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The Effects of Citric Acid and Stearic Acid Compatibilizers on the Degradation Behavior of TPS/LDPE Blends for Mulch Films

Sitrik Asit ve Stearik Asit Uyumlaştırıcılarının TPN/AYPE Karışımı Malç Filmlerinin Bozunma Davranışı Üzerine Etkileri

Research Article

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ABSTRACT

Low density polyethylene (LDPE) is one of the most widely used plastic in agriculture and the degradability of mulch film is increased by introducing thermoplastic starch (TPS) into the LDPE. In this study, TPS/LDPE blends were prepared by twin screw compounder and TPS content is varied from 20 to 40%. To improve the interfacial adhesion and dispersion of TPS, citric acid and stearic acid were added as compatibilizers. To accelerate the degradation cobalt(II)acetylacetonate was used as a pro-oxidant. The blended mulch films were buried in soil inoculated with *Coriolus versicolor* (L.) Quél. and *Postia placenta* (Fr.) M.J. Larsen & Lombard for 180 days for the degradation. The changes in the chemical structures of the films were evaluated by FTIR spectroscopy before and after soil burial treatment. The weight loss of all samples achieved after 180 days of biodegradation and increasing starch content speeded up the weight loss. The effects of compatibilizers on thermal, tensile and morphological properties of blends were determined by TGA, mechanical and SEM analysis. When cobalt(II)acetylacetonate used together with citric acid, the thermal stability of TPS in films was enhanced. It was also found that samples with citric acid exhibited higher elongation at break values compared to films with stearic acid.

Key Words
LDPE, thermoplastic wheat starch, pro-oxidant, compatibilizer.

ÖZ

Az yoğunluklu polietilen (AYPE) tarımda yaygın olarak kullanılan plastiklerden biridir ve LDPE'den üretilen malç filmlerin bozunabilirliği termoplastik nişasta (TPN) eklenmesi ile artırılmaktadır. Bu çalışmada, bileşiminde %20'den %40'a kadar değişen oranlarda TPN bulunan TPN/LDPE karışımları çift vidalı karıştırıcı kullanılarak hazırlandı. TPN'nın ara yüzey yapışmasını geliştirmek ve matris içinde daha iyi dağılmasını sağlamak için, sitrik asit ve stearik asit uyumlulaştırıcıları ilave edildi. Bozunmayı hızlandırmak için kobalt(II) asetilasetonat pro-oksidan olarak kullanılmıştır. Malç filmler bozunması için 180 gün *Coriolus versicolor* (L.) Quél ve Postia plasenta (Fr.) M.J. Larsen & Lombard ile aşılanmış topraklara gömüldü. Filmlerin kimyasal yapılarındaki değişiklikler toprağa gömülmeden önce ve sonra FTIR spektroskopisi ile değerlendirildi. Tüm örneklerin ağırlık kaybı 180 gün biyobozunmadan sonra ölçüldü ve artan nişasta içeriği ile ağırlık kaybının hızlandığı görüldü. Uyumlaştırıcıların, malç karışımların ısıl, mekanik ve morfolojik özelliklerine etkileri TGA, mekanik testler ve SEM ile belirlenmiştir. Kobalt(II)asetilasetonat sitrik asit ile birlikte kullanıldığında TPN'nın filmlerdeki ısıl kararlılığı gelişmiştir. Aynı zamanda, sitrik asit ile hazırlanan filmler stearik asit ile kıyasla kopma anında daha yüksek uzama değerleri göstermiştir.

Anahtar Kelimeler
AYPE, termoplastik buğday nişastası, pro-oksidan, uyumlaştırıcı.

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INTRODUCTION

Polyethylene (PE), has been widely used as plastic bags, packaging materials and mulching films. Mulching is the practice of covering the top of the soil with low density polyethylene (LDPE) and its copolymers films. The main benefits of mulching are to control radiation and soil temperature, conservation of moisture, limit weed growth and insect infestation, improve crop yield [1,2]. The annual production of PE has increased to meet the growing demand. However, the hydrophobic character of PE causes the non-biodegradable properties under compost conditions. These plastics turn to solid waste after service life and leading to environmental and waste management problems. The environmental impact caused by persistent plastic waste has resulted in a research interest aiming to replace conventional non degradable polymers with degradable polymers [3,4]. To reduce the volume of plastic waste partially degradable mulch films can be obtained by blending with a biodegradable polymers and additives [5]. Starch is considered as one of the most important biodegradable materials due to its abundance, renewable, low cost and degradable natural biopolymer [6-9]. It is expected that the incorporation of a starch into the LDPE matrix results in an enhancement in degradability of the blend. However, blends of the higher starch contents result in a poor compatibility and interfacial adhesion due to the polar character of starch. The compatibility of starch with PE was improved by the transformation of the native starch into the thermoplastic starch (TPS) by adding plasticizers such as glycerol [10], water [11] and urea formamide [12]. The starch is gelatinized by the water and the action of heat. The hydrogen bonds between the polysaccharide chains are destroyed and the new hydrogen bonds are formed between the plasticizer and starch molecules. The addition of plasticizer causes to change the granular morphology and the crystalline/amorphous parts of starch. The TPS has a different mechanical behavior e.g. it becomes ductile and when it is mixed with other polymer it behaves like a polymer-polymer blend. When blended with starch, PE films degraded by the microbial attack in soil environment and this attack cause to void formation and disintegration. It is needed to obtain a controlled degradable polymer which degrades at a predictable rate. Thus, the controlling the degradation time is important for manufacturing of degradable polymer [13]. The chemical and photodegradation of these materials are increased by introducing some transition metal compounds containing special groups e.g. carbonyl, ester, ketone. The prooxidants contribute to the initiation and the propagation of radical reactions in photo and thermo-oxidative degradation [14-17].

The aim of this study was the formulation of partially biodegradable PE-TPS blends with high TPS contents. The effect of cobalt(II) acetylacetonate as a pro-oxidant on degradation was evaluated by different techniques. In order to increase interfacial adhesion and bring compatilibility between TPS and LDPE, introduction of compatibilizers to these blends was considered. Hence, to enhance the compatibility, chemicals containing a reactive functional group capable of hydrogen bonding or reacting group with starch hydroxyls were introduced. Citric acid and stearic acid were added to blends as compatibilizers and the effects of these compatibilizers on biodegradation and mechanical properties were also examined.

Experimental

Materials

LDPE (F2-12 grade) was supplied by Turkish Petrochemical Industry, PETKIM. The wheat starch and the cobalt (II) acetylacetonate with 97% purity were purchased from Sigma-Aldrich. 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

For the preparation of thermoplastic starch (TPS) the 48% wheat starch, 33% glycerol and 19% deionized water by weight were mixed for 10 minutes by mechanical stirrer at 900 rpm. The suspension was then left to stand for 1 hour to allow the starch granules to swell. The starch/glycerol/water mixture was heated for 8-10 minutes at 70-75°C and then it was dried at 60°C

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

Code	TPS+LDPE		Compatibilizer		Pro-oxidant
	TPS	LDPE	Citric acid	Stearic acid	Cobalt(II) acetylacetonate
W20	20%	80%	-	-	-
W20C	20%	80%	-	-	0.5%
W20Cca	20%	80%	2%	-	0.5%
W20Csa	20%	80%	-	2%	0.5%
W30	30%	70%	-	-	-
W30C	30%	70%	-	-	0.5%
W30Cca	30%	70%	2%	-	0.5%
W30Csa	30%	70%	-	2%	0.5%
W40	40%	60%	-	-	-
W40C	40%	60%	-	-	0.5%
W40Cca	40%	60%	2%	-	0.5%
W40Csa	40%	60%	-	2%	0.5%

in vacuum oven for 48 hours. After the TPS was prepared, polymer blend preparation was carried out with LPDE, cobalt(II)acetyl acetonate, citric acid and stearic acid. The compositions contain 20%, 30%, and 40% of TPS by weight according to total weight of LDPE and TPS. The amount of pro-oxidant cobalt (II) acetyl acetonate) in each composition equals to 0.5% according to total weight LDPE and TPS. Selected compositions contain 2% of compatibilizers (stearic acid or citric acid) by weight according to total weight of LDPE and TPS. The compositions of different blends prepared in this study are shown in Table 1.

To prevent confusion about types of blends, they are coded as e.g. W30Cs.a, where "W" represents thermoplastic wheat starch, the number "30" written represents the 30% of starch by weight, the "C" represents the cobalt(II)acetylacetonate 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.

Sample Processing

DSMxplore Netherlands, micro 15cc twin screw compounder was used for the preparation of the blends. The temperatures of the three zones were 145°C-150°C–145°C. The screw speed was kept at 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 Spectroscopy

BRUKER VERTEX 70 model FTIR Spectroscopy was used 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.

Thermogravimetric Analysis (TGA)

Perkin-Elmer, Pyris model Thermo gravimetric analyser was used to characterize the degradation behavior of samples. The thermal gravimetric 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 Testing

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.

Morphology Studies

The surfaces and fractures of blend films were examined using JEOL JSM-7600F scanning electron microscope operated at 5 kV. The films were fractured in liquid nitrogen and all the samples were coated with gold before scanning.

Soil Preparation and Inoculation

The soil was collected from farmland soil on Yeşilyurt/Muğla Turkey. The soil was sieved (<2 mm) and stored at 4°C sealed in plastic container. The two fungal isolates used in this study included a white-rot fungus *Coriolus versicolor* (L.) Quél. (COV-1030- from Wood Research

Institute, Kyoto University) and a brown-rot fungi *Postia placenta* (Fr.) M.J. Larsen & Lombard (Mad-698 (USDA Forest Product Lab, Madison, WI, USA)) which were maintained through periodic transfer at 4°C on petri dishes containing 20g 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 either *C.versicolor* or *P. placenta*, 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* or *P. placenta* 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 25 cmx19 cmx33 cm were filled with the sieved soil. The sterile blended film samples were cut into pieces with dimensions 6 cmx7 cm 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 [21]. 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 formula;

Equation 1;
Percentage Weight Lost = [[(Weight Initial-
Weight Final)]/Weight Final] x 100

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 LDPE and its blends with the 20%, 30% and 40% of TPS containing samples show the similar characteristics, so only the 40% of TPS containing blends are given in Figure 1. In the spectrum of the LDPE film, peaks around 2918 and 2841 cm^{-1} correspond to $-CH_2$ asymmetric and symmetric stretching, respectively. The absorption band around 1464-1305 cm^{-1} is attributed to the $-CH_2$ bending vibrations. The strong absorption at 712 cm^{-1} shows the $-CH_2$ rocking. In the spectrum of thermoplastic starch, a broad peak in the range of 3593-3013 cm^{-1} corresponds to the –OH stretching and –CH stretching can be seen as a weak peak at 2942 and 2879 cm^{-1}. –CH bending in the structure was appeared as a broad band at around 1438-1330

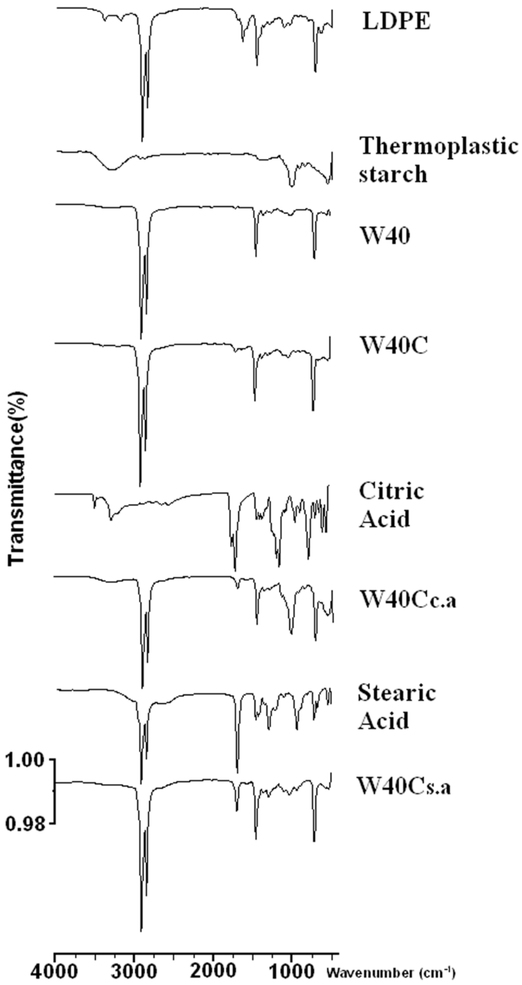

Figure 1. FTIR spectra of W40C, W40Cc.a and W40Cs.a.

cm^{-1}. The characteristic C-O stretching can be seen as a sharp peak at 1018 cm^{-1}. In the spectrum of $W_4$0, the peaks corresponding to LDPE and starch in the polymer structure are seen. The strong peaks at around 2918, 2847, 1457 and 718 cm^{-1} are related to the LDPE parts , the broad peak at 3370 cm^{-1} and the peak at 1030 cm^{-1} correspond to the starch units in the blend structure. Thus, incorporation of starch into the LDPE was achieved successfully.

The citric acid and stearic acid were added to the blend system to increase the compatibility between LDPE and TPS. Stearic acid has long alkyl groups and the carboxylic acid group in its structure. The peaks at 1706 cm^{-1} and at 1707 cm^{-1} in the spectra of the blends are the characteristic –C=O groups of citric acid and the stearic acid, respectively. The -OH stretching at around 3000 cm^{-1} related to the starch units was not observed in the blends with these additives, because of the interaction between the –OH groups in starch and the carboxylic acid groups of stearic acid and citric acid.

Cobalt(II) acetylacetonate, which accelerate the photo and thermo oxidation of the polymers, causes a polymer more susceptible to biodegradation. The absorption at 1712 cm^{-1} in the blends containing cobalt(II)acetylacetonate is attributed to the stretching of the carbonyl (C=O) group in cobalt acetylacetonate.

Thermogravimetric Analysis Before Soil Burial Treatment

The thermal analysis of LDPE, TPS and the blends were performed to determine the degradation temperatures and the weight loss patterns during degradation.

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

Code of the sample	Evaporation Temperature of Glycerol (^{0}C)	Decomposition Temperature of Starch (^{0}C)	Decomposition Temperature of LDPE (^{0}C)
W20C	259	329	482
W20Cca	240	330	482
W20Csa	262	328	482
W30C	255	329	477
W30Cca	249	331	482
W30Csa	256	326	471
W40C	249	328	482
W40Cca	240	332	481
W40Csa	254	324	481

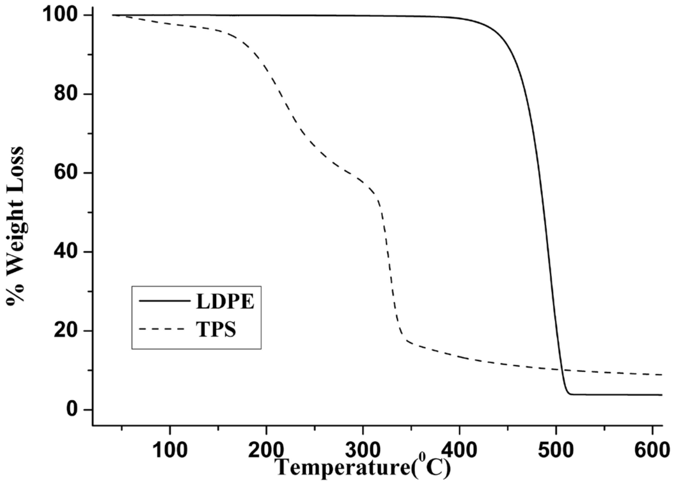

Figure 2. TGA curves of LDPE and TPS.

The TGA thermograms of LDPE and TPS are displayed in Figure 2. The TGA curve for pure LDPE indicates one stage of degradation, at 490°C due to the carbonated chains decomposition. Thermoplastic starch showed three decomposition stages. The first stage was observed at around 100°C, which was attributed to the loss of moisture absorbed by the starch particles. The second degradation zone was observed around 210°C, attributed to the loss evaporation of glycerol. The last stage was observed near 321°C, in which decomposition of wheat starch was observed.

The TGA curves of the blends are displayed in the Figure 3 and the decomposition temperatures are given in the Table 2. Four well defined weight loss stages can be observed in all the samples and the first stage was attributed to the loss of moisture around 100°C. The second one was due to the evaporation of glycerol. The third one is attributed to thermal degradation of the wheat starch and the last stage was attributed to the degradation of LDPE.

The results reveal that blending TPS with LDPE changed the decomposition temperature of starch and LDPE. The decomposition temperature of the starch in neat TPS was 321°C, but the decomposition temperatures of the starch in the blends were between 323°C and 332°C. The decomposition temperature of the neat LDPE was 490°C whereas this value varied from 477 to 482°C for the blends (Table 2). Addition of citric acid with cobalt(II)

Table 3. Decomposition temperatures of blend films before and after soil burial treatment.

Code of the sample	Evaporation temperature of glycerol (^oC)		Degradation temperature of wheat starch (^oC)		Degradation temperature of LDPE (^oC)	
	Before soil burial	After soil burial	Before soil burial	After soil burial	Before soil burial	After soil burial
W20C	259	-	329	326	482	477
W20Csa	240	269	330	329	482	482
W20Cca	262	238	328	329	482	482
W30C	255	-	329	326	477	489
W30Cca	249	-	331	329	482	486
W30Csa	256	-	326	326	471	466
W40C	249	-	328	326	482	484
W40Cca	240	-	332	326	481	484
W40Csa	254	-	323	328	481	490

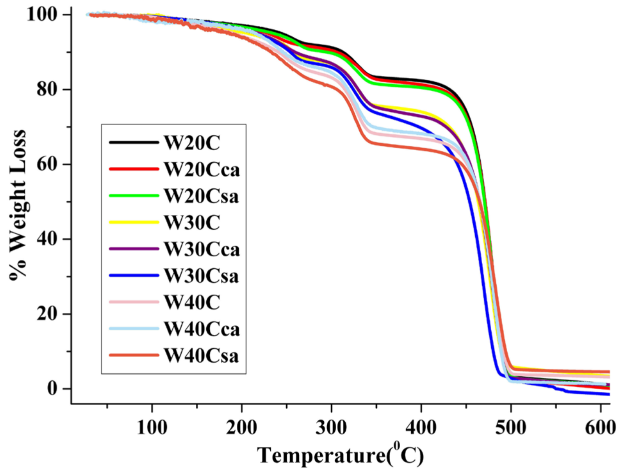

Figure 3. TGA curves of the blends before soil burial.

acetylacetonate has decreased the evaporation temperature of glycerol since citric acid can form stronger hydrogen bonds with starch than glycerol. This effect was highly pronounced at the films with 40% of TPS loadings. The addition of citric acid together with cobalt(II)acetylacetonate improved the thermal stability of starch in the blends. Addition of stearic acid together with cobalt (II) acetylacetonate slightly increased the evaporation temperature of glycerol, which may indicate that the addition of stearic acid increased the interaction of glycerol with starch. Moreover, the addition of stearic acid together with cobalt(II)acetylacetonate, slightly decreased the thermal stability of starch.

Soil Burial Treatment

The films had been buried under soil for 180 days. In order to investigate the degradation, weights of the films were measured and they were characterized by FTIR, subjected to mechanical testing and thermo gravimetric analysis. Soil has extensive microbial diversity, 1g of soil contains more than 10^7 prokaryotic cells and relatively, a large percent of them have not been identified. Microorganisms such as bacteria and fungi are involved in this process. Mainly, because of the

Table 4. Mechanical properties of the blend films before and after soil burial treatment.

Code of the sample	Tensile Strength[a] (MPa)		Elongation at Break[a] (%)		Tensile Strength[b] (MPa)		Elongation at Break[b] (%)	
	Before soil burial	After soil buria	Before soil burial	After soil buria	Before soil burial	After soil buria	Before soil burial	After soil buria
LDPE	14.8	-	475.4	-	14.8	-	475.4	-
W20	8.5	8.3	176.4	56.4	8.5	8.1	176.4	26.4
W20C	9.1	7.1	235.9	70.2	9.1	8.3	235.9	32.5
W20Cca	8.4	8.2	303.7	72.6	8.4	7.4	303.7	48.2
W20Csa	8.9	7.9	295.6	66.7	8.9	7.9	295.6	31.6
W30	6.9	6.4	65.2	34.6	6.9	6.7	65.2	17.6
W30C	7.7	7.2	154.6	50.7	7.7	7.1	154.6	29.3
W30Cca	5.8	6.1	176.8	42.6	5.8	6.8	176.8	35.8
W30Csa	6.8	6.7	169.5	33.9	6.8	6.6	169.5	23.2
W40	4.2	3.9	78.4	24.7	4.2	4.1	78.4	9.3
W40C	5.9	4.4	110.0	69.3	5.9	5.2	110.0	15.8
W40Cca	5.5	4.2	113.7	19.7	5.5	5.4	113.7	11.9
W40Csa	5.3	5.1	57.3	22.5	5.3	5.1	57.3	6.3

[a] *Coriolus versicolor* [b] *Postia placenta*

low percolation rate, the soil burial method is known to be a slow process, but it reflects the real life conditions and gives key points about the biodegradation process taking place [18].

Weight Loss Records for the Control Group

The percentage weight of the films from control group with respect to time are displayed in the Figure 4. The graphs were plotted according to formula given in Equation 1.

The control group films were degraded soil in which fungi was not incorporated in degradation medium. At the end of 180 days, total weight loss for W20 was 0.17% of its initial weight. For W30, the weight loss was recorded as 2.34% and for the sample coded as W40 total weight loss was 4.98% of its initial weight. The entire amount of starch was not removed during the soil burial test. The explanation for this result is that TPS in some area of the blends were well protected by LDPE and not easily accessible to microbial action.

Increasing starch content in the blends speeded up the weight loss as it was expected and as mentioned in literature. Since dispersed parts of TPS became more interconnected and continuous, for films with 30% and 40% TPS content, the weight loss became more significant. These results are in close agreement with the percolation analysis performed by Peanasky and Wool [18]. These authors claimed that the microbial attack started from the top and bottom of the polymer films by computer simulation. The percolation threshold is the minumum level of starch needed to connectivity between starch domains. The accessibility of starch is highly dependent on an apparent percolation threshold near 30% by volume or approximately 40% by weight of starch. Below the percolation threshold the consumption of starch by microorganisms is not efficient [18]. Thus for high TPS containing blends, a very small amount of TPS was protected by the LDPE, as a result higher degradation rates were observed.

Weight Loss Records for the Blends

The percentage weights of the films are displayed in Figure 5a and Figure 5b. The degradation

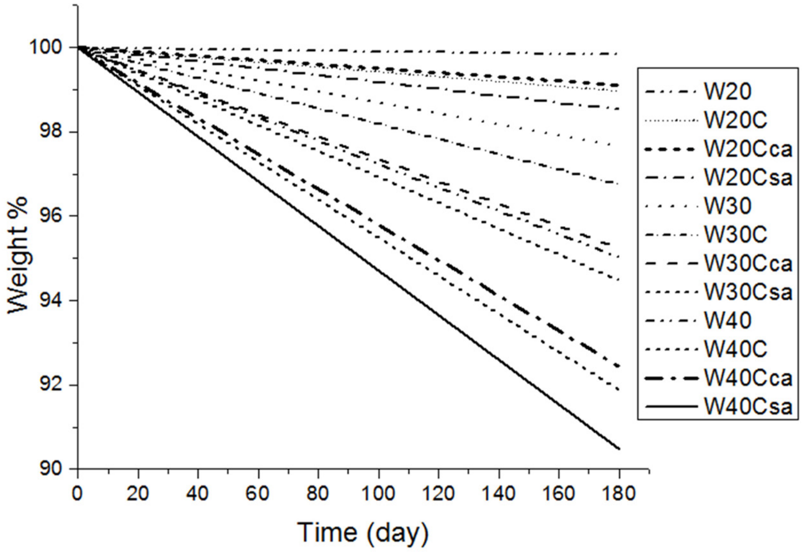

Figure 4. The percentage weight of the films from control group (no inoculation of fungi, just soil) versus time.

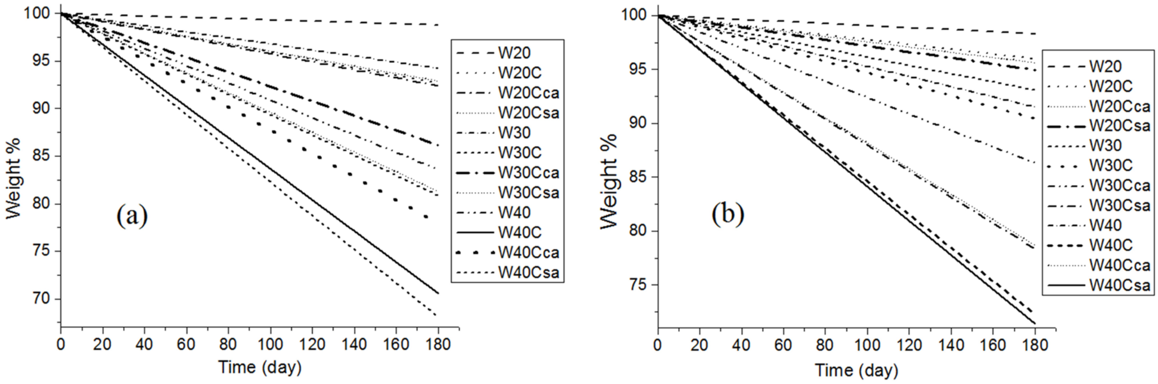

Figure 5. a. *Coriolus versicolor* b. *Postia placenta* The percentage weight of the blend films versus time.

of LDPE/TPS blend films in *Coriolus versicolor* inoculated soil was compared with the degradation in *Postia placenta* inoculated soil. The weight loss of the films which degraded in fungi (both *Coriolus versicolor* and *Postia placenta*) inoculated soil were higher than the control group. Besides, the efficieny of *Coriolus versicolor* in weight loss was better than *Postia placenta*. In *Coriolus versicolor* entered soil, for high loadings of starch, the weight loss for W40C, W40Cca and W40Csa were 29.42%, 22.07% and 31.89% of their initial weight, respectively. Since degradation started by starch consumption, the weight loss was due to the fact that loss of glycerol, citric and starch. The weight loss data show that the films with citric acid content showed the least weight loss. Since starch and citric acid may form strong interactions in the presence of cobalt(II) acetylacetonate, causing stability and resulting low consumption of starch.

FTIR Analysis after Soil Burial Treatment

The FTIR spectra of the samples from control group and the blend films with 40% TPS loadings are displayed in Figures 6 and 7, respectively. The spectra of the films recovered from soil are notified with star. A broad peak around 3500 cm^{-1} related to –OH stretching was observed in the spectra of the films recovered from soil. That shows that degradation starts from starch, more –OH group became free. This trend is more dominant for films with 40% of starch and for the films with citric acid and stearic acid. Since, these additives interacted with the –OH group of starch, with removal of these additives by microorganisms, more –OH group

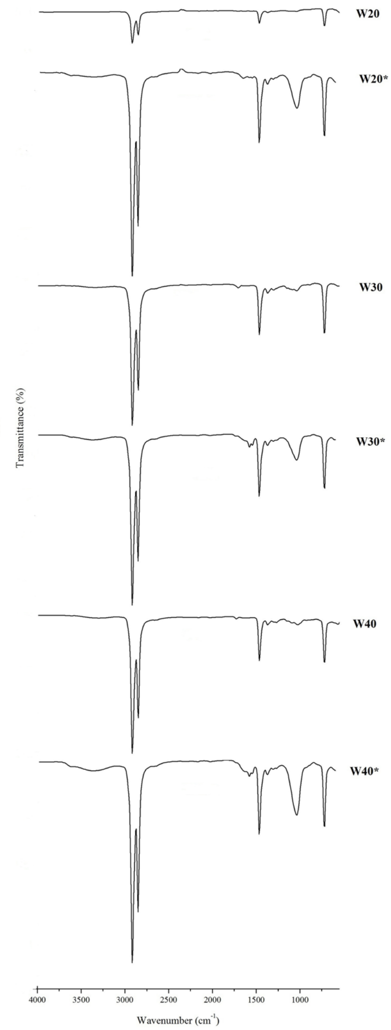

Figure 6. FTIR spectra of the films with 40% TPS loadings before and after soil burial treatment,* denotes after soil burial degradation.

became free, and stronger peaks were observed compared to before soil burial. The characteristics -C=O peaks around 1700 cm^{-1} for citric acid and stearic acid were not observed in the structure of the films after soil burial. This indicates that during soil burial these additives were removed by micro-organisms. FTIR spectra of the samples recovered from soil show that a broad peak around 1640 cm^{-1} assigned to -OH band was observed since the films under soil absorbed water.

Thermogravimetric Analysis After Soil Burial Treatment

Thermogravimetric analysis was performed for the films, which were exposed to *Coriolus versicolor* inoculated soil environment up to 180 days. The TGA curves of the films recovered from soil are displayed in Figure 8. The onset temperatures of the films before and after burial are tabulated in Table 3.

The first degradation peak around 1000C was attributed to the loss of water which was absorbed by starch granules (Figure 8). Except the samples coded as W20Cs.a and W20Cc.a, the stage which was attributed to evaporation of glycerol was not observed. It suggests that all the glycerol in the samples except W20Csa and W20Cca was removed during soil burial treatment. For films with 30% and 40% TPS, the onset temperatures for the degradation of TPS slightly decreased except the sample coded as W40Csa. When the TGA curves of the films recovered from the soil are compared

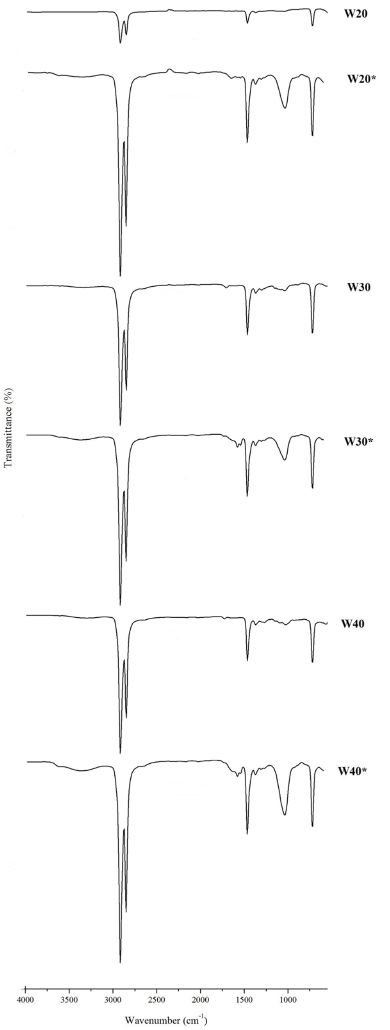

Figure 7. FTIR spectra of 40% TPS loaded films with additives before and after soil burial treatment, * denotes after soil burial degradation.

to that of the films before soil burial treatment, it is found that the weight losses during the shifts attributed to degradation of starch decreased. It was a result of removal of starch by microorganisms.

Mechanical Properties of Blends Before and After Soil Burial Treatment

The tensile properties of the blends are given in Table 4. When TPS was introduced into the polymer matrix, a decrease in tensile properties was observed. At higher TPS contents, this effect was more pronounced.

At higher loadings of TPS, starch granules have tendency to form aggregates. Because of the poor adhesion between TPS and LDPE, plus no compatibilizer was present in the blends; the transfer of stress through the blend was not efficient. Moreover, the tensile strength of the starch is lower than the tensile strength of LDPE [19]. All these factors resulted in decrease in tensile strength for as the TPS content is increased (UTS values 8.5, 6.9, 4.2 for W20:W30:W40 blends). Since physical incorporation of starch in the matrix of LDPE that weakens the forces between LDPE layers and the fact that TPS (starch is a low molecular weight polymer) has lower elongation compared to LDPE, reduction at elongation break was observed [20].

The tensile properties of the blends, which is prepared to see the effects of other additives on the mechanical properties and degradation rates

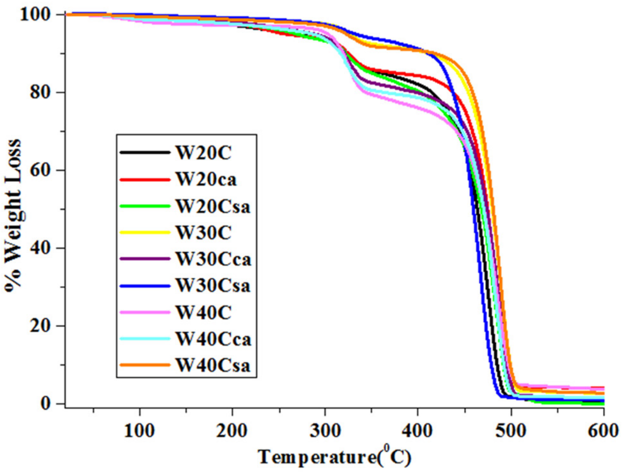

Figure 8. TGA curves of the blends after soil burial.

are also given in Table 4. The general increase in the tensile strength and elongation at break values compared the samples with no compatibilizer group, is an evidence of cobalt(II) acetylacetonate also act as a compatibilizer.

Before soil burial the elongation at break increases with the introduction of stearic acid and citric acid in to the blend. It indicates that citric and stearic acid increased the interfacial adhesion between LDPE and TPS. The samples with citric acid exhibited higher elongation at break values compared to films with stearic acid. Even at high loadings of TPS, for W40Cca 113.7% elongation at break was observed, whereas this value was 57.3% for W40Csa. The elongation at break for W40 which does not contain any pro-oxidant and compatibizer was 78.4% (Table 4). The effect of citric acid when it is used with cobalt(II)acetylacetonate was seen more dramatically at high loadings of TPS. Due to the loss of integrity, by consumption of the starch, the elongation at break values for the blend films dropped dramatically. It was also evaluated the effect of different fungi inoculated soil on biodegradation of LDPE/TPS blends. The first group films were degraded in *Coriolus versicolor* inoculated soil and the second group films were buried in *Postia placenta* inoculated soil. After the soil burial of films the comparison of mechanical properties of films which degraded in two different fungi inoculated soil showed different tensile strength and percentage elongation. Most of the blends in first group showed lower tensile strength and higher percentage elongation as compared to that of second group films. In other words, *Coriolus versicolor* containing soil environment had a profound effect on the decrease in tensile strength of films. Meanwhile, the tensile strength of the second group films which degraded in *Postia placenta* inoculated soil was not affected significantly. The mechanical results showed good agreement with the weight loss records and *Coriolus versicolor* provided a better degradation for LDPE/TPS blends.

SEM Analysis

The surface and fracture morphologies of W40Csa and W40Cca films before and after soil burial treatment were investigated by SEM. The SEM micrographs of W40Csa blend film before soil treatment for surface and fracture are given in Figure 9a and Figure 9b, respectively. The W40Csa sample contains a high amount of TPS (40%) and stearic acid was used as a compatibilizer. The surface view of the W40Csa film showed the uniform, continuous matrix (Figure 9a). The cross section of the film also showed that the TPS was homogenously dispersed into the LDPE matrix and there is no phase separation. Thus, the stearic acid improved the interfacial adhesion which resulted in a higher miscibility. Similar observations were reported on polyethylene-grafted maleic anhydride corn starch blends [22]. Figure 9c and 9d show the surface and fracture morphologies of the W40Cca film after soil burial treatment for 180 days. After degradation, fungus created some holes and an irregular surface (Figure 9c). The fracture of W40Cca film clearly showed the voids created due

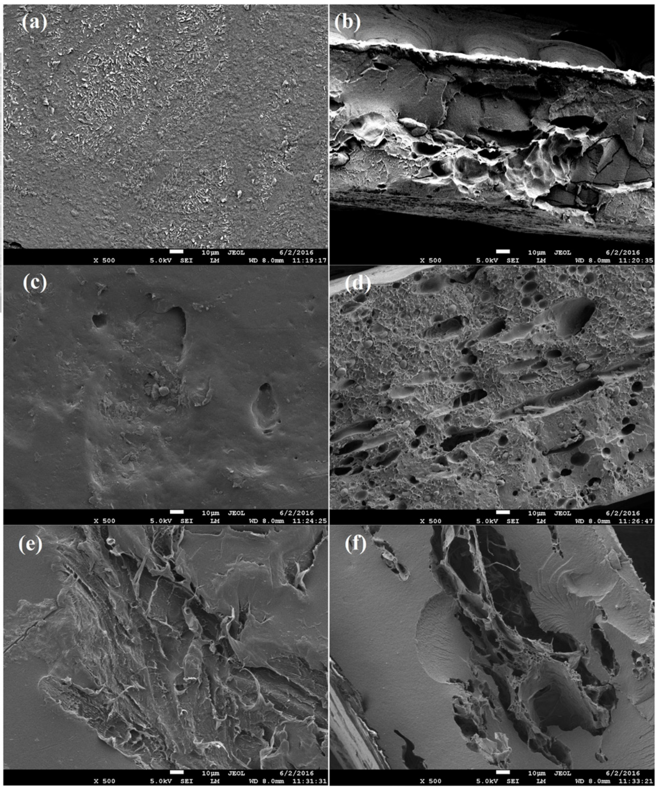

Figure 9. SEM micrographs of TPS/LDPE (40/60) films (a) W40Csa surface before, (b) W40Csa fracture before, (c)W40Cca surface after, (d) W40Cca fracture after, (e)W40Csa surface after, (f) W40Csa fracture after soil burial treatment.

to the partial removal of starch. However, when the surface and fracture morphologies of W40Csa film after soil treatment were investigated, many long cracks and voids were clearly noticed (Figure 9e and 9f). The effect of stearic acid compatibilizer can be seen and W40Csa film exhibited very smooth and continuous surface (Figure 9f). Besides, after degradation, in the stearic acid formulated films the surface erosion was much higher than that of citric acid compatibilized films. A high degree of degradation results correlated with weight loss measurements.

CONCLUSIONS

It can be seen that degradation starts by the consumption of starch when the films were buried in soil without direct exposure to sunlight. The highest biodegradation rate was observed in the blends with 40% TPS content. The film which is coded as W40Cs lost 31.98% of its weight after soil burial treatment. The films achieved a maximum weight loss in *Coriolus versicolor* inoculated soil after 180 days. The mechanical properties of the films decreased with increasing starch content. W20Cca showed the highest elongation at break, W20C had the highest tensile strength among the blends containing 20% TPS. After *Coriolus versicolor* inoculated soil burial treatment, percentage elongations at break of the films were highly affected, whereas the tensile strengths of the films which were degraded in *Postia placenta* inoculated soil were not affected dramatically. One of the results of the study was the interaction between compatibilizers and pro-oxidants. When cobalt(II) acetylacetonate used together with citric acid the thermal stability of TPS in films were enhanced. The mechanical properties were also improved.

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