

# Combined Effect of a Bio-Filler and Pro-Oxidants on the Degradation of Linear Low Density Polyethylene

**Anna Dilfi K. F.**

School of Civil Engineering  
Harbin Institute of Technology  
Harbin, China  
anna.dilfi@hit.edu.cn

**Thomas Kurian**

Department of Polymer Science and Rubber Technology  
Cochin University of Science and Technology  
Kochi – 682 022, India

**Raghul Subin S., and Saritha G. Bhat**

Department of Biotechnology  
Cochin University of Science and Technology  
Kochi – 682 022, India

*Abstract— Linear low density polyethylene (LLDPE) was blended with a bio-filler (starch, 15 weight %, 300 mesh size) by melt mixing. Various dosages (0.25, 0.5, 0.75 and 1 weight %) of pro-oxidants [iron oxide, manganese dioxide, titanium dioxide (anatase and rutile grades)] were added to this LLDPE-starch blend. The combined effect of the bio-filler and the pro-oxidant in every composition was determined by evaluating the mechanical properties, differential scanning calorimetry and melt flow indices. The biodegradation of the compositions was established by subjecting the samples to biodegradation in a shake culture flask containing amylase producing vibrios and soil burial. The extent of biodegradation was established by measurement of mechanical properties and weight loss. The morphology of the samples before and after biodegradation was also carried out using scanning electron microscope (SEM). The photodegradation of the linear low density polyethylene containing both the bio-filler and pro-oxidant was established by exposing the samples to ultraviolet (UV) radiation for 240 hours and checking the mechanical properties before and after UV irradiation. The results suggest that the combination of a bio-filler and a pro-oxidant improves the biodegradation and photodegradation of linear low density polyethylene.*

**Keywords— bio-filler; pro-oxidant; biodegradation; photodegradation**

## 1. INTRODUCTION

Plastics have attained a unique position in packaging industry because of their favourable features such as high strength, water resistance, light weight, energy effectiveness and low cost [1]. It has been estimated that about 2% of all plastics eventually reach the environment, thus contributing considerably to a currently acute ecological problem. For this reason, there have been several attempts towards the preparation of degradable natural or synthetic polymers or natural/synthetic polymer blends [2]. Linear low density polyethylene (LLDPE) is regarded as an inert bulk polymer and its degradability is very low compared to hydrolysable polymers such as thermoplastic polyesters [3]. One of the methods to accelerate the biodegradation of inert polymers is the incorporation of biopolymers to produce plastic films with a porous structure, which enhances the accessibility of the plastic to oxygen and micro-organisms [4-11]. Pro-oxidants too improve the degradability of plastics when exposed to sunlight [4,5].

In the present study, linear low density polyethylene (LLDPE) was blended with a bio-filler (starch, 15 weight %, 300 mesh size) and various dosages (0.25, 0.5, 0.75 and 1 weight %) of pro-oxidants [iron oxide, manganese dioxide, titanium dioxide (anatase and rutile grades)] by melt mixing. The combined effect of the bio-filler and the pro-oxidant in every composition was determined by evaluating the mechanical properties, differential scanning calorimetry, biodegradation, photodegradation and melt flow indices.

## 2. EXPERIMENTAL

### 2.1 Materials

The film grade linear low density polyethylene (LLDPE 20FS010) used in this study was provided by Reliance Industries Limited, Mumbai, India. The bio-filler (starch, 300 mesh size) used in this study was provided by Jemsons Starch and Derivatives, Aroor, Kerala, India. Various metal oxides [iron oxide, manganese dioxide, titanium dioxide (anatase and rutile grades)] were used as pro-oxidants in this study. The iron oxide was supplied by Merck Specialities Pvt. Ltd., Mumbai, manganese dioxide was supplied by Qualigens Fine Chemicals, Mumbai, and titanium dioxide (anatase and rutile grades) were supplied by Associated Chemicals, Edappally, Kerala.

## 2.2 Mixing

The compounds were prepared in a Thermo HAAKE PolyLab System equipped with roller type rotors. The mixing was done at a rotor speed of 30 rpm and at a temperature of 150°C. Initially the LLDPE was allowed to melt for 2 minutes, and then the bio-filler was added. Mixing was continued for another 1 minute. Then the pro-oxidant was added. Mixing was continued for another 5 minutes. Four compositions with each pro-oxidant and LLDPE-biofiller blend were prepared.

## 2.3 Preparation of test specimens

The test specimens were prepared from the compounds by moulding in an electrically heated hydraulic press for 5 minutes at 150°C under a pressure of 20MPa. After moulding the samples were cooled under pressure.

## 2.4 Mechanical testing

The stress-strain properties were evaluated as per ASTM D-882 [12] in a Shimadzu Autograph AG-I series Universal Testing Machine at a crosshead speed of 50 mm/min using a load cell of 10KN capacity. An average of at least five measurements was taken to represent each data point.

## 2.5 Differential scanning calorimetry

Crystallinity of the samples were studied using a TA Q-100 thermal analyzer (TA Instruments) performed under nitrogen with a heating rate of 10°C/min. Samples of 5-10mg were heated in a nitrogen atmosphere from -50°C to 170°C at a heating rate of 10°C/min, kept at 170°C for 3 min in order to erase thermal history. Then a cooling was performed at a rate of 10°C/min from 170 to -50°C followed by a second heating from -50 to 170°C at the same rate. Polymer crystallinity was calculated from the melting enthalpy obtained by endothermic peak integration and as reference the melting enthalpy of a perfect LLDPE crystal (289J/g).

## 2.6 Biodegradation studies

### 2.6.1 Using shake culture flask

The biodegradation studies on the blends were carried out according to ASTM D 6691 [13]. Biodegradability of the blends was tested using a shake culture flask containing the selected amylase producing *Vibrios*. *Vibrios* with the ability to produce amylase enzyme were selected for checking the biodegradability of the samples. The inoculum was prepared as follows. The individual isolates of the consortium were grown overnight at 37°C at 120 rpm on an Orbitek shaker (Scigenics Pvt. Ltd, Chennai, India) in nutrient broth (Himedia, Mumbai) pH 7.0 ±0.3 with 1% NaCl. The cells were harvested by centrifugation at 5000 rpm (2292g) for 20 minutes, washed with physiological saline and then pooled. 5 ml of this pooled culture (OD<sub>660</sub> = 1) was used to inoculate 50mL amylase minimal medium [14] lacking starch. The bioplastic strips previously wiped with 70% alcohol were added to this medium and these strips acted as the sole source of carbon. Incubation was in the Orbitek environmental shaker at 37°C and 120 rpm for a total period of 4 months with regular sampling. The medium without the inoculum with corresponding starch-plastic blends and subjected to the same treatment as above were used as controls. After 4 months the percentage decrease in tensile strength and weight was measured for determining the degree of degradation.

### 2.6.2 Soil burial test

The soil burial test was also carried out for evaluating the biodegradability of the blends. The soil was taken in pots and the plastic strips were placed in it. The bacterial culture was supplied to the soil. Care was taken to ensure that the samples were completely covered with soil. The pot was then kept at room temperature. The percentage decrease in tensile strength was measured after thorough washing with water and drying in oven until constant weight to determine the extent of biodegradability.

### 2.6.3 Scanning electron microscopic analyses (SEM)

In the present study, morphological characterisation of the fractured surfaces of the tensile test specimens (before and after biodegradation) was carried out using scanning electron microscope (JEOL Model JSM - 6390LV) after sputter coating the surface with platinum.

## 2.7 Photodegradability studies

The plastic film samples were cut to 8x1 cm size and exposed under a 30-watt shortwave UV lamp at a distance of 30 cm. The plastic films were then taken out at different time intervals, viz., 48, 120 and 240 hours to determine tensile strength using a Universal testing machine. The tensile strength of the samples was then compared with that of non-degraded samples.

## 2.8 Melt flow rates

An extrusion plastometer was used for measuring the melt flow index of polymer melts according to ASTM D-1238 [15]. The rate of extrusion through a die of specified length and diameter was measured under prescribed conditions of temperature and load as a function of time. Melt index is calculated and reported as g/10min. This index is inversely related to molecular weight.

The melt flow index (MFI) of each blend of LLDPE with filler was measured using a CEAST Modular Line Melt Flow Indexer in accordance with ASTM method D-1238 using a 2.16 kg load at a melt temperature of 190°C.

## 3. RESULTS AND DISCUSSION

### 3.1 Mechanical properties

The variation of tensile strength and elastic modulus of LLDPE-starch-prooxidant compositions are shown in Figs. 1a and 1b. The tensile strength of all the compositions shows a decreasing tendency with the addition of pro-oxidants. In the case of LLDPE-starch-prooxidant compositions, the elastic moduli were lower as compared to LLDPE-starch blends. This suggests that the metal oxides have no significant reinforcing effect on the blends.

The bio-filler used in this study is hydrophilic, as it contains hydroxyl groups on its surface. Thus, the formation of strong interfacial bonds like hydrogen bonds with LLDPE and the biofiller is not feasible due to the hydrophobicity of the polymer matrix [16-18].

### 3.2 Differential Scanning Calorimetry

The DSC thermograms of LLDPE-starch-prooxidant compositions are shown in Fig. 2. The melting temperature, crystallisation temperature, heat of fusion, heat of crystallisation and degree of crystallinity of LLDPE, LLDPE-starch and LLDPE-starch-prooxidant compositions are shown in Table 1. The melting and crystallisation temperatures of the blends are similar to neat LLDPE. This suggests that the fillers and the polymer are incompatible and the filler-polymer interactions are weak.

The degree of crystallinity of the blends are calculated by dividing heat of fusion of blends with heat of fusion of 100% pure crystalline polymer. The degree of crystallinity of the pro-oxidant containing blends was lower as compared to the neat polymer. This observation is in conformity with the lower tensile strength observed in presence of the pro-oxidants in the case of LLDPE-starch blends.

### 3.3 Biodegradation Studies

#### 3.3.1. In shake culture flask

The Figs. 3a, 3b, 3c and 3d show the variation in tensile strength of LLDPE-starch-prooxidant blends after immersing the strips in shake culture flask containing amylase producing vibrios, which were isolated from marine benthic environment, for 4 months. After 4 months of immersion, the strips were retrieved and the tensile strength measurements were carried out for determining the extent of biodegradation. There is significant variation in tensile strength of the LLDPE sample containing starch alone as the bio-filler indicating higher degree of biodegradation as compared to neat LLDPE. When pro-oxidants were incorporated in the LLDPE-starch blend and subjected to biodegradation in shake culture flask for 4 months, it was observed that the extent of biodegradation for the pro-oxidant containing blends were lower (Table 2) as compared to the LLDPE containing starch alone as bio-filler. The mechanical damage of LLDPE macrochain might have caused by swelling and bursting of the growing cells of the invading micro-organisms or the micro-organisms in the culture medium [19].

Table 2 shows the percentage decrease in tensile strength of LLDPE-starch blends, and LLDPE-starch-prooxidant (1 weight %) blends after biodegradation in shake culture flask for 4 months. Though the tensile strength of the LLDPE-starch blend showed 36.84% loss in tensile strength after the biodegradation in shake culture flask for 4 months, the blends containing the pro-oxidants showed lower loss in tensile strength after the biodegradation. The results show that the pro-oxidants used in this study adversely affect the biodegradation of LLDPE.

#### 3.3.2. Soil burial test

The variation in tensile strength of the samples prepared from the blends after burial in soil for 4 months determined using a Shimadzu Autograph AG I series universal testing machine are shown in Figs. 4a, 4b, 4c, and 4d. The tensile strength of the blends decreased after burial in soil for 4 months. The results suggest that the blends are partially biodegradable.

#### 3.3.3. Scanning electron microscopic analyses

The scanning electron photomicrographs of LLDPE-starch-prooxidant compositions, before and after biodegradation in shake culture flask for 4 months, are shown in Figs. 5a, 5b, 5c, 5d, 5e, 5f, 5g, and 5h. Smooth surfaces were observed in the case of the

scanning electron photomicrographs of the samples prepared from LLDPE-starch-prooxidant compositions, before biodegradation. During the incubation period, the degradation of LLDPE-starch-prooxidant compositions occurred and the characteristic change in morphology was observed in the scanning electron photomicrographs. The formation of cavities in the blends after biodegradation is attributed to the removal of bio-filler by the microorganisms. It shows that the bio-filler in the blends favour the microbial accumulation throughout the surface [20]. Apparently, the micro-organism in the culture medium attacks the plastic strips as their nutritional source and the bio-filler were removed from the surface. As the concentration of pro-oxidant in the blends increased, a decrease in the rate of biodegradation was observed. The scanning electron photomicrographs also give evidence for the dispersion of filler particles in the LLDPE matrix.

### 3.4 Photodegradability studies

The reduction in tensile strength after placing the samples under ultraviolet radiation for 240 hours are shown in Figs. 6a, 6b, 6c and 6d. There is considerable decrease in tensile strength after 240 hours of UV exposure in all the samples. The samples containing metal oxides as pro-oxidants show more variation in tensile strength after UV irradiation as compared to the LLDPE-starch blends. It was observed that the decrease in tensile strength was higher for blends containing more amount of pro-oxidant. The results suggest that the metal oxide content in the blends accelerates the photo-oxidation of linear low density polyethylene by generating free radicals which in turn may be accelerating the degradation process.

Table 3 shows the percentage decrease in tensile strength of LLDPE-starch blends, and LLDPE-starch-prooxidant (1 weight %) blends after UV irradiation for 240 hours. Comparing the decrease in tensile strength of the LLDPE-starch blend and the LLDPE-starch-prooxidant blends it was observed that the blends containing the pro-oxidants showed higher loss in tensile strength after UV irradiation. The results show that the pro-oxidants used in this study are effective in enhancing the rate of photodegradation of LLDPE.

### 3.5 Melt Flow Test

The melt flow index has been widely used as a common measure for judging the processability of polymers [21]. It is an indirect measure of viscosity. In Table 4 the melt flow indices of LLDPE-starch-prooxidant compositions are compared with those of neat LLDPE and LLDPE-starch blends.

On comparing the melt flow indices of neat LLDPE, LLDPE-starch, and LLDPE-starch-prooxidant blends, it was observed that the blends containing pro-oxidants have lower melt flow indices as compared to the neat LLDPE and the LLDPE-starch blends. The incorporation of starch into neat LLDPE also decreased the melt flow rate of LLDPE. This may be due to the increased entanglement of the polymer chains of LLDPE and the starch [22,23]. The addition of metal oxides as pro-oxidants to the LLDPE-starch blend might have decreased the movement of the polymer chain by increasing the viscosity of the blend, which eventually decreased the melt flow rate of the blends containing the pro-oxidants. The presence of the bio-filler and the pro-oxidants in LLDPE matrix apparently restricts the melt movement by increasing viscosity, which implies a hardening effect of the fillers [23].

## 4. CONCLUSION

The mechanical properties of LLDPE-starch blend containing pro-oxidants suggest that the metal oxides used as pro-oxidants have no significant reinforcing effect on the blends. The differential scanning calorimetric analyses show that the degree of crystallinity of the pro-oxidant containing blends was lower as compared to the LLDPE-biofiller blends. The biodegradation of the samples in shake culture flask and in soil for 4 months suggest that the LLDPE-biofiller blends containing the pro-oxidants show lower extent of biodegradation as compared to the LLDPE-biofiller blends. The results show that the metal oxides used as pro-oxidants in this study adversely affect the biodegradation of LLDPE. The photodegradability studies show that the pro-oxidants are effective in enhancing the rate of photodegradation of LLDPE. The scanning electron microscopic analyses reveal that the biofillers in the blends favour the microbial accumulation throughout the surface of the blends. The melt flow indices of the LLDPE-biofiller blends decreased on incorporating the pro-oxidants, and the values decreased as the concentration of the pro-oxidant increased suggesting that the pro-oxidants in LLDPE-biofiller matrix apparently restricts the melt movement by increasing the melt viscosity.

## 5. ACKNOWLEDGMENT

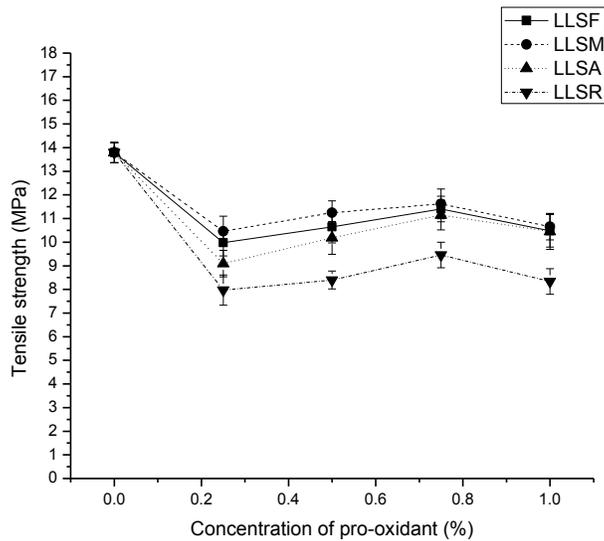
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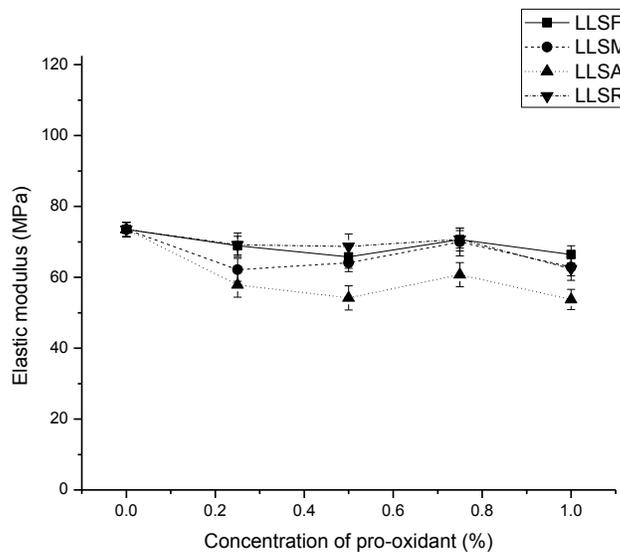
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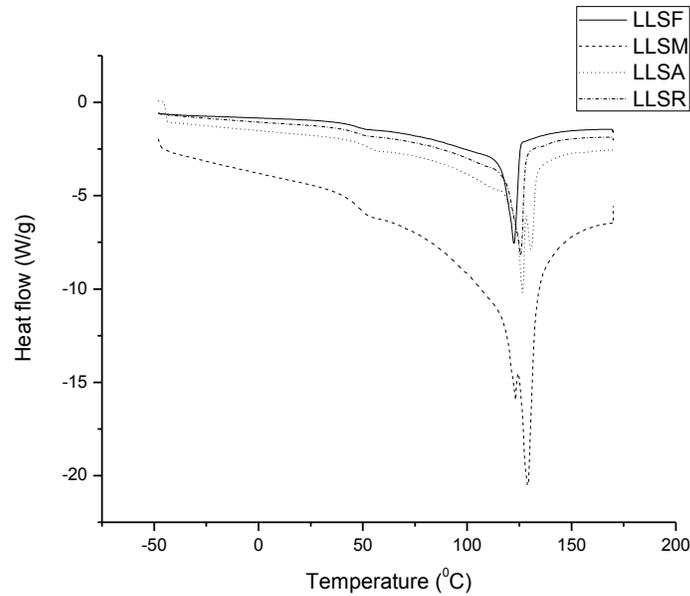
Figures



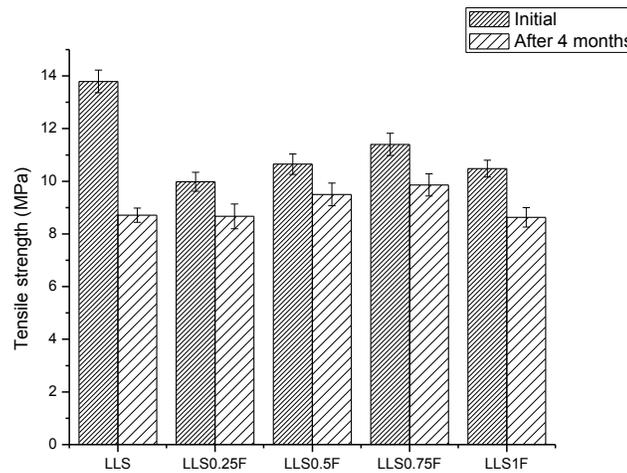
**Fig. 1a.** Variation of tensile strength with concentration of pro-oxidants in LLDPE-starch blends [LLSF = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>, LLSM = LLDPE-starch-MnO<sub>2</sub>, LLSA = LLDPE-starch-TiO<sub>2</sub> (anatase), LLSR = LLDPE-starch-TiO<sub>2</sub> (rutile)]



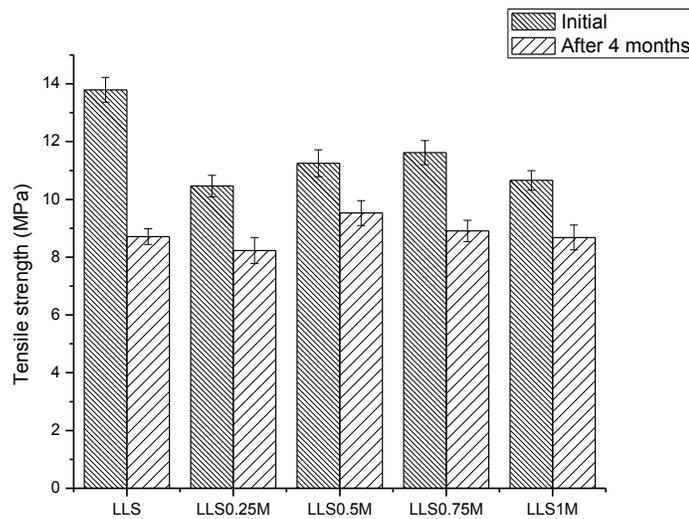
**Fig. 1b.** Variation of elastic modulus with concentration of pro-oxidants in LLDPE-starch blends [LLSF = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>, LLSM = LLDPE-starch-MnO<sub>2</sub>, LLSA = LLDPE-starch-TiO<sub>2</sub> (anatase), LLSR = LLDPE-starch-TiO<sub>2</sub> (rutile)]



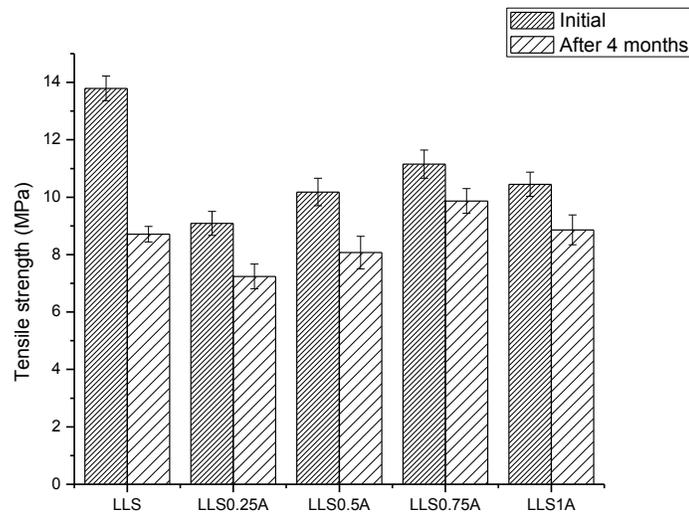
**Fig. 2.** DSC thermograms of LLDPE-starch blends with various pro-oxidants [LLSF = LLDPE-starch- $Fe_2O_3$ , LLSM = LLDPE-starch- $MnO_2$ , LLSA = LLDPE-starch- $TiO_2$  (anatase), LLSR = LLDPE-starch- $TiO_2$  (rutile)]



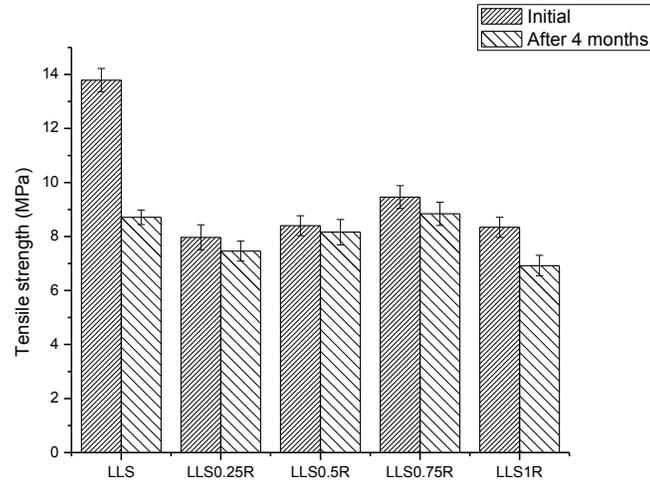
**Fig. 3a.** Variation in tensile strength of LLDPE-starch- $Fe_2O_3$  blends after biodegradation of plastic strips in shake culture flask for 4 months [LLS = LLDPE-starch, LLS0.25F = LLDPE-starch- $Fe_2O_3$ (0.25%), LLS0.5F = LLDPE-starch- $Fe_2O_3$ (0.5%), LLS0.75F = LLDPE-starch- $Fe_2O_3$ (0.75%), LLS1F = LLDPE-starch- $Fe_2O_3$ (1%)]



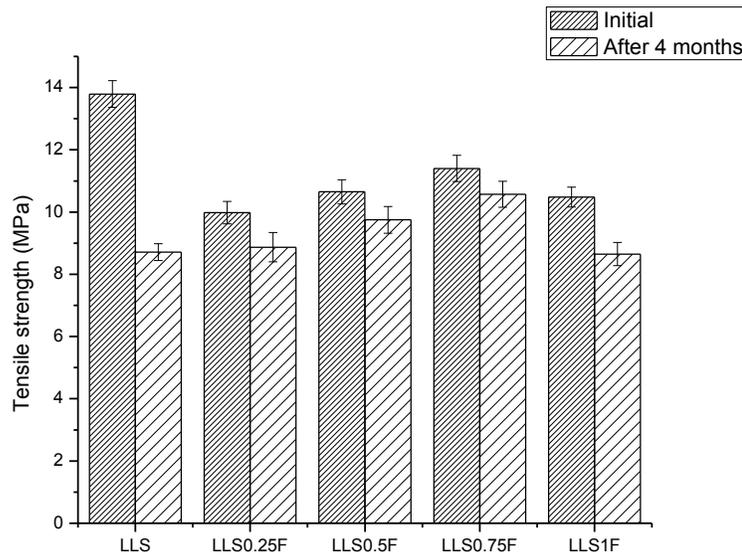
**Fig. 3b.** Variation in tensile strength of LLDPE-starch-MnO<sub>2</sub> blends after biodegradation of plastic strips in shake culture flask for 4 months [LLS = LLDPE-starch, LLS0.25M = LLDPE-starch-MnO<sub>2</sub>(0.25%), LLS0.5M = LLDPE-starch-MnO<sub>2</sub>(0.5%), LLS0.75M = LLDPE-starch-MnO<sub>2</sub>(0.75%), LLS1M = LLDPE-starch-MnO<sub>2</sub>(1%)]



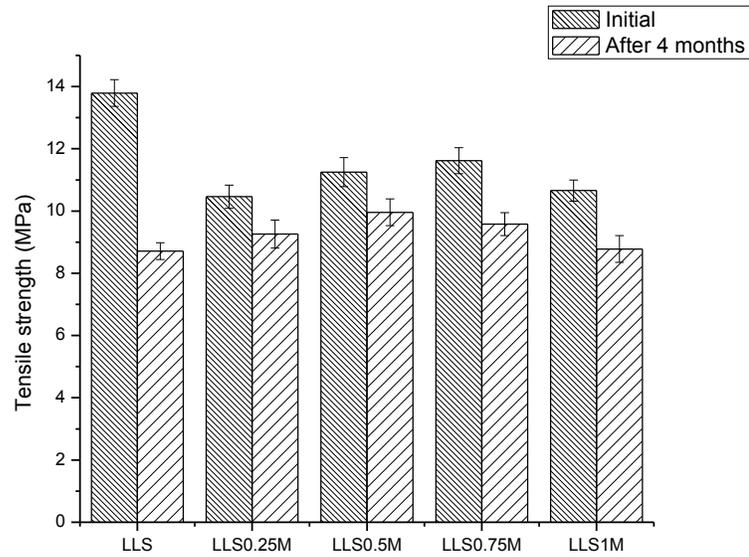
**Fig. 3c.** Variation in tensile strength of LLDPE-starch-TiO<sub>2</sub>(anatase) blends after biodegradation of plastic strips in shake culture flask for 4 months [LLS = LLDPE-starch, LLS0.25A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.25%), LLS0.5A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.5%), LLS0.75A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.75%), LLS1A = LLDPE-starch-TiO<sub>2</sub>(anatase-1%)]



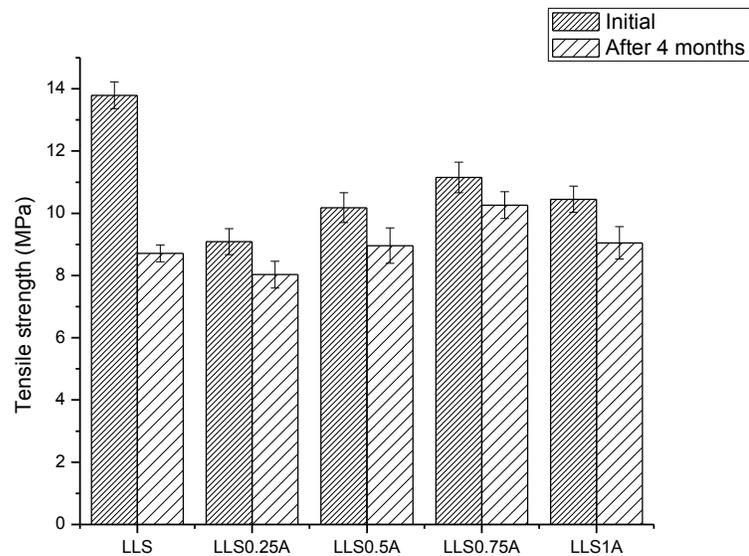
**Fig. 3d.** Variation in tensile strength of LLDPE-starch-TiO<sub>2</sub>(rutile) blends after biodegradation of plastic strips in shake culture flask for 4 months [LLS = LLDPE-starch, LLS0.25R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.25%), LLS0.5R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.5%), LLS0.75R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.75%), LLS1R = LLDPE-starch-TiO<sub>2</sub>(rutile-1%)]



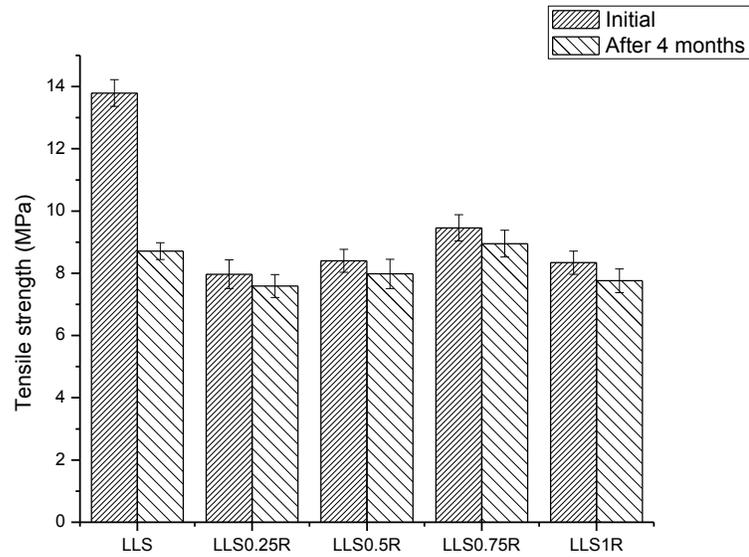
**Fig. 4a.** Variation in tensile strength of LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub> blends after soil burial test for 4 months [LLS = LLDPE-starch, LLS0.25F = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(0.25%), LLS0.5F = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(0.5%), LLS0.75F = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(0.75%), LLS1F = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(1%)]



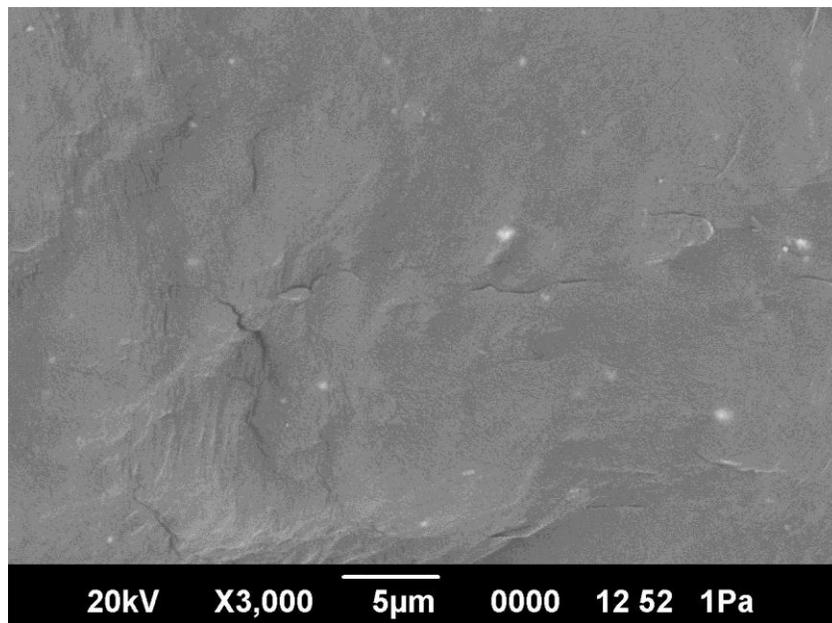
**Fig. 4b.** Variation in tensile strength of LLDPE-starch-MnO<sub>2</sub> blends after soil burial test for 4 months [LLS = LLDPE-starch, LLS0.25M = LLDPE-starch-MnO<sub>2</sub>(0.25%), LLS0.5M = LLDPE-starch-MnO<sub>2</sub>(0.5%), LLS0.75M = LLDPE-starch-MnO<sub>2</sub>(0.75%), LLS1M = LLDPE-starch-MnO<sub>2</sub>(1%)]



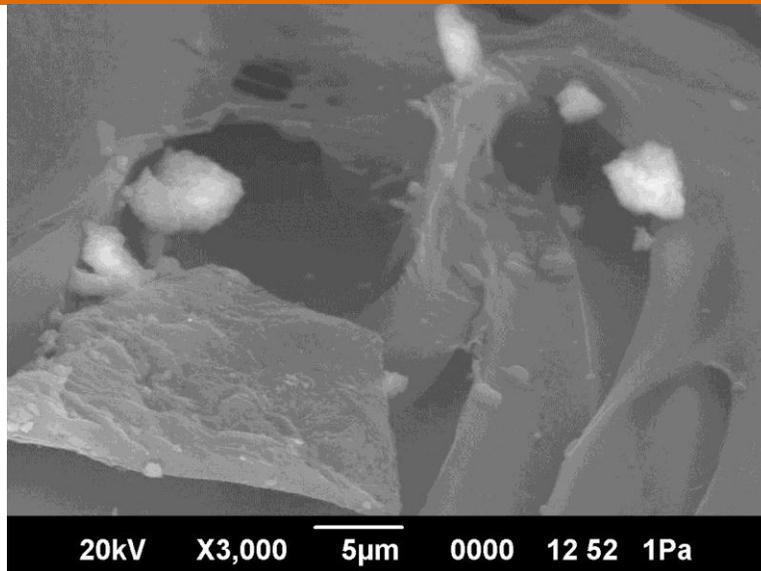
**Fig. 4c.** Variation in tensile strength of LLDPE-starch-TiO<sub>2</sub>(anatase) blends after soil burial test for 4 months [LLS = LLDPE-starch, LLS0.25A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.25%), LLS0.5A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.5%), LLS0.75A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.75%), LLS1A = LLDPE-starch-TiO<sub>2</sub>(anatase-1%)]



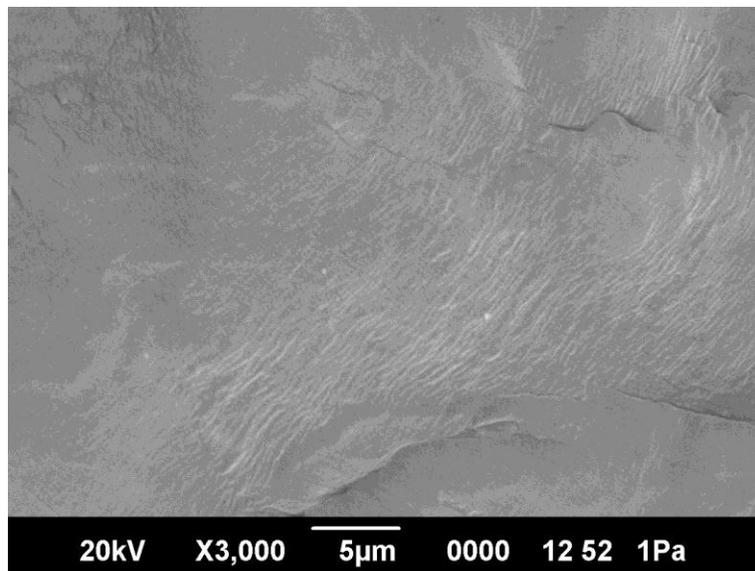
**Fig. 4d.** Variation in tensile strength of LLDPE-starch-TiO<sub>2</sub>(rutile) blends after soil burial test for 4 months [LLS = LLDPE-starch, LLS0.25R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.25%), LLS0.5R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.5%), LLS0.75R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.75%), LLS1R = LLDPE-starch-TiO<sub>2</sub>(rutile-1%)]



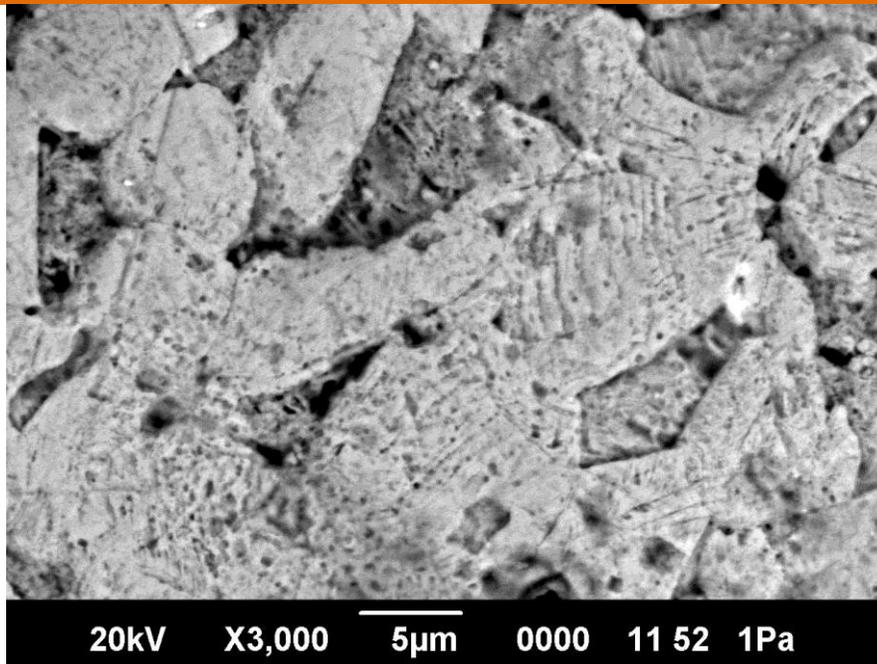
**Fig. 5a.** Scanning electron photomicrograph of LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub> blends – before biodegradation



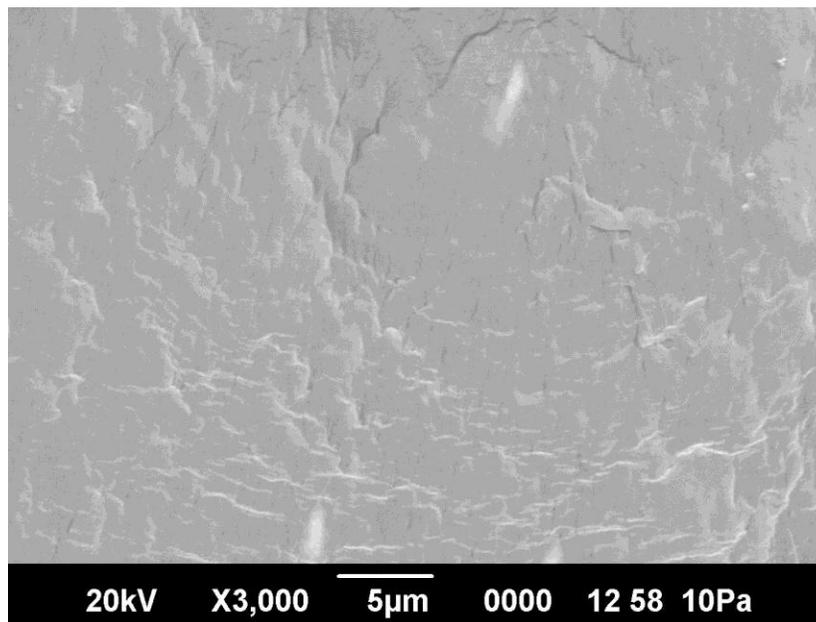
**Fig. 5b.** Scanning electron photomicrograph of LLDPE-starch- $\text{Fe}_2\text{O}_3$  blends – after biodegradation in shake culture flask for 4 months



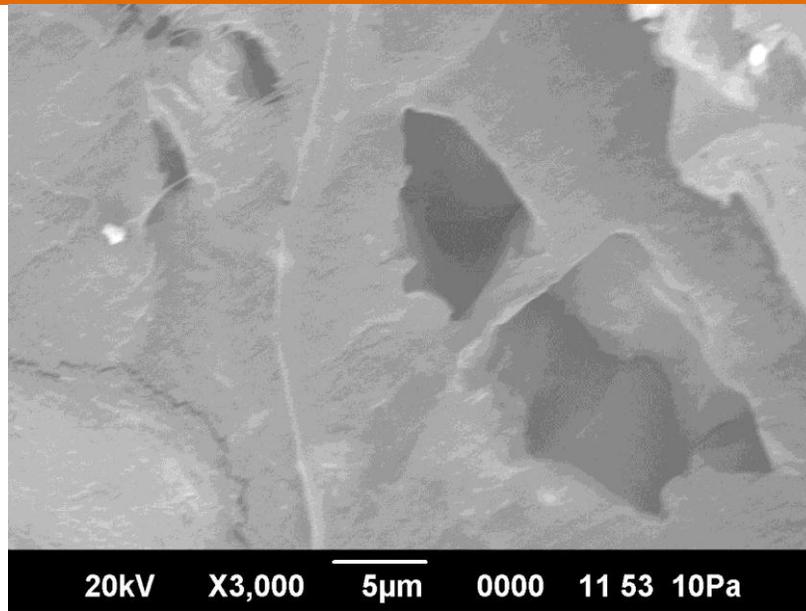
**Fig. 5c.** Scanning electron photomicrograph of LLDPE-starch- $\text{MnO}_2$  blends – before biodegradation



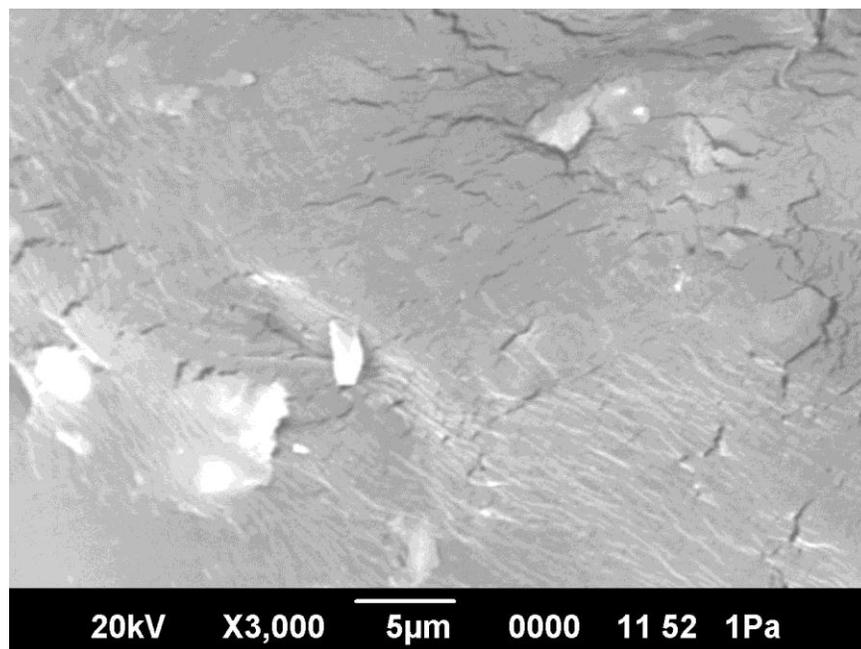
**Fig. 5d.** Scanning electron photomicrograph of LLDPE-starch-MnO<sub>2</sub> blends – after biodegradation in shake culture flask for 4 months



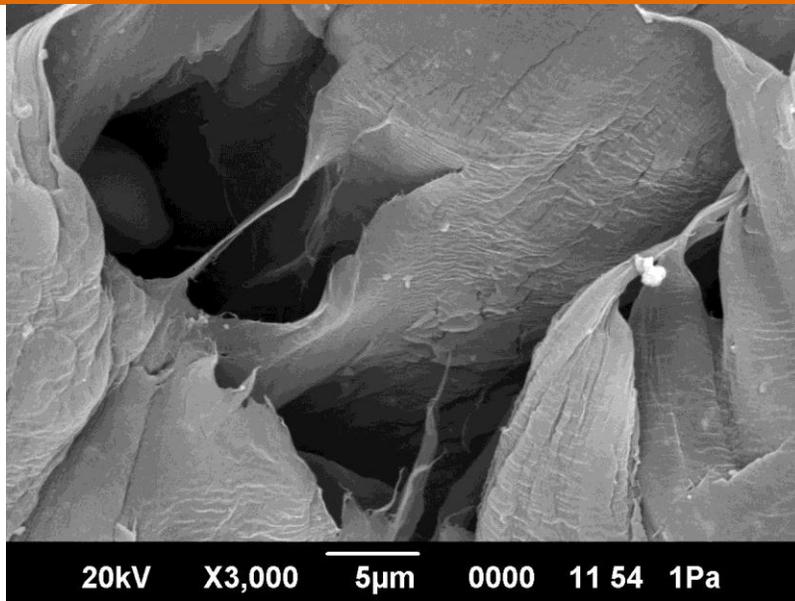
**Fig. 5e.** Scanning electron photomicrograph of LLDPE-starch-TiO<sub>2</sub>(anatase) blends – before biodegradation



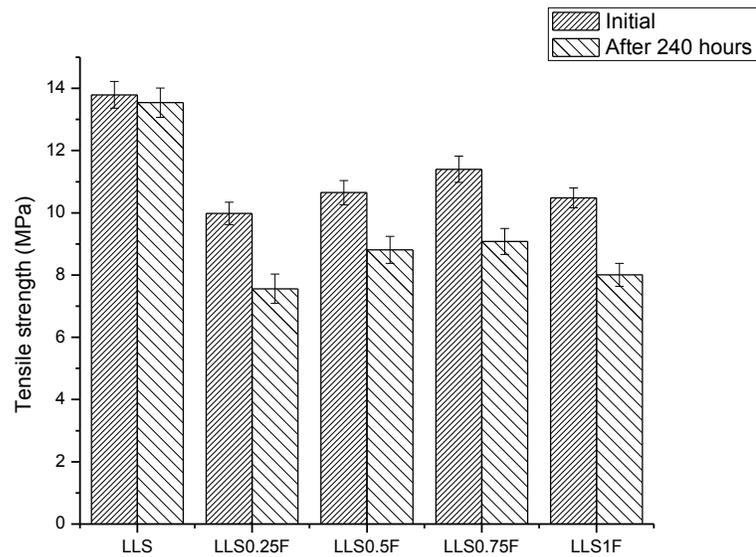
**Fig. 5f.** Scanning electron photomicrograph of LLDPE-starch-TiO<sub>2</sub>(anatase) blends – after biodegradation in shake culture flask for 4 months



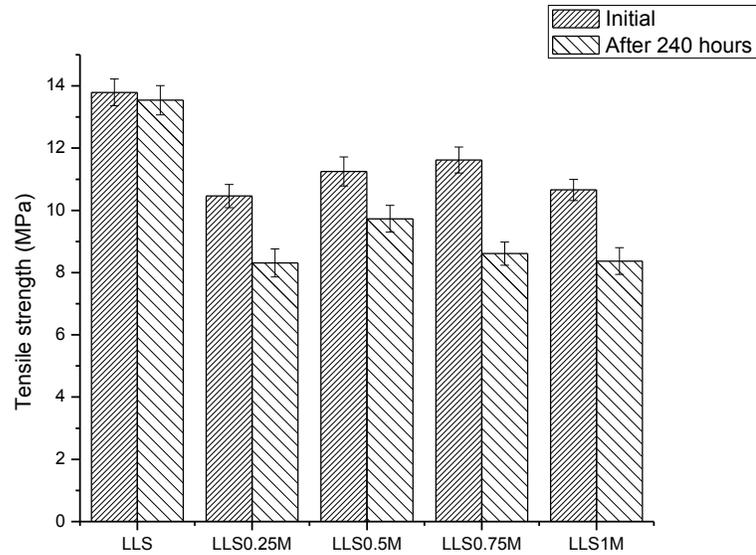
**Fig. 5g.** Scanning electron photomicrograph of LLDPE-starch-TiO<sub>2</sub>(rutile) blends – before biodegradation



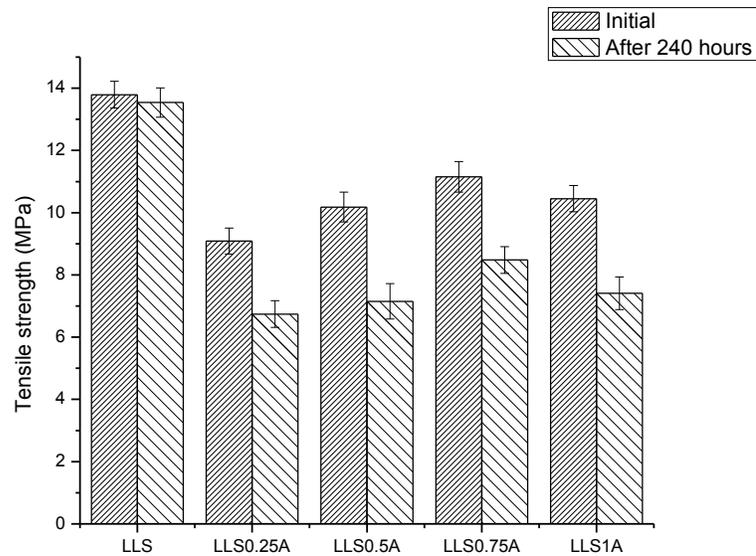
**Fig. 5h.** Scanning electron photomicrograph of LLDPE-starch-TiO<sub>2</sub>(rutile) blends – after biodegradation in shake culture flask for 4 months



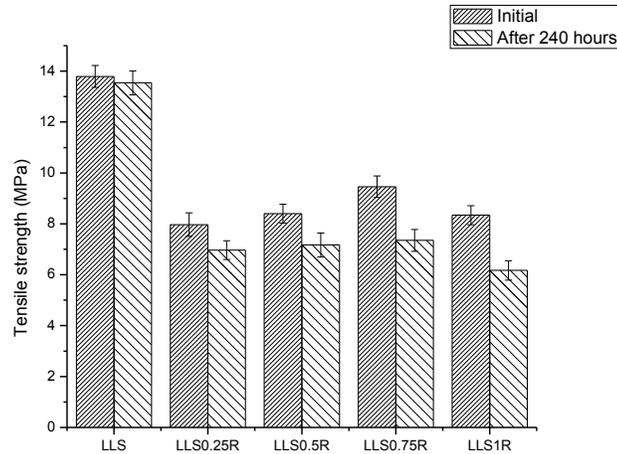
**Fig. 6a.** Variation in tensile strength of LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub> blends after UV irradiation for 240 hours [LLS = LLDPE-starch, LLS0.25Fe = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(0.25%), LLS0.5Fe = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(0.5%), LLS0.75Fe = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(0.75%), LLS1Fe = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>(1%)]



**Fig. 6b.** Variation in tensile strength of LLDPE-starch-MnO<sub>2</sub> blends after UV irradiation for 240 hours [LLS = LLDPE-starch, LLS0.25Mn = LLDPE-starch-MnO<sub>2</sub>(0.25%), LLS0.5Mn = LLDPE-starch-MnO<sub>2</sub>(0.5%), LLS0.75Mn = LLDPE-starch-MnO<sub>2</sub>(0.75%), LLS1Mn = LLDPE-starch-MnO<sub>2</sub>(1%)]



**Fig. 6c.** Variation in tensile strength of LLDPE-starch-TiO<sub>2</sub>(anatase) blends after UV irradiation for 240 hours [LLS = LLDPE-starch, LLS0.25A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.25%), LLS0.5A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.5%), LLS0.75A = LLDPE-starch-TiO<sub>2</sub>(anatase-0.75%), LLS1A = LLDPE-starch-TiO<sub>2</sub>(anatase-1%)]



**Fig. 6d.** Variation in tensile strength of LLDPE-starch-TiO<sub>2</sub>(rutile) blends after UV irradiation for 240 hours [LLS = LLDPE-starch, LLS0.25R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.25%), LLS0.5R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.5%), LLS0.75R = LLDPE-starch-TiO<sub>2</sub>(rutile-0.75%), LLS1R = LLDPE-starch-TiO<sub>2</sub>(rutile-1%)]

## Tables

**Table 1.** Results from differential scanning calorimetry [LLS = LLDPE-starch, LLSF = LLDPE-starch-Fe<sub>2</sub>O<sub>3</sub>, LLSM = LLDPE-starch-MnO<sub>2</sub>, LLSA = LLDPE-starch-TiO<sub>2</sub> (anatase), LLSR = LLDPE-starch-TiO<sub>2</sub> (rutile)]

| Sample | T <sub>m</sub> (°C) | ΔH <sub>f</sub> (J/g) | T <sub>c</sub> (°C) | ΔH <sub>c</sub> (J/g) | % Crystallinity |
|--------|---------------------|-----------------------|---------------------|-----------------------|-----------------|
| LLDPE  | 126                 | 58                    | 106                 | 59                    | 20              |
| LLS    | 125                 | 57                    | 107                 | 53                    | 19              |
| LLSF   | 122                 | 39                    | 108                 | 41                    | 13              |
| LLSM   | 128                 | 40                    | 107                 | 46                    | 14              |
| LLSR   | 125                 | 38                    | 108                 | 40                    | 13              |
| LLSA   | 123                 | 36                    | 108                 | 42                    | 12              |

**Table 2.** Percentage decrease in tensile strength of LLDPE-starch-prooxidant (1%) blends after biodegradation of plastic strips in shake culture flask for 4 months

| Composition      | Initial tensile strength (MPa) | Tensile strength after 4 months (MPa) | Percentage loss in tensile strength |
|------------------|--------------------------------|---------------------------------------|-------------------------------------|
| LLDPE+S300 (15%) | 13.79                          | 8.71                                  | 36.84                               |
| LLS1Fe           | 10.48                          | 7.63                                  | 17.65                               |
| LLS1Mn           | 10.66                          | 8.68                                  | 18.57                               |
| LLS1A            | 10.45                          | 8.86                                  | 15.22                               |

|       |      |      |       |
|-------|------|------|-------|
| LLS1R | 8.34 | 7.52 | 17.03 |
|-------|------|------|-------|

**Table 3.** Percentage decrease in tensile strength of LLDPE-starch-prooxidant (1%) blends after UV irradiation for 240 hours

| Composition      | Initial tensile strength (MPa) | Tensile strength after 4 months (MPa) | Percentage loss in tensile strength |
|------------------|--------------------------------|---------------------------------------|-------------------------------------|
| LLDPE+S300 (15%) | 13.79                          | 13.54                                 | 1.81                                |
| LLS1Fe           | 10.48                          | 8.01                                  | 23.57                               |
| LLS1Mn           | 10.66                          | 8.37                                  | 21.48                               |
| LLS1A            | 10.45                          | 7.41                                  | 29.09                               |
| LLS1R            | 8.34                           | 6.17                                  | 26.02                               |

**Table 4.** Melt flow rates of LLDPE-starch-prooxidant blends

| Sample   | MFI (g/10 min) |
|--|----------------|
| LLDPE  | 1.09           |
| LLDPE-starch*                                    | 0.75           |
| LLDPE-starch-0.25%Fe <sub>2</sub> O <sub>3</sub> | 0.71           |
| LLDPE-starch-1%Fe <sub>2</sub> O <sub>3</sub>    | 0.58           |
| LLDPE-starch-0.25%MnO <sub>2</sub>               | 0.75           |
| LLDPE-starch-1%MnO <sub>2</sub>                  | 0.61           |
| LLDPE-starch-0.25%TiO <sub>2</sub> (rutile)      | 0.72           |
| LLDPE-starch-1%TiO <sub>2</sub> (rutile)         | 0.57           |
| LLDPE-starch-0.25%TiO <sub>2</sub> (anatase)     | 0.69           |
| LLDPE-starch-1%TiO <sub>2</sub> (anatase)        | 0.61           |