The Degradation Behavior of TPS/LDPE Blend Mulch Films Prepared with Different Pro-oxidants

Farklı Pro-oksidanlar ile Üretilmiş TPN/AYPE Karışım Malç Filmlerin Bozunma Davranışı

Research Article

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ABSTRACT

Low density polyethylene (LDPE) was blended with thermoplastic starch (TPS) by twin screw compounder to prepare partially degradable mulch films. In the present study, ferric stearate and manganese(II) stearate were used as pro-oxidant and the effect of different pro-oxidants on the degradation of the blends were investigated. The blended mulch films were buried in soil inoculated with *Coriolus versicolor* (L.) Quél. for 180 days for the degradation. The chemical structures of the films were evaluated by FTIR spectroscopy and the weight loss of all samples was measured before and after soil burial treatment. The effects of two different pro-oxidants on thermal and tensile properties of blends were determined by TGA and mechanical analysis. A synergetic effect between ferric stearate and citric acid was observed. Using both in the blends resulted in higher thermal stability of TPS in the blends. Significant improvement of the mechanical properties was also observed. However, when manganese(II) stearate used together with citric acid a decrease in the mechanical properties was observed compared blends with stearic acid.

Key Words
LDPE, thermoplastic starch, pro-oxidant, ferric stearate, manganese(II) stearate.

ÖZ

Kısmen bozunabilen malç filmleri hazırlamak için az yoğunluklu polietilen (AYPE), termoplastik nişasta (TPN) ile çift vidalı ekstruder yardımıyla karıştırıldı. Bu çalışmada, demir(III) stearat ve manganez(II) stearat pro-oksidan olarak kullanılmışve farklı pro-oksidanların karışımların bozunması üzerindeki etkisi incelenmiştir. Malç filmler *Coriolus versicolor* (L.) Quel ile aşılanmış toprağa gömülerek 180 gün boyunca degrede edilmiştir. Filmlerin kimyasal yapıları FTIR spektroskopisi ile belirlenmiş ve tüm numunelerin ağırlık kaybı toprakta bozunma öncesi ve sonrası ölçülmüştür. İki farklı pro-oksidanın, malç karışımların ısıl ve germe özellikleri üzerine etkisi TGA ve mekanik analiz ile tespit edilmiştir. Demir (III) stearat ve sitrik asitin birlikte kullanılmasıyla sinerjik bir etki gözlenmiştir. Her ikisinin birlikte kullanıldığı karışımlarda TPN'nin yüksek ısıl kararlılık gösterdiği bulunmuştur. Ayrıca, mekanik özelliklerinde belirgin düzelme gözlenmiştir. Bununla birlikte, manganez(II) stearat sitrik asit ile birlikte kullanıldığında stearik asitli karışımlarına kıyasla daha zayıf mekanik özellikler göstermiştir.

Anahtar Kelimeler
AYPE, termoplastik nişasta, pro-oksidan, demir stearat, manganez(II) stearat.

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INTRODUCTION

Low density polyethylene (LDPE) and its copolymers have been widely used in agricultural purposes such as greenhouses, low tunnel and mulching films. Mulching is the practice of covering the top of the soil with a plastic film as has been done by leaves or straw in nature. The mulch films are mostly made from LDPE and the mulch films which are spread over large areas and then removed from the field after the harvest [1]. When the film was left in the soil do not degrade and stay in the soil as a macro pollutants [2]. Degradable mulch films may offer an economical alternative and become a solution for ultimate disposal problem. Starch has potential to provide a solution to environmental concerns, the mixing of starch with the matrix of LDPE, can cause the degradation of LDPE partially. The native starch is converted to the thermoplastic starch (TPS) by using glycerol and water for better distribution in LDPE [3]. Blending TPS with LDPE enhances the accessibility of the LDPE to oxygen and microorganisms. To initiate and propagate radical degradation, the special additives called pro-oxidants can be added to the blend system. Pro-oxidants are transition metal (Fe, Co, Mn) complexes of stearate or acetyl acetonate ligands and they accelerate the photo- or thermo-oxidation. After the decomposition of peroxides, radical chain reactions start, as a result chains are shortened and molecular weight was decreased [4]. Many researchers suggest fungi inoculation in soil to accelerate this degradation process of polyethylene/starch blends. Fungi play vital role in biomass degradation in nature. Orhan and Büyükgüngör evaluated the biodegradation of LDPE/starch blend films in *Phanerochaete chrysosporium* (ATCC 34541) inoculated soil for 6 months and they showed that inoculation of soil with *P. chrysosporium* enhances the biodegradation of LDPE/starch blend [5]. The biodegradability of maleic anhydride grafted LLDPE/starch blends have been investigated in mixed fungi inoculum. Blends were placed in sterile petri dishes containing spores of *Aspergillus niger*, *Penicilliurn funiculosum*, *Chaetomium globosum*, *Gliocladiurn virens* and *Pullularia pullulans* [6].

In our previous study, cobalt(II)acetyl acetonate pro-oxidant added TPS/LDPE blends were degraded in two different fungi (*Coriolus versicolor* (L.) Quél. and *Postia placenta* (Fr.) M.J. Larsen & Lombard) inoculated soil for 180 days [7]. It was found that the efficieny of *Coriolus versicolor* in weight loss was better than *Postia placenta* and *Coriolus versicolor* containing soil environment had a profound effect on the decrease in tensile strength of films. In this study, the soil was inoculated with one type of fungi (*Coriolus versicolor* (L.) Quél) and two different types of pro-oxidants were used. The effects of ferric stearate and manganese(II) stearate pro-oxidants on degradation of TPS/LDPE blends were compared by weight loss, FTIR spectroscopy, thermogravimetric analysis and mechanical tests.

EXPERIMENTAL

Materials

LDPE (F2-12 grade) was supplied by Turkish Petrochemical Industry, PETKIM. The wheat starch (Sigma-Aldrich), ferric stearate (MP Biomedicals) and manganese(II) stearate (90%, Santa Cruz Chemicals) were used as received. The glycerol of reagent grade with purity 99.5%, the compatibilizers stearic acid with purity 95% and citric acid with purity 99% were obtained from Sigma-Aldrich and they were all used as received.

Sample Preparation

TPS/LDPE blend films were prepared as reported earlier [7]. In brief, to prepare thermoplastic starch (TPS), the 48% wheat starch, 33% glycerol and 19% deionized water by weight were mixed and heated for 8-10 minutes at 70-75°C and then dried at 60°C in vacuum oven for 48 hours. After the TPS was prepared, LDPE, ferric stearate and manganese(II) stearate pro-oxidants, citric acid and stearic acid compatibilizers were blended. The compositions contain 20%, 30%, and 40% of TPS by weight according to total weight of LDPE and TPS. The amount of pro-oxidant (ferric stearate or manganese(II) stearate) in each composition equals to 0.5% and the amount of compatibilizer (stearic acid or citric acid) equals to 2% by weight according to total weight of LDPE and TPS. The compositions of different blends prepared in this study are shown in Table 1.

Table 1. The recipe of materials used for blends prepared by extrusion.

Code	TPS+LDPE		Compatibilizer		Pro-oxidant	Code	TPS+LDPE		Compatibil.		Pro-oxidant
	TPS (%)	LDPE (%)	Citric Acid (%)	Stearic Acid (%)	Ferric stearate		TPS (%)	LDPE (%)	Citric acid (%)	Stearic acid (%)	Manganese (II) stearate
W20	20	80	-	-	-	W20	20	80	-	-	-
W20F	20	80	-	-	0.5%	W20M	20	80	-	-	0.5%
W20Fca	20	80	2	-	0.5%	W20Mca	20	80	2	-	0.5%
W20Fsa	20	80	-	2	0.5%	W20Msa	20	80	-	2	0.5%
W30	30	70	-	-	-	W30	30	70	-	-	-
W30F	30	70	-	-	0.5%	W30M	30	70	-	-	0.5%
W30Fca	30	70	2	-	0.5%	W30Mca	30	70	2	-	0.5%
W30Fsa	30	70	-	2	0.5%	W30Msa	30	70	-	2	0.5%
W40	40	60	-	-	-	W40	40	60	-	-	-
W40F	40	60	-	-	0.5%	W40M	40	60	-	-	0.5%
W40Fca	40	60	2	-	0.5%	W40Mca	40	60	2	-	0.5%
W40Fsa	40	60	-	2	0.5%	W40Msa	40	60	-	2	0.5%

To prevent confusion about types of blends, they are coded as e.g. W40Fsa, where "W" represents thermoplastic wheat starch, the number "40" written represents the 40% of starch by weight, the "F" represents the Ferric stearate and the "sa" represents the stearic acid (and also "ca" represents the citric acid). A control group is composed of three samples, containing 20%, 30% and 40% of TPS without pro–oxidants and compatibilizers in order to see the effects of these chemicals' influence on mechanical properties and degradation rates of the samples. Blends were prepared by DSMxplore Netherlands, micro 15cc twin screw compounder. The temperatures of the three zones were 145°C - 150°C - 145°C. The screw speed was 100 rpm and the die temperature was 138°C. The blends were compression moulded in Pneumo Hydraulic Press at 150°C for 4 minutes and the films prepared are stored at 4°C for further investigation.

Characterization

FTIR analyses were performed with BRUKER VERTEX 70 model FTIR Spectroscopy for the chemical characterization of the blends. FTIR spectra of all samples were recorded by using ATR technique with a resolution of 16 cm^{-1} and number of 32 scans per sample in a spectral range of 4000–600 cm^{-1}. The FTIR spectra of the samples were recorded before and after soil burial treatment. Perkin-Elmer, Pyris model Thermo gravimetric analyser was used to characterize the degradation behavior of samples. The TGA analyses of samples were carried out in the nitrogen atmosphere at heating rate of 10°C/ min from 25°C up to 600°C. Tensile strength and percentage strain were measured by LLYOD LR 5K at room temperature with crosshead speed of 50 mm/min. The six specimens were tested for each blend. The thicknesses of the films were 100 microns. The mechanical properties of the films were measured before and after soil burial.

Soil Preparation and Inoculation

The soil was collected from farmland soil on Yeşilyurt/Muğla. The soil was sieved (<2 mm) and stored at 4°C sealed in plastic container. The *Coriolus versicolor* (L.) Quél. (COV-1030- from Wood Research Institute, Kyoto University) fungi which were maintained through periodic transfer at 4°C on petri dishes containing 20 g malt extract and 15 g agar (both from Merck) per one liter of water. Freshly prepared agar plates were inoculated with a 1-cm diameter plug of *C.versicolor*, taken from the edge of an actively growing colony and incubated at 27°C until the plates were sufficiently covered with mycelium. Incubation were carried out 27°C in the dark by pre inoculating 300 ml of potato dextrose broth (24 g/l) containing 0.5% yeast extract in 500 ml shaken flasks with a 4x1-cm diameter plug of the *C.versicolor* mycelia. 50 ml of a 5-day-old culture were transferred in 1 liter flasks containing 450 ml of broth. The cultures were incubated in the dark at 27°C. After 10–12 day of incubation, the fungal cultures were ready to be inoculated aseptically in soil.

Soil Burial

The plastic box having approximate dimensions 25cmx19cmx33cm were filled with the sieved soil. The sterile blended film samples were cut into pieces with dimensions 6x7cm and buried in fungi inoculated or uninoculated soil at the depth of 8 cm and stored in a sterilized chamber at 24°C and 40% relative humidity. The soil was fed with 3K basal mineral solution containing KH_2PO_4, 0.7; K_2HPO_4, 0.7; $MgSO_4.7H_2O$, 0.7; NH_4NO_3, 1.0; NaCl, 0.005; $MnSO_4.7H_2O$, 0.001; $ZnSO_4.7H_2O$, 0.002; $FeSO_4$, 0.002; in terms of gram per liter, at pH 6.5 [5]. The specimens were taken from the soil and the soil was removed for the weight loss measurements. Weight loss of the specimens with time was used to measure the degradation rate in the soil. Before burial and 180 days after the burial, the weights of the specimens were measured and recorded.

Weight Loss

The blend films were weighed by analytical balance before degradation and after soil treatment, samples were recovered, washed, dried and weighed and the weight loss was determined by using the below Equation 1;

$$Percentage\ Weight\ Loss = \frac{(Weight\ initial - Weight\ final)}{Weight\ initial} x100$$

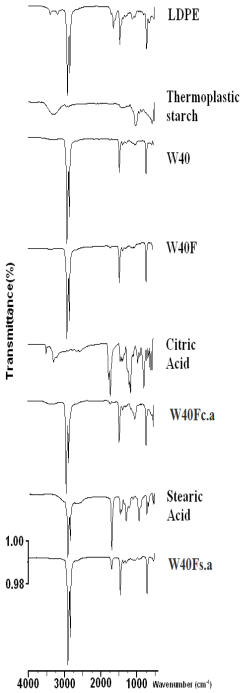

Figure 1. FTIR spectra of W40F, W40Fca and W40Fsa.

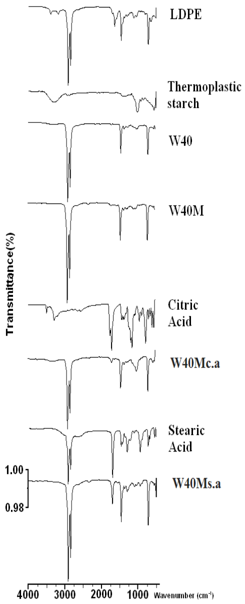

Figure 2. FTIR spectra of W40M,W40Mca and W40Msa.

RESULTS and DISCUSSION

FTIR Analysis Before Soil Burial Treatment

The chemical structures of the films were identified by ATR-FTIR spectroscopy. The FTIR spectra of 40% of TPS containing blends are given in Figure 1 and Figure 2 for ferric stearate and manganese(II) stearate pro-oxidants, respectively. In the spectrum of the LDPE, the characteristic $-CH_2$ asymmetric and symmetric stretching can be seen around 2918 and 2840 cm^{-1}, respectively. The $-CH_2$ bending and $-CH_2$ rocking gave peaks at around 1461-1301cm^{-1} and 712 cm^{-1}, respectively. The characteristic bands for

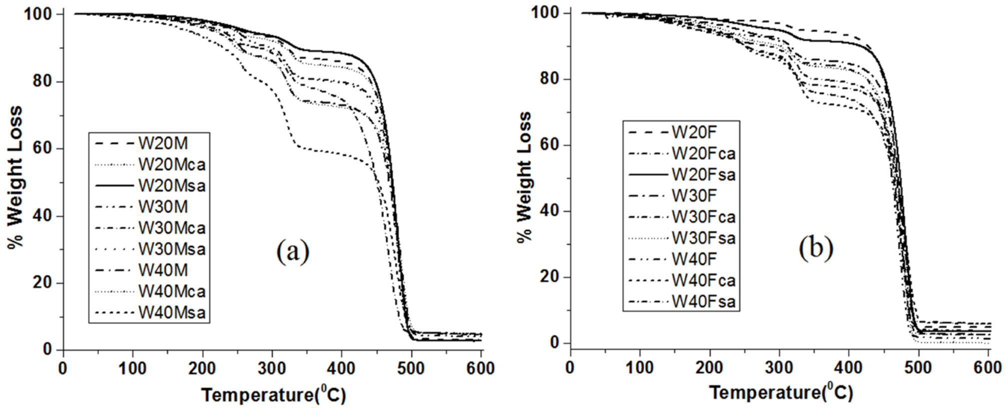

Figure 3. TGA curves of the blends before soil burial, a) manganese(II) stearate group, b) ferric stearate group.

thermoplastic starch can also be seen in Figure 1 and Figure 2 A broad O-H stretching absorbance in the 3289 cm^{-1} region and strong C-O stretching peak at the 1020 cm^{-1} were identified. All the characteristic peaks of LDPE (2918, 2844, 1464 and 719 cm^{-1}) and starch (3309 cm^{-1} and 1026 cm^{-1}) units have appeared in the W40 blend. The citric acid and stearic acid were added as compatibilizer and the characteristic –C=O group of stearic acid was seen at 1702 cm^{-1} (Figure 1) for W40Fsa blend. The peak at 1710 cm^{-1} was related to the carbonyl group of citric acid in the spectrum of W40Mca (Figure 2). Prooxidants accelerates the photo and thermooxidation of the polymers, so consequent polymer chain cleavage makes the polymer more susceptible to biodegradation. Thus, ferric stearate and manganese(II) stearate were added to the LDPE/starch blends and the spectra comprising a blend of LDPE, starch ferric stearate and manganese(II) stearate can be seen in Figure W40F and Figure W40M, respectively.

Thermogravimetric Analysis Before Soil Burial Treatment

The degradation temperatures and the weight loss patterns during thermal degradation of neat LDPE and neat TPS were performed in our previous study [7]. The TGA curves revealed that, pure LDPE indicates one stage of degradation (490°C), whereas thermoplastic starch showed three decomposition stages (100°C, 210°C and 321°C). The first stage (at 100°C) corresponds to the absorbed water, the second one (210°C) attributed to the glycerol evaporation and the last degradation stage (321°C) was observed due to the decomposition of starch. In the present study, the TGA curves of manganese (II) stearate group and ferric stearate group are displayed Figures 3a and 3b, respectively. The decomposition

Table 2. The decomposition temperatures for the blends before soil burial treatment.

Code of the sample	Evaporation Temperature of Glycerol (°C)	Decompo. Temperature of Starch (°C)	Decompo. Temperature of LDPE (°C)	Code of the sample	Evapor. Temp. of glycerol (°C)	Decomp. Temp. of starch (°C)	Decomp. Temp. of LDPE (°C)
W20M	259	322	481	W20F	-	319	478
W20Mca	245	326	481	W20Fca	-	328	479
W20Msa	261	324	481	W20Fsa	-	319	479
W30M	259	321	481	W30F	247	319	479
W30Mca	241	326	473	W30Fca	242	328	477
W30Msa	259	325	481	W30Fsa	247	319	477
W40M	251	321	481	W40F	-	327	475
W40Mca	238	321	481	W40Fca	249	330	481
W40Msa	254	321	477	W40Fsa	251	321	481

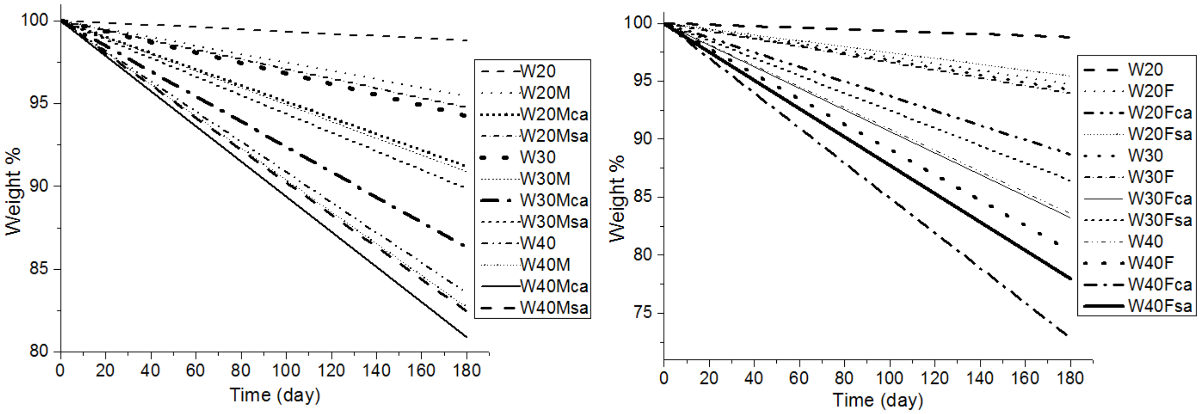

Figure 4. The percentage weight of the blend films versus time, a) manganese(II) stearate group, b) ferric stearate group.

temperatures of both prooxidants are given in the Table 2. Four well defined weight loss stages were observed for all blends, except for the W20F, W20Fca and W20Fsa blends. For these 20% of TPS loaded ferric stearate group, three well defined weight loss stages can be observed and the mass loss which was attributed to evaporation of glycerol was not observed (Table 2). The TGA thermograms of both prooxidant groups showed that the decomposition temperatures of TPS and LDPE were changed in blends. The starch was degraded at around 321-326°C for manganese (II) stearate group and at 319-330°C for ferric stearate group. These values are higher than the degradation temperature of neat starch, which was 321°C. Besides that, the decomposition temperature of the neat LDPE was lowered from 490°C to 473-481°C for the both prooxidant group blends. It was also found that the citric acid increased the thermal stability of starch when compared with the stearic acid. In addition to that, citric acid lowered the evaporation temperature of glycerol since the citric acid can form stronger hydrogen bonds with starch than glycerol and then glycerol became free.

When the thermal stabilities of the starch in the blends are compared, it is obvious that prooxidants play an important role in this case. When ferric stearate used together with citric acid, a significant increase in the thermal stability of the starch was observed. Addition of manganese (II) stearate had a moderate effect on the thermal stability of starch in the blends. When stearic acid is used together with this prooxidant a slight increase in the thermal stability of the starch in the blends. This effect was a result of high similarity between the structures of stearic acid and manganese(II) stearate.

Soil Burial Treatment

The blend films were degraded in *Coriolus versicolor* inoculated soil for 180 days. After the soil burial, the characterizations were carried out in terms of their gravimetric (weight loss), thermogravimetric and mechanical properties. The chemical structures of TPS/LDPE blend films were also characterized by FTIR spectroscopy after the degradation.

Weight Loss Records for the Blends

The percentage weights of the films are displayed in Figure 4a and Figure 4b, which corresponds to the manganese (II) stearate group and ferric stearate group, respectively. The graphs were plotted according to the formula given in Equation1. The degradation of manganese (II) stearate pro-oxidant added TPS/LDPE blend films in *Coriolus versicolor* inoculated soil was compared with the degradation of ferric stearate pro-oxidant added TPS/LDPE blend films. For both pro-oxidant groups, it is evident that increasing starch content resulted in increasing weight loss. In high TPS containing blends, a very small part of TPS was surrounded by LDPE and the dispersed parts of TPS became more interconnected and continuous. Hence, for high loadings for starch more possible substrates were created for the microorganism attacks. The weight loss of the films with ferric stearate pro-oxidant were higher than that of the manganese (II) stearate group. In ferric stearate group, for high loadings of starch, the weight loss

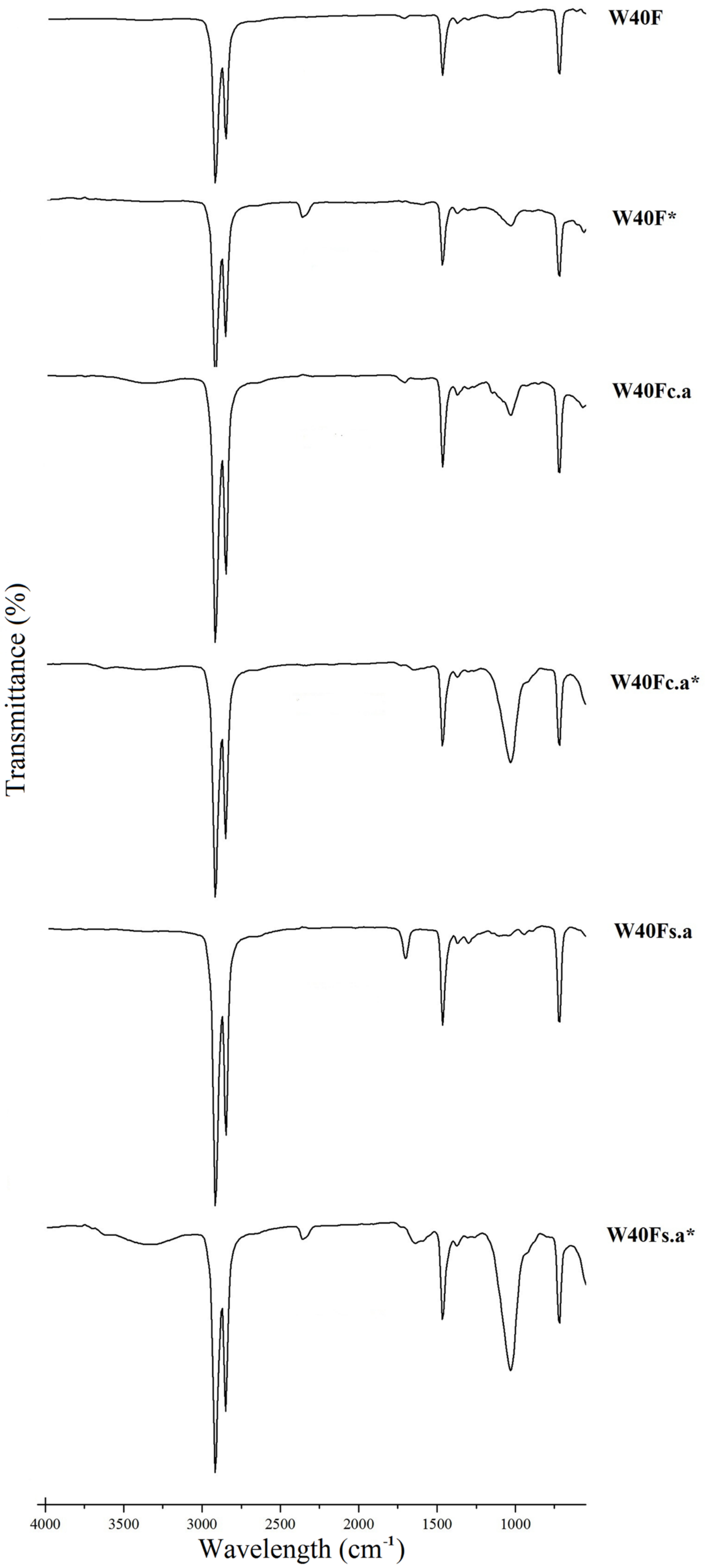

Figure 5. FTIR spectra of the ferric stearate group films with 40% TPS loadings before and after soil burial treatment,* denotes after degradation.

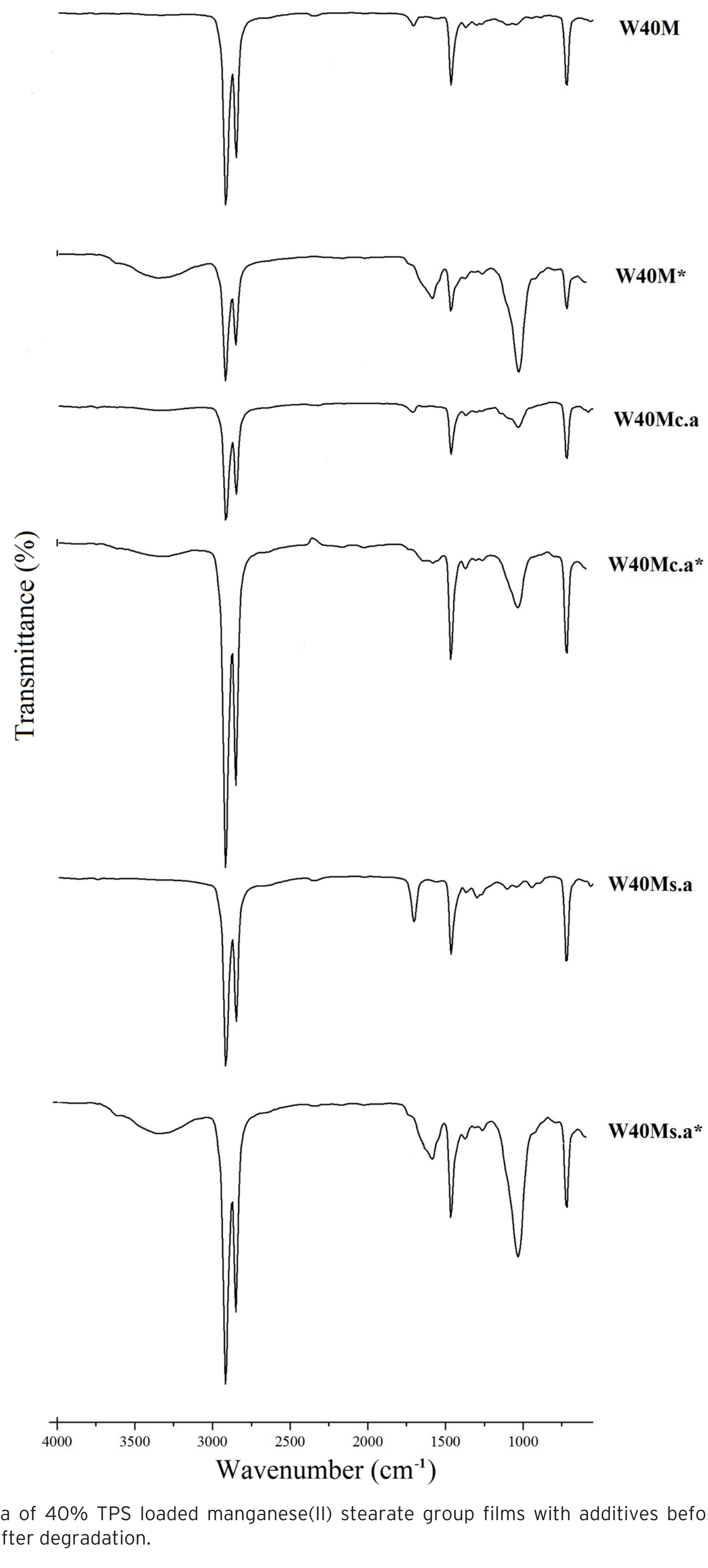

Figure 6. FTIR spectra of 40% TPS loaded manganese(II) stearate group films with additives before and after soil burial treatment, * denotes after degradation.

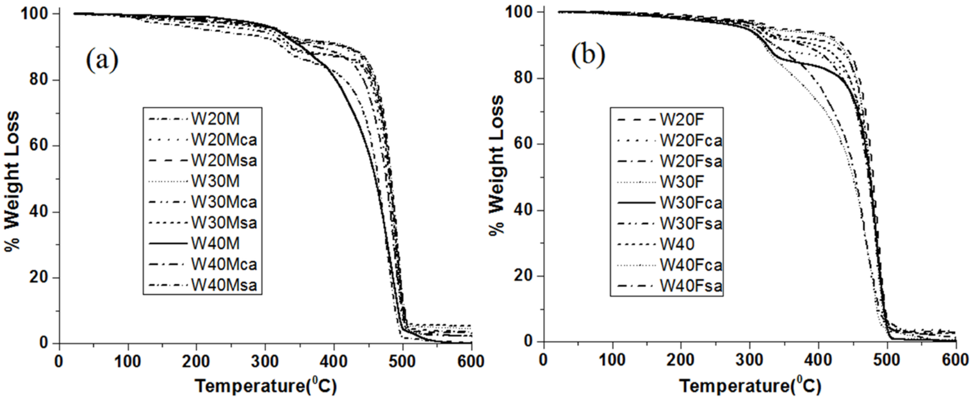

Figure 7. TGA curves of the blends after soil burial, a) manganese(II) stearate, b) ferric stearate groups.

for W40F, W40Fca and W40Fsa were 19.6%, 27.1 % and 22.0% of their initial weight, respectively. Meanwhile, the weight loss for W40M, W40Mca and W40Msa were 17.3%, 19.1% and 17.6% of their initial weight. The samples with ferric stearate showed higher weight loss compared to the samples with manganese (II) stearate pro-oxidant and this can be attributed to the different oxidation states of the central metals. The central iron metal has +3 oxidation state in ferric stearate, whereas the manganese central metal has +2 oxidation state in manganese (II) stearate. A higher oxidation state of iron (Fe^{3+}) may cause the decomposition of hydroperoxides subsequently leads to the formation of carboxylic groups and these groups are very sensitive to the photo and thermal degradations. Some of the studies showed that the oxidation state of central metal play an important role in photo- or thermooxidative degradations of LDPE films [8,9]. It was also found that the highest weight loss was observed in the blends with citric acid. Since citric acid caused badly acidolysis of starch, deteriorated the rigid structured of starch and eased the consumption by the micro-organisms, high amounts of degradation was evidenced for the samples with citric acid.

FTIR Analysis After Soil Burial Treatment

Figures 5 and 6 show the changes in the FTIR spectra of both ferric stearate and manganese (II) stearate pro-oxidant groups after degradation. The most significant changes were observed in the –OH stretching related broad band around

Table 3. Decomposition temperatures of blend films with manganese(II) stearate pro-oxidant before and after soil burial treatment.

Code of the sample	Evaporation temperature of glycerol (°C)		Degradation temperature of wheat starch (°C)		Degradation temperature of LDPE (°C)	
	Before soil burial	After soil burial	Before soil burial	After soil burial	Before soil burial	After soil burial
W20M	259	-	322	326	481	479
W20Mca	246	-	326	330	481	486
W20Msa	261	-	324	326	481	490
W30M	258	-	321	328	481	489
W30Mca	241	-	326	329	473	490
W30Msa	258	-	325	329	481	489
W40M	251	-	321	324	481	486
W40Mca	238	-	321	326	481	489
W40Msa	254	-	321	326	477	489

Table 4. Decomposition temperatures of blend films with ferric stearate pro-oxidant before and after soil burial treatment.

Code of the sample	Evaporation temperature of glycerol (°C)		Degradation temperature of wheat starch (°C)		Degradation temperature of LDPE (°C)	
	Before soil burial	After soil burial	Before soil burial	After soil burial	Before soil burial	After soil burial
W20F	-	-	319	323	478	486
W20Fca	-	-	328	323	479	484
W20Fsa	-	-	319	319	479	468
W30F	247	-	319	321	479	484
W30Fca	242	-	328	326	477	486
W30Fsa	247	-	319	326	477	484
W40F	-	-	327	323	475	484
W40Fca	249	-	330	324	481	479
W40Fsa	251	-	321	319	481	484

3300 cm^{-1} for both citric acid and stearic acid blends. After 180 days soil burial treatment, with the removal of these compatibilizers by *Coriolus versicolor* fungi, more –OH group became free, and stronger peaks were observed during the degradation period. The characteristics -C=O peaks around 1700 cm^{-1} for these compatibilizers were not observed after soil burial. FTIR spectra of the samples recovered from soil indicate that the thermoplastic starch is preferentially removed, leaving the LDPE matrix. Hence, the LDPE related characteristic peaks around 2916, 2844, 1464, 1032 and 717 cm^{-1} can be seen after the blend films degradation.

Thermogravimetric Analysis After Soil Burial Treatment

The TGA curves of the manganese (II) stearate and ferric stearate pro-oxidant added films, which were recovered from *Coriolus versicolor* inoculated soil, are presented in Figure 7a and 7b, respectively. The degradation temperatures of both manganese and ferric group blends for before and after soil burial treatment are given in Tables 3 and Table 4, respectively.

Before degradation the main decomposition temperature of pure LDPE was around 490°C and the addition of TPS into the LDPE lowered the decomposition temperature for blends. However, after the soil burial treatment the degradation temperature of the LDPE mostly increased. The increment in degradation temperature of LDPE might be the reduction of starch content after degradation. Exposure to fungi inoculated soil degradation of blend films caused to loss of some of glycerol and starch and then, the thermal degradation of LDPE occurred in higher temperature range.

In manganese(II) stearate group, the degradation stage which corresponds to the evaporation of glycerol was not seen in all blends, since the glycerol in TPS was removed during soil burial treatment (Table 3). A similar thermal behavior was also observed for the ferric stearate group (Table 4). Additionally, after degradation when compare the two pro-oxidants, the thermal stabilities of the blends with ferric stearate were slightly lower than the blends with manganese(II) stearate. The shift of the degradation temperature of the LDPE in somewhat higher degrees was due to the phase compatibility between the TPS and LDPE [10,11].

Mechanical Properties of Blends Before and After Soil Burial Treatment

The effects of different compatibilizers and pro-oxidants in blend composition were evaluated by tensile tests. The mechanical properties of blends before and after soil burial treatment were given in Table 5. It is known that, fillers generally reduce

Table 5. Mechanical properties of the blend films before and after soil burial treatment.

Code of the sample	Tensile Strength (MPa)		Elongation at Break (%)		Code of the sample	Tensile Strength (MPa)		Elongation at Break (%)	
	Before soil burial	After soil burial	Before soil burial	After soil burial		Before soil burial	After soil burial	Before soil burial	After soil burial
LDPE	14.8	-	475.4	-	LDPE	14.8	-	475.4	-
W20	8.5	8.3	176.4	56.4	W20	8.5	8.3	176.4	56.4
W20M	9.0	7.4	195.1	57.1	W20F	8.1	6.4	183.2	71.7
W20Mca	7.1	6.4	103.5	26.1	W20Fca	7.7	7.4	262.9	29.9
W20Msa	8.5	9.3	248.1	30.9	W20Fsa	7.9	5.9	114.0	5.1
W30	6.9	6.4	65.2	34.6	W30	6.9	6.4	65.2	34.6
W30M	6.8	4.5	42.5	22.1	W30F	6.0	5.2	27.4	27.5
W30Mca	5.5	5.6	63.6	17.8	W30Fca	6.7	5.5	211.4	61.9
W30Msa	6.1	5.8	93.9	44.2	W30Fsa	5.2	6.3	26.9	6.6
W40	4.2	3.9	78.4	24.3	W40	4.2	3.9	78.4	24.3
W40M	6.1	5.7	29.1	8.4	W40F	5.3	5.2	23.7	14.7
W40Mca	4.5	3.1	24.0	15.5	W40Fca	5.3	5.4	82.3	22.6
W40Msa	5.6	3.1	22.2	4.1	W40Fsa	5.7	5.1	35.4	4.4

the tensile strength of matrix due to the poor filler-matrix interactions [8]. This is also valid for high TPS content blends (W20, W30 and W40). Starch cannot elongate as LDPE and so, the drop in elongation at break (EB) can be seen in high loading of TPS. The effects of citric acid and stearic acid compatibilizers were also compared before degradation. Especially, for the ferric stearate pro-oxidant group, the samples with citric acid elongated more than the samples with stearic acid (EB values 262.9, 211.4, 82.3 for W20Fca:W30Fca:W40Fca blends). W40 Fca was the one having the highest EB value among the 40% TPS containing films. Hence, citric acid provided better compatibility between TPS and LDPE phases (Table 5).

After the degradation of films in *Coriolus versicolor* inoculated soil, a comparison was done between the mechanical properties of manganese(II) stearate and ferric stearate groups. After degradation the mechanical properties of blends were deteriorated. The UTS and EB values decreased all through the manganese and ferric groups. However, this decay was seen more clearly for the ferric stearate pro-oxidant group. Faster decomposition occurred in ferric group which supported the weight loss results.

CONCLUSION

The effect of ferric stearate and manganese(II) stearate pro-oxidants on the degradation behavior of the TPS/LDPE blends were compared. The addition of the pro-oxidant in formulations of TPS/LDPE blends accelerated the degradation, particularly for ferric stearate pro-oxidant. Besides, using a small amount of citric acid compatibilizer together with ferric stearate caused to improved thermal stability of thermoplastic starch. During the degradation of blends in *Coriolus versicolor* inoculated soil, some of the TPS were consumed by fungi and so, the thermal degradation temperature of the remaining LDPE was increased. W40Fca blend showed the highest weight loss and the use of ferric stearate synergize with citric acid for increased weight loss. Because citric acid made starch partial acidolysis and reduced the size of the molecules as well as. After the soil burial, the mechanical properties of TPS/LDPE blends were very poor and the tensile strength and the elongation at break of the blends decreased greatly.

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