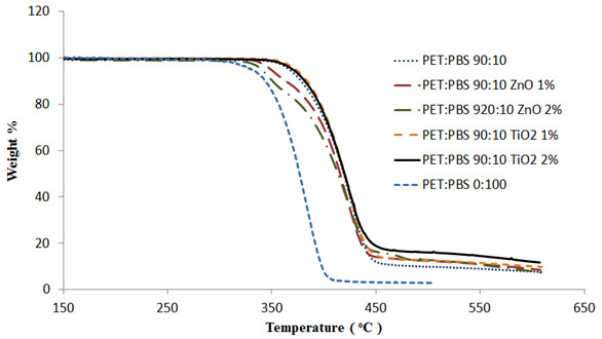


Fig. 6 TGA curves of PET/PBS blends with TiO_2 and ZnO at 1% and 2%wt

3.2.4 Tensile Properties

Table 5 illustrated tensile properties such as Young's modulus (YM), tensile strength (TS) and percentage of elongation (EB) of PET/PBS thin films with either TiO_2 or ZnO. Young's modulus value slightly increased by incorporating of TiO_2 and ZnO powder because of their high stiffness of TiO_2 and ZnO particles. However, tensile strength were not affected by the addition of TiO_2 and ZnO. Furthermore, the addition of TiO_2 could slightly increase percentage elongation at break value in comparison with PET/PBS blends thin film. The higher contents of TiO_2 at 2% would have no impact to percentage elongation at break. However, it was evident that the addition of ZnO had no influence on percentage elongation at break value of PET/PBS blends thin film.

Table 5 Tensile properties of PET/PBS thin films with TiO_2 and ZnO at 1% and 2%wt

Filler	YM (*MPa*)	TS (*MPa*)	EB (*%*)
0	1820 ± 61	27.0 ± 1.6	1.78 ± 0.24
TiO_2 1%	1882 ± 54	27.7 ± 2.6	2.10 ± 0.18
TiO_2 2%	1906 ± 82	27.1 ± 2.0	2.10 ± 0.18
ZnO 1%	1966 ± 67	27.3 ± 2.4	1.90 ± 0.28
ZnO 2%	1862 ± 96	27.6 ± 2.3	1.89 ± 0.22

3.2.5 Antibacterial activity against E.coli and S.aureus

In this study, the relative antibacterial activity of thin film of PET/PBS blend at the ratio of 90:10 with TiO_2 or ZnO at 1 and 2% wt were studied by dynamic shake flask test method. *E.coli* is gram-negative bacteria while *S.aureus* is gram-positive bacteria. Both *E.coli* and *S.aureus* had different components on their cell walls. Reactive oxygen species were created by chemical mechanism (Fig. 7) to execute the antibacterial activity of *E.coli* and *S.aureus* in the presence of TiO_2 and ZnO [5, 13]. Such oxygen species released from the surface of ZnO by both UV and visible light activation could cause mortality to those microorganisms. Electron-hole pairs (e^- h^+) can be generated and enable to separate water molecule into $^{\cdot}OH$ and H^+. Dissolved oxygen molecules are converted to superoxide radical anions ($^{\cdot}O_2^-$), which could react with H^+ to generate ($HO_2^{\cdot}$) radicals. Then the subsequent collision with electrons would generate hydrogen peroxide anions (HO_2^-) and in the presence of hydrogen ions to generate molecules of H_2O_2. And such the strong chemical as hydrogen peroxide (H_2O_2) could migrate through the cell membrane and cause fatality to those bacteria [13].

$$ZnO + h\nu \longrightarrow e^- + h^+$$
$$h^+ + H_2O \longrightarrow {}^{\cdot}OH + H^+$$
$$e^- + O_2 \longrightarrow {}^{\cdot}O_2^-$$
$${}^{\cdot}O_2^- + H^+ \longrightarrow HO_2^{\cdot}$$
$$HO_2^{\cdot} + H^+ + e^- \longrightarrow H_2O_2$$

Fig. 7 Mechanism of reactive oxygen species (ROS).

The filler content of either TiO_2 or ZnO at 1 and 2%wt was taken into consideration for our study. It was found that PET/PBS thin film with TiO_2 and ZnO could exhibit inhibitory effect for *E.coli* and *S.aureus* as seen in Table 6. At any given filler type and content, percentage of antibacterial ratio for *S.aureus* bacteria was higher than *E.coil* bacteria. This indicated that the antibacterial effect of PET/PBS film with both TiO_2 and ZnO for *E.coli* was weaker than that for *S.aureus.* Coherently, the percentage of antibacterial ratio of PU film with 1%wt of modified ZnO was at 13% for *E. coli* and 42% for *S. aureus* [14]. As per our SEM images (Fig. 4), the comparison between TiO_2 and ZnO particles were made. Apparently, TiO_2 had smaller particles than ZnO particles**.** Smaller particle size exhibited the enhanced surface activity of antibacterial agents because of large surface area to volume ratio. Therefore, TiO_2 particles were more effective for energy receptibility on their relatively larger surface area. Upon the exposure of UV light, PET/PBS blend film with TiO_2 could generate more hydrogen peroxide and thus more effective to antibacteria activity of both *E. coli* and *S. Aureus* than the one with ZnO as seen in Table 6.

Table 6 Antimicrobial ratio against E.coli and S.aureus

Filler Content	Antibacterial ratio (%)	
	S. aureus	*E. coli*
0	0	0
TiO_2 1%	54.82	27.56
TiO_2 2%	77.96	38.97
ZnO 1%	51.12	23.33
ZnO 2%	56.56	32.31

Considering the higher content namely at 2%wt for both fillers, PET/PBS thin film could illustrate better antibacterial effect than the one at 1%wt. In conclusion, the type of filler as well as quantity and particle size of the inorganic material added to thin film showed significant contribution on the inhibitory effect of microorganisms.

4. Conclusions

In this research, the ratio of PET and PBS of 90:10 was found to be the most clarity. The more PBS content in the blends it was, the more haziness of the thin film it would be. The compatibility of PET and PBS blends was investigated by differential scanning calorimeter and found that the melting temperature of PET/PBS blends were completely separated due to immiscibility of polymer blend. Thermal stability was investigated by thermogravimetric analyzer. A noticeable drop of the degradation temperature of PET/PBS blends was observed with the addition of PBS at higher content. Mechanical properties of PET/PBS blends thin film were studied by universal tensile testing and showed the decrement of tensile strength, young's modulus and percentage elongation at break compared with pure PET thin film.

The addition of TiO_2 made film less transparency than ZnO because TiO_2 particles were physically smaller than ZnO particles. In addition, we found that TiO_2 increased thermal stability of PET/PBS blends. The addition of TiO_2 and ZnO would not significantly increase tensile strength, young's modulus and percentage elongation at break. The result of antibacterial testing of PET/PBS blends thin film with TiO_2 exhibited better performance of inhibiting *E.coli* and *S.aureus* bacteria than the one with ZnO.

Acknowledgement

This research was supported by Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University. The authors would like to thank Labtech engineering Co., Ltd. for twin screw extruder and flat film extrusion machines.

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