Investigation of physical and rheological properties of LDPE/HDPE/thermoplastic starch biodegradable blend films

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Abstract
In this work, low-density polyethylene/high density polyethylene/thermoplastic starch (LDPE/HDPE/TS) films were prepared with different compositions to obtain environmentally friendly materials. LDPE/HDPE/TS blends, at ratios of 95:5:15, 90:10:15, 85:15:15, 85:15:20, 85:15:25 and 85:15:30, were processed into thin films by single-step single-screw extrusion. Fourier transform infrared (FTIR) spectra confirmed the immiscibility of matrices and TS in the blend, also in the SEM micrographs of the films no miscibility between the PE and starch was observed. In addition, the SEM micrographs showed a fairly good dispersion of TS (at low wt%) in the blend. Differential scanning calorimetry (DSC) analysis depicted an increase in the percentage of crystallinity with increasing HDPE and a decrease in the percentage of crystallinity with increasing TS. With the increase of HDPE content at low wt% of TS in the blend, an improvement was obtained in oxygen barrier property of the prepared films when compared to LD film. Water absorption of the samples decreased to some extent with increasing HDPE and the absorption increased with increasing TS. The rheological properties of LDPE/HDPE/TS blends were investigated before and after biodegradation. Results were fitted with well-known rheological models to achieve more valuable data about the effect of the composition as well degradation condition on the blend property. By adding HDPE in the presence of TS, rheological properties close to the LDPE were obtained for LDPE/HDPE/TS samples.

1 Introduction
Synthetic polymers are widely used in common essential applications because of their good mechanical properties, thermal stability, and their performance as good barriers to carbon dioxide, oxygen and aromatic compounds, and they are widely available and relatively low cost. Polyethylene (PE) is one of the mass-produced synthetic polymers which is utilized in many applications such as packaging, electrical insulations, construction and daily consumer products. Flexible polymeric packages made of synthetic polymers like PE are very durable during their all-life cycle and present serious environmental problems because are not degraded by microorganisms in the environment. Among the PE, low-density polyethylene (LDPE) is more susceptible to the attack of microorganisms. The resistance of polyethylene (PE) to biological attack is related to its hydrophobicity, high molecular weight, and lack of functional groups recognizable by microbial enzymatic systems. All of these properties limit its applications in which biodegradability is a desirable attribute. To overcome the non-degradability of synthetic plastics, one method is the preparation of bio-blends. Blending synthetic polymers such as polyethylene (LDPE) with a natural polymer such as starch helps to enhance PE chain oxidation reactions; microbial consumption of starch causes to raise the PE surface area by generating pores and improves oxygen-based reaction. As microorganisms consume the natural and bioplastic polymers, they lose their structural integrity which leads to enhance the biodegradation mechanisms and deterioration of the properties to facilitate integrated waste management approaches.
Starch is a hydrocolloid biopolymer that can be found in a variety of agricultural feedstocks such as wheat, corn, rice, beans, and potatoes. Starch is a high molecular weight ($M_w$) polymer of hydro-glucose units linked by a-D glycoside bonds that are composed of two types of alpha-glucans, linear amylose and branched amyllopectin, which represent approximately 98–99% of the dry weight. Amylopectin with molecular weight in the range of 50–500 million is much larger molecule than amylose. Starch is not a true thermoplastic, but in the presence of plasticizers at high temperature and under shear it can readily melt and flow, allowing for its use as an extruded or injected material, similar to most conventional synthetic thermoplastic polymers. 

Two major technologies for starch addition to plastics have been developed. One is based on the use of gelatinized starch molecules as an integral part of the polymeric structure, and the other is based on the use of granular starch as filler. Because the nature of PE is nonpolar and starch is polar, therefore they are incompatible and adding starch as filler to PE creates poor properties (physical/mechanical, rheological). To overcome this drawback and to achieve the expected properties, many attempts have been conducted on modifying either starch or PE. In addition, using a plasticizer to provide a good dispersion of starch in the polymer matrix and an increase in susceptibility to biodegradation has been approved. Glycerol owing to its low cost and availability is the most widely used plasticizer to prepare a material known as thermoplastic starch (TS).

Several studies have reported the development of biodegradable polymers by incorporating starch into LDPE and the characterization of this synthesized polymer. All these studies, in addition to biodegradability, have focused on improving the properties of the binary mixture of LDPE/starch due to unavoidable reduction in properties when starch content increases in the blend. In this work, the effect of blending of HDPE, with superior properties compared to LDPE, and LDPE has been investigated and its melt mixing with TS was studied. Here, an attempt was made to test environmentally friendly materials with potential capabilities in film applications. For this purpose, LDPE/HDPE blend with different ratios was melt compounded with TS (15, 20, 25 and 30wt%) in a single-screw extruder, followed by the blowing process to provide films and the physical, rheological and degradation properties of the mixtures were investigated.

2 Materials And Experimental Methods

2.1 Material

Two commercial film grades of polyethylene were used: 1) LDPE with a melt flow index (MFI) of 1.2 g/10min and a density of 0.924 g/cm$^3$; 2) HDPE with MFI of 0.1 g/10min (190 °C, 2.16 kg) and a density of 0.951 g/cm$^3$, which supplied by Petrochemical Commercial Company, Iran. The native corn starch (30wt% amylose) was obtained from Glucosan Company, Iran. Glycerol (KLK OLEO chemical producer, Malaysia) as a plasticizer for starch was prepared.

2.2 Methods
2.2.1 Preparation of the blends

Before blending, all ingredients were dried in a vacuum oven at 80 °C for 24 h. Thermoplastic starch was prepared by melt mixing the homogenous compound of native starch and 30wt% glycerol in a Haake internal mixer at 140 °C with a rotor speed of 60 rpm for 8 min. After the preparation of TS, the blends of LDPE/HDPE/TS at ratios of 95:5:15, 90:10:15, 85:15:20, 85:15:25 and 85:15:30, were processed into thin films (thickness of 50–90 micrometer) in single-step single-screw extrusion. The extruder had a barrel diameter (d) of 30 mm and the length to diameter ratio (L/D) was 25. The temperature profile along the five heating zones of the extruder barrel was 210-235-240-240-250 (from feed zone to die) and the torque was set at 12.4 N.m. The blend formulations and sample codes are summarized in Table 1.

Table 1. The blend formulations and sample codes.

<table>
<thead>
<tr>
<th>sample</th>
<th>LDPE</th>
<th>HDPE</th>
<th>Starch+Glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%100</td>
<td>%85</td>
<td>%15</td>
</tr>
<tr>
<td>LD</td>
<td>%100</td>
<td>%65</td>
<td></td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>%95</td>
<td>%85</td>
<td>%10</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>%90</td>
<td>%65</td>
<td></td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>%85</td>
<td>%10</td>
<td></td>
</tr>
<tr>
<td>LD85/HD15/TS20</td>
<td>%85</td>
<td>%80</td>
<td>%20</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>%75</td>
<td>%85</td>
<td>%25</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>%70</td>
<td>%85</td>
<td>%30</td>
</tr>
</tbody>
</table>

2.2.2 Fourier transform infrared (FTIR) spectroscopy

Typical infrared spectra of LDPE/HDPE/TS films were taken using an FTIR Spectrophotometer (Brucker, Tensor II, Germany). Film spectra were recorded with a resolution of 4cm\(^{-1}\) in the 400-4000cm\(^{-1}\) wave number range.

2.2.3 Differential scanning calorimetry (DSC)

The thermal behaviour of LDPE/HDPE/TS films was characterized by differential scanning calorimetry (Mettler Toledo DSC 822e Thermal Analyzer, Switzerland) in a nitrogen atmosphere under a flow rate of 50 mL/min. A sample weight of 7 mg in a sealed aluminum pan was heated from 25 °C to 190 °C at a rate of 10 °C/min and held at this temperature for 5 min. Then, the sample was cooled back to 25 at a rate of 10 and finally, heating it from 25 to 190 at the same rate was performed. Before starting the tests, the heat flow and temperature of the instrument were calibrated using standard materials, such as indium and zinc. The melting thermograms were recorded from the second heating cycle. The melting
temperature was determined from the DSC diagrams, and the percentage of crystallinity was calculated using Eq. (1):

\[
\%X_c = \frac{\Delta H_f(PE)}{\Delta H_f^0(PE)} \times \frac{1}{w_{PE}} \times 100
\]

Where \( \Delta H_f(PE) \) is the heat of fusion for PE in the sample, and \( \Delta H_f^0(PE) \) is the heat of fusion of 100% crystalline PE which is 287.6 j/g. \( w_{PE} \) is also the weight fraction of PE.

### 2.2.4. Determination of oxygen permeability

Film samples were cut into circular pieces with 12 cm in diameter and then conditioned in a closed chamber containing saturated calcium chloride salt solution at 25°C (30% RH) for 48h before measurement. Oxygen transmission rate (OTR) of the samples was measured according to ASTM D3985-802 using an oxygen permeation analyzer at 23°C and 0% RH. Three specimens were tested for each Sample. Oxygen permeability of the sample was then computed from Eq. (2) \(^{17} \):

\[
OP = \frac{OTR \times L}{\Delta P}
\]

where OP is the oxygen permeability (mol /m.sec.Pa), OTR is the measured oxygen transmission rate through a sample (mol/m².sec), L is the mean sample thickness (m) and \( \Delta P \) is the oxygen partial pressure difference between the two sides of the sample (Pa). The OP data were averaged from three replicates to obtain a mean value ± standard deviation.

### 2.2.5 Scanning electron microscopy (SEM)

Morphology of the typical films was studied by scanning electron microscopy (TESCAN, Tescan-Vega3, Czech Republic), operating at an accelerating voltage of 15kV. Before the test, the samples were cryogenically fractured in liquid nitrogen for 2 min using a glass knife and then sputter-coated with a thin layer of gold to avoid electrostatic charging and poor resolution during the examination. SEM micrographs were taken at a magnification of ×1000.

### 2.2.6 Water absorption

Water absorption test was carried out according to ASTM Standard D750-95. The three specimens (2.0×3.5cm) of each composition were dried in an oven under a vacuum for 6 h at 50 ± 3°C and cooled in a desiccator and immediately weighed to the nearest 0.001g. The conditioned container of distilled samples was placed in maintained water at 23 ± 2°C. The samples were then removed weekly from the water once at a time, gently blotted with tissue paper to remove the excess water on the surface, weighed to the nearest 0.001 g immediately, and replaced in the water. The weightings were repeated at the end of every week for 4 weeks and the average of three values was recorded. The percentage increase in weight during immersion was calculated by Eq. (3):
where $W_f$ is the final increased weight percentage, $W_w$ the wet weight and $W_C$ the conditioned weight of the testing samples.

### 2.2.7 Rheology

Dynamic frequency scan measurements including storage and loss moduli of the samples were conducted on a Rheometric Mechanical Spectrometer (RMS) (Anton Paar MCR-302, Austria) with the geometry of the parallel plates. Complex viscosity ($\eta^*$) of the molten granules of LDPE/HDPE/TS blends was also measured. All measurements were performed under a nitrogen atmosphere in the angular frequency range of 0.01–628 (rad/s) with a strain amplitude of 0.5% at 190 °C.

### 2.2.8 Degradation

#### Soil

A degradation study was performed on polymer samples in the form of three samples of each film in a square shape (5×5 cm) for three months. The phenomenon of degradation through mass loss and changes in peak FTIR and changes in rheological properties were investigated. Before burial, the polymer samples were characterized by weighing and recording their initial mass using an electronic balance with a resolution of 0.1 mg. After one month of burial, the samples were dug out and cleaned to ensure the complete removal of soil/mud. Samples were then placed in an area with sufficient ventilation for natural drying. The dried degraded samples were weighed using the same electronic balance as carried out before starting degradation. Measurements were performed once a month for three months. Subsequently, the percentage of mass loss of the respective sample was calculated with Eq. (4):

$$%MassLoss = \frac{M_i - M_f}{M_i} \times 100$$

where $M_i$ is the initial mass (i.e., mass before degradation) and $M_f$ is the final mass (i.e., mass after degradation).

#### Environment

Degradation study was performed on the polymer samples in the form of square shape (5×5 cm) during a degradation period up to 90 days. The films were degraded in Natural weathering (environment), which includes ambient conditions during the day and night. The phenomenon of degradation through mass loss and changes in peak FTIR and changes in rheological properties were investigated. Prior to degradation, the polymer samples were characterized by weighing and recording their initial mass using an electronic balance with a resolution of 0.1 mg. After one month, the degraded samples were weighed
using the same electronic balance as carried out before starting degradation. Measurements were performed once a month for three months. Subsequently, the percentage of mass loss of the respective sample was measured from Eq. (4).

3 Results And Discussion

3.1 FTIR

Figure 1 shows the FT-IR spectra of the LDPE and the LDPE/HDPE/TS blend films in the wave numbers of 4000–450 cm$^{-1}$. The FT-IR spectrum of LDPE shows accentuated peaks at 2914–2847 cm$^{-1}$ (CH stretching), 1464 cm$^{-1}$ (CH$_3$ bending), 719–729 cm$^{-1}$ (skeletal vibration of CH$_2$)\textsuperscript{13,18}. By adding TS, the bands appeared at regions of 3200–3400, 2850–2900 cm$^{-1}$, 1600–1700 cm$^{-1}$, 1300–1450 cm$^{-1}$ and 850–950 cm$^{-1}$ are attributed to O-H stretching and CH$_2$ stretching vibrations, -C-C- stretching, O-H bending and -C-C-bending, respectively. In addition, the bands at region of 960–1190 cm$^{-1}$ correspond to a strong set of C-O bending and stretching of the characteristic peaks for starch\textsuperscript{18–20}. There was no change in LDPE peaks when blend with starch, that indicating PE and starch are immiscible. The peak of 1721 cm$^{-1}$ has appeared in the LD85/HD15/TS30 specimen, which may be related to the carbonyl group and possibly regarding to the oxidation reaction during the extrusion process.

3.2 DSC

Table 2 shows the gas permeability ($o_2$) and DSC data including melting peak temperature ($T_m$), melting enthalpies ($\Delta H_m$), and percent of crystallinity ($X_c$) of LDPE, LD95/HD5/TS15, LD90/HD10/TS15, LD85/HD15/TS15, LD85/HD15/TS25. Melting curve obtained from second heating run of the LDPE and LDPE/HDPE/TS blends are given in Fig. 2.

Table 2. DSC and gas permeability Analysis for the LDPE/HDPE/TS blend films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak temperature ($^\circ$C)</th>
<th>$\Delta H_f$ (kJ g$^{-1}$)</th>
<th>$%X_c$</th>
<th>Gas Permeability ($o_2$, mol. m$^{-1}$ s$^{-1}$ Pa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>114.2</td>
<td>75</td>
<td>26</td>
<td>1.00±(.13) × 10$^{-14}$</td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>113.7</td>
<td>57</td>
<td>21</td>
<td>1.37± (.11) × 10$^{-14}$</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>115.3</td>
<td>79</td>
<td>31</td>
<td>8.75± (.57) × 10$^{-15}$</td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>113.5,123.3</td>
<td>61</td>
<td>25</td>
<td>1.11± (.09) × 10$^{-14}$</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>111.2,124.7</td>
<td>34</td>
<td>16</td>
<td>1.54± (.09) × 10$^{-14}$</td>
</tr>
</tbody>
</table>

There exists a basic disagreement over the issue of miscibility of HDPE with LDPE, it was agreed that branch content of branched component was the major molecular factor that controls miscibility of HDPE/LDPE blends. PE blends could be miscible, partially miscible or immiscible depending on molecular parameters such as molecular weight, molecular weight distribution, branch content and distribution and composition\textsuperscript{21}. 

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As can be seen in the Fig. 2, due to the presence of one peak in samples containing 5 and 10wt% of HDPE, polyethylenes are miscible, but at 15wt% of HDPE (based on matrix) they are immiscible and two melting peaks have appeared. In connection with the weak interactions of two polymers, it can be concluded that the HDPE forms well-organized spherulite's with a high degree of crystallinity and rigid amorphous layers between the lamellae, and LDPE forms irregular aggregates with low crystallinity and mobile amorphous layers between the lamellae, therefore HDPE and LDPE may be completely miscible in the melt; however, they are segregated into separate lamellar stacks during cooling from the melt to room temperature particularly at higher content of HDPE. Therefore, by incorporating HDPE tensile strength of the films were improved (about 20%) due to raising crystallinity; however, this improvement was dependent on ST content (Results not shown).

In sample LD90/HD10/TS15, the presence of HDPE in the matrix increases the degree of crystallinity, Also, it causes a higher melting temperature than virgin LDPE which indicates that HDPE can crystallize more easily and rapidly than LDPE because there are no branched chains that can restrict polyethylene molecules entering their crystal lattice. The molecules of HDPE dispersed in the LDPE matrix crystallize earlier at a higher temperature and act as nuclei for the crystallization of LDPE. These nuclei are densely distributed in the LDPE matrix and facilitate the crystallization process.

In the LD95/HD5/TS15 and LD85/HD15/TS25 samples, the degree of crystallinity is reduced. In the absence of starch, the material surrounding the crystalline particles is composed of amorphous phases of both polyethylenes. It is reasonable to expect that the starch particles predominantly present in the amorphous phase surrounding the crystalline particles. Starch acts as a rigid dispersed phase and reduces chain flexibility of PEs and inhibited close packing of the PEs chains during the cooling process which in turn decreases the $X_c$ value. Therefore, as TS content increases, the crystallinity of the samples decreases. Another reason for the decrease in the $X_c$ value with the increase of starch is the decrease of the PE in the blend.

According to the oxygen permeability results in Table 2, by comparing the prepared samples with the LDPE, the addition of TS has increased the oxygen permeability except for the LD90/HD10/TS15 sample. The improvement of oxygen barrier property in the LD90/HD10/TS15 sample can be due to the higher crystallinity of the sample compared to other samples. This behavior can be explained in terms of a decrease in oxygen diffusivity as a consequence of higher crystalline phase which is impermeable to oxygen. The increased oxygen permeability with starch content may be as a result of incompatibility between polyethylenes and starch which caused phase separation with a weak interface between two phases. It should be noted that blending LDPE with HDPE could improve gas barrier property of the biodegradable films.

### 3.3 SEM

The surface morphology of the LDPE/starch blend films was studied using scanning electron microscope (SEM). Scanning electron microscopy (SEM) micrographs of the tensile fracture surface of LDPE and
starch filled LDPE/HDPE are shown in Fig. 3. As evident from Fig. 3b-g, a layer like structure of LDPE/HDPE and the starch filler as dispersed phase is observed which indicating a two-phase morphology resulting from immiscibility of starch and LDPE/HDPE.

As shown in Figs. 3b and c the blends containing 15wt% TS exhibit a good dispersion of starch particles into the LDPE/HDPE matrix, and phase separation between matrix and starch is rarely seen. The smooth and uniform continuous surface in the images can be due to the relatively good surface adhesion between the matrix and the starch which can be attributed to the presence of HDPE and glycerol. The HDPE forms well organized spherulites with a high degree of crystallinity and rigid amorphous layers between the lamellae, when HDPE is blended with LDPE creates rigid amorphous layers between the lamellae in the matrix, and since starch particles are predominantly in the amorphous phase surrounding the crystalline particles, it is expected that by adding HDPE thermoplastic starch will be well embedded into the matrix. The role of glycerol as a plasticizer reduces the interfacial energy between the starch and matrix phases and makes them more compatible in these weight ratios. Since the study of the linear viscoelastic behaviour of the polymer blends can be a useful tool to quantify the morphology, by examining the rheological properties in the following, we confirm the positive impact of HDPE in the mixture in the presence of 15wt% of TS.

In LDPE/HDPE/TS blends different surface morphologies are observed depending on the amount of starch. In SEM micrographs, it can be seen that the degree of phase separation has increased with increasing starch content in the matrix/TS films. According to Figs. 3f and g with increasing starch content in the blends, the finer distribution of starch particles decreased and when the starch content increased to 30 wt%, particles agglomeration at the cross section of the specimen was observed that the separation of particles and surface holes created is due to such agglomeration. Surface holes formed by removal of loosely embedded starch particles were detected, which is due to the incompatibility of the starch and the matrix due to the difference in their polarity. This morphology is usually for incompatible mixtures which results in poor mechanical properties.

### 3.4 Water absorption

The percentage of water uptake for the LDPE film and LDPE/HDPE/TS film blends with a weekly immersion time is given in Table 3 and Fig. 4.
Table 3
Data of Percentage of water uptake for the LDPE/HDPE/TS film blends with immersion time with weekly intervals as (a) increase the percentage of HDPE and (b) increase the percentage of TS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Week 1</th>
<th>Week 2</th>
<th>Week 3</th>
<th>Week 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>0.571 ± 0.050</td>
<td>1.142 ± 0.130</td>
<td>1.142 ± 0.083</td>
<td>1.142 ± 0.066</td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>2.692 ± 0.062</td>
<td>3.846 ± 0.230</td>
<td>4.230 ± 0.097</td>
<td>4.230 ± 0.042</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>2.564 ± 0.085</td>
<td>3.846 ± 0.097</td>
<td>4.166 ± 0.170</td>
<td>4.166 ± 0.220</td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>2.439 ± 0.048</td>
<td>3.252 ± 0.190</td>
<td>4.065 ± 0.082</td>
<td>4.065 ± 0.077</td>
</tr>
<tr>
<td>LD85/HD15/TS20</td>
<td>2.836 ± 0.094</td>
<td>3.546 ± 0.084</td>
<td>4.255 ± 0.250</td>
<td>4.255 ± 0.037</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>3.448 ± 0.065</td>
<td>4.023 ± 0.270</td>
<td>4.597 ± 0.087</td>
<td>4.597 ± 0.320</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>3.703 ± 0.064</td>
<td>4.320 ± 0.093</td>
<td>4.732 ± 0.395</td>
<td>4.732 ± 0.072</td>
</tr>
</tbody>
</table>

As can be seen, the addition of HDPE and starch affects the water absorption of the composites. Increasing HDPE has reduced water absorption (see Fig. 4a). This decrease is almost observed in samples LD90/HD10/TS15 and LD85/HD15/TS15 compared to sample LD95/HD5/TS15. Increasing starch content has increased water absorption. Starch-based materials tend to absorb water, because the hydroxyl group in starch can form a hydrogen bond with water. In other words, water absorption is related to the amount of its penetration into the blends which increased with the starch content (the Lack of a smooth and uniform continuous surface causes better water penetration, which can be seen in SEM analysis by increasing the starch wt% in the blends) (see Fig. 4b). Rapid water uptake was observed for all specimens in the first two weeks of immersion, but gradually decreased over time and eventually reached steady. Regarding to water penetration into the composites and bonding to the hydroxyl group of starch granules which swelled and reduced the gap between their molecules, it was difficult for water to diffuse; thus, the rate of water absorption was reduced.

### 3.5 Rheological properties

#### 3.5.1 Elasticity

The rheology of thermoplastic blends provides a concept for the relationship between microscopic structure and their processing capability. Figure 5 and Fig. 6 show the storage modulus ($G'$) and the loss modulus ($G''$) versus angular frequency ($\omega$) for the specimens, respectively.
Regarding the increase of the dynamic modulus with increasing frequency, it can be said, the loss modulus reflects the strength of the internal friction, which becomes more drastic as the shear rate increases. On the other hand, two factors affect the storage modulus: the number of oriented chain segments will increase obviously as the shear rate increases and, simultaneously, the oriented chain segments will have less time for disorientation. Therefore, at high frequencies, entangled chains have a short time to relax and increase the amount of storage modulus. It was also observed that the storage modulus ($G'$) and the loss modulus ($G''$) increase with an increasing weight percentage of HDPE and TS in the blends.

The values $G'$ and $G''$ in the specimens shows a crossover point. The frequency ($\omega$) at which the point of intersection occurs is called the cross-over frequency $\omega_c$. $1/\omega_c$ is the relaxation time. The location of the cross-over in oscillatory data (where $G' = G''$) is often regarded as the boundary between solid-like and liquid-like behavior. At frequencies higher than the crossover point, the material is unable to relax sufficiently quick within the timescale of the applied oscillations and exhibits significant elastic behaviour ($G'$ dominates over $G''$). Conversely, at lower frequencies, the relaxation behaviour is faster than the applied oscillations and the material exhibits viscous characteristics. According to Table 4, the crossover frequency for HDPE is lower than that of LDPE which shows that the elastic region of HDPE starts at lower frequencies. So, the increment in HDPE content in LDPE/HDPE/TS blends has increased $\lambda$. The addition of starch except for sample LD85/HD15/TS30 increased the crossover frequency (observing Fig. 7 and Fig. 8 for a better comparison). In the following, we also use the generalized Maxwell model to compare with the times obtained from crossover point.
Maxwell's generalized model is defined as follows, Eq. (5):

\[ G(t) = \sum_{i=1}^{n} G_i \left[ \exp \left( -\frac{t}{\lambda_i} \right) \right] \]

Since all linear viscoelastic behaviour is governed by the Boltzmann superposition principle, which is based on the single material function, \( G(t) \), it is possible to relate the response to any sufficiently small or slow deformation to the linear relaxation modulus. In the case of small amplitude oscillatory shear, for example, it can be shown that \( G'(\omega) \) and \( G''(\omega) \) are the Fourier sine and cosine transforms of the relaxation modulus as Eq. (6) and Eq. (7), respectively:

\[ G'(\omega) = \omega \int_{0}^{\infty} G(s) \sin(\omega s) \, ds \]

\[ G''(\omega) = \omega \int_{0}^{\infty} G(s) \cos(\omega s) \, ds \]
If a generalized Maxwell model is used to represent the relaxation modulus, the resulting functions are:

\[ G'(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega \lambda_i)^2}{1 + (\omega \lambda_i)^2} \]

\[ G''(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega \lambda_i)}{1 + (\omega \lambda_i)^2} \]

Experimental values of storage or loss modulus can also be used to determine a set of Maxwell parameters. In this case suggests that the parameters be chosen such that:

\[ \sum_{k=1}^{m} \left[ (G'(\omega_k) - G'_k)^2 + (G''(\omega_k) - G''_k)^2 \right] = \text{minimum (10)} \]

where \( G'(\omega_k) \) and \( G''(\omega_k) \) are calculated by means of Equations (8) and (9). It was started by selecting the \( \lambda_i \) equal to integer powers of ten from \( 10^{-4} \) s to \( 10^3 \) s. Then the \( G_i \)'s were estimated by use of Eq. (10). \( G'_k \) and \( G''_k \) are experimental data. Additional information is available in the book of John M. Dealy et al.\(^{37}\). By writing the code using MATLAB, we can achieve the desired results.

Tables 5 and 6, show the results including statistical parameters and the relaxation module as well as the relaxation times of the generalized Maxwell model for PEs and LD/HD/TS film blends which were obtained by fitting the experimental data of storage modulus and loss modulus versus angular frequency. Figures 9 and 10 show \( \lambda \) and \( G \) resulting from the Maxwell model with increasing the percentage of HDPE and TS for the LDPE/HDPE/TS film blends, respectively). The mean relaxation time (\( \bar{\lambda} \)) was extracted from the relaxation spectra calculated using \( G' \) and \( G'' \) plot.
Table 5
λ and G resulting from the Maxwell model with increasing the percentage of HDPE for the LDPE/HDPE/Ts film blends. (Comparison with experimental data of storage and loss modulus).

<table>
<thead>
<tr>
<th>sample</th>
<th>LD</th>
<th>HD</th>
<th>LD95/HD5/Ts15</th>
<th>LD90/HD10/Ts15</th>
<th>LD85/HD15/Ts15</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-square</td>
<td>0.9946</td>
<td>0.9941</td>
<td>0.9970</td>
<td>0.9970</td>
<td>0.9972</td>
</tr>
<tr>
<td>λ₁ [s]</td>
<td>0.0013</td>
<td>0.0011</td>
<td>0.0008</td>
<td>0.0009</td>
<td>0.0011</td>
</tr>
<tr>
<td>λ₂ [s]</td>
<td>0.0217</td>
<td>0.0151</td>
<td>0.0127</td>
<td>0.0147</td>
<td>0.01601</td>
</tr>
<tr>
<td>λ₃ [s]</td>
<td>0.2102</td>
<td>0.2256</td>
<td>0.2349</td>
<td>0.2547</td>
<td>0.2554</td>
</tr>
<tr>
<td>G₁ [Pa]</td>
<td>174611</td>
<td>489580</td>
<td>239847</td>
<td>202999</td>
<td>207636</td>
</tr>
<tr>
<td>G₂ [Pa]</td>
<td>56217</td>
<td>198995</td>
<td>67990</td>
<td>56591</td>
<td>61497</td>
</tr>
<tr>
<td>G₃ [Pa]</td>
<td>21113</td>
<td>72496</td>
<td>28699</td>
<td>23025</td>
<td>27014</td>
</tr>
<tr>
<td>_</td>
<td>0.1631</td>
<td>0.1877</td>
<td>0.2043</td>
<td>0.2186</td>
<td>0.2189</td>
</tr>
</tbody>
</table>

\[ \lambda [s] = \left( \sum \lambda_i^2 \right) G_i \]

Table 6
λ and G resulting from the Maxwell model with increasing the percentage of Ts for the LDPE/HDPE/Ts film blends. (Comparison with experimental data of storage and loss modulus).

<table>
<thead>
<tr>
<th>Sample</th>
<th>LD85/HD15/Ts15</th>
<th>LD85/HD15/Ts20</th>
<th>LD85/HD15/Ts25</th>
<th>LD85/HD15/Ts30</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-square</td>
<td>0.9972</td>
<td>0.9965</td>
<td>0.9971</td>
<td>0.9938</td>
</tr>
<tr>
<td>λ₁ [s]</td>
<td>0.0011</td>
<td>0.0008</td>
<td>0.0009</td>
<td>0.0011</td>
</tr>
<tr>
<td>λ₂ [s]</td>
<td>0.0160</td>
<td>0.0119</td>
<td>0.0119</td>
<td>0.0121</td>
</tr>
<tr>
<td>λ₃ [s]</td>
<td>0.2554</td>
<td>0.2390</td>
<td>0.1700</td>
<td>0.3335</td>
</tr>
<tr>
<td>G₁ [Pa]</td>
<td>207636</td>
<td>221206</td>
<td>262720</td>
<td>232499</td>
</tr>
<tr>
<td>G₂ [Pa]</td>
<td>61497</td>
<td>77067</td>
<td>87492</td>
<td>73910</td>
</tr>
<tr>
<td>G₃ [Pa]</td>
<td>27014</td>
<td>29791</td>
<td>36691</td>
<td>30174</td>
</tr>
<tr>
<td>_</td>
<td>0.2189</td>
<td>0.2080</td>
<td>0.1425</td>
<td>0.3003</td>
</tr>
</tbody>
</table>

by comparing the relaxation modulus and the relaxation time resulting from the intersection point, also the relaxation modulus and the relaxation times resulting from the model for the LDPE and HDPE, it can
be seen that parameter values for HDPE values are significantly higher than LDPE. The change in storage modulus is directly related to the orientation and disorientation of the chain segments, which are affected by frequency, temperature, molecular weight and molecular weight distribution. The occurrence of branching is often accompanied by a broadening of the molecular weight distribution (LDPE has a broad molecular weight distribution than HDPE). Physically, the introduction of long branches has two opposing effects. First, the radius of gyration $R_g$ is decreased compared to that of a linear chain of the same molecular weight. The decreased $R_g$ results in fewer entanglements and lower viscosity. The second effect of branching occurs when the branch length is sufficiently long to be entangled, i.e., when the molecular weight of the branch becomes comparable to the critical molecular weight for entanglement of a linear chain ($M_e$). The overall entanglement network then has a much longer lifetime than that of a linear polymer network. The viscoelastic relaxation spectrum is extended to much longer relaxation times. This behaviour is consistent with the reptation model. A linear chain relaxes by diffusing out of its entanglement "tube." A branched-chain is attached at its branch points to at least two other chains, each in their own tubes. It cannot, therefore, diffuse out independently, and relaxation can occur only by processes requiring much longer times.

According to the MFI, the molecular weight of HDPE is higher than that of LDPE. When the molecular weight is above $M_c$ (the critical molecular weight for entanglements) the relaxation time of fractions with different molecular weights are separated widely. The fractions with a low molecular weight can relax quickly, while the fractions with a high molecular weight contribute to the dynamic moduli because of their slower relaxation. Polymer chains with a higher molecular weight form a more stable entanglement network which makes it difficult for the orientation of the chain segments along the direction of the shear flow. Thus, regarding the hindrance effect of the entanglements of the fractions with high molecular weight, the number of the oriented chain segments will not increase as much as the fractions with low molecular weight do with the shear rate increases. Therefore, the dynamic moduli of the polymers with a higher molecular weight will have a weaker dependence on the frequency than the polymers with lower $M_w$. So, the relaxation times and moduli for HDPE are higher when compared to LDPE.

Increasing the weigh percent of HDPE in the blends, regarding that HDPE, does not have a long side branch and has a higher molecular weight than LDPE, causes pack closer of matrix chains and creates a better entanglement network, so it increases the relaxation time resulting from the crossover point and $\lambda_i$s resulting from the model. According to Table 4, the relaxation time for the sample LD90/HD10/TS15 is very close to that of the LDPE and for the LD95/HD5/TS15 specimen is less than that of the LDPE. In the LD95/HD5/TS15 specimen with the lower content of HDPE the greater the effect of starch particles results in a weaker entanglement network, so less relaxation time was observed.

Except for LD85/HD15/TS30, increasing starch loading, has reduced the relaxation time obtained from the crossover point and the generalized Maxwell model. This reduction can be attributed to the dispersion of starch particles within LDPE/HDPE chains and reduction of the close packing in the polymeric chains. But at higher loading of the filler, where the particle-particle interactions are stronger than the particle-
matrix ones, the agglomeration of particles may occur and results in the immobilization of the polymeric chains which retards the stress relaxation rate. Therefore, the melt behavior tends to be more solid-like \(^2\). in the LD85/HD15/TS30 specimen (see Fig. 8 and Fig. 10), relaxation time was increased. The storage modulus of thermoplastic starch is higher than the loss modulus in the whole frequency range of 0.01–100 rad/s, so in this blend the behaviour of TS is dominant and the crossover point occurs at low frequencies \(^4\).

It should be noted that calculated mean relaxation times are in accordance with frequency crossover data. With respect to the small statistical errors in fitting the generalized Maxwell model to rheological data, with comparison of the relaxation time and modulus values of LDPE/HDPE/TS blends more knowledge about the structure of the blends can be achieved.

### 3.5.2 Viscosity

Figure 11 shows the relationship between complex viscosity \(\eta^*\) and frequency \((\omega)\) for the samples. It is clear that the complex viscosity of all samples decreases with increasing angular frequency, which indicates the shear-thinning behaviour of the prepared melts \(^4\). According to the Fig. 11a and b it is observed that with increasing the content of HDPE and TS in the composite films, the complex viscosity of their melts increases which is more obvious at lower frequencies. The increasing complex viscosity with an increment TS loading is due to the attractive interaction between matrix and thermoplastic starch.

To obtain zero shear viscosity and other flow properties of the prepared samples with considering Cox-Merz rule (the term Cox-Merz rule generally refers to the (near) equality between the shear rate \(\dot{\gamma}\) dependence of the nonlinear steady-state shear viscosity \(\eta\) and the angular frequency dependence of the linear complex viscosity \(\eta^*)\) \(^4\) complex viscosity data are fitted by the Cross (see Eq. (11)) and Power law models (see Eq. (13)) which are given in the following.

\[
\eta^* = \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^c}
\]

where \(\eta^*\) is the viscosity at the shear rate \(\dot{\gamma}\), the parameters \(\eta_0\) and \(\eta_\infty\) are the limit values of the viscosity at \(\dot{\gamma} = 0\) and \(\dot{\gamma} = \infty\) and \(\lambda\) is a characteristic time constant which is related to the relaxation time of the chains. For polymer melts it is \(\dot{\gamma} \gg \infty\) so we have \(\eta_\infty \ll 1\) and the Eq. (11) can be converted to the Eq. (12):

\[
\eta^* = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^c}
\]

\[c = 1-n\] which \(n\) is the Power law behavior index \(^4\).
Table 7
Cross model parameters for the LDPE/HDPE/TS film blends.

<table>
<thead>
<tr>
<th>sample</th>
<th>(\eta_0) [Pa. s]</th>
<th>(\lambda) [s]</th>
<th>(n)</th>
<th>R-square</th>
<th>Adj-Rsq</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>(2.217 \times 10^4)</td>
<td>1.820</td>
<td>0.3661</td>
<td>0.9971</td>
<td>0.9969</td>
</tr>
<tr>
<td>HD</td>
<td>(8.242 \times 10^4)</td>
<td>1.925</td>
<td>0.2179</td>
<td>0.9827</td>
<td>0.9800</td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>(2.241 \times 10^4)</td>
<td>2.201</td>
<td>0.4149</td>
<td>0.9999</td>
<td>0.9999</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>(2.517 \times 10^4)</td>
<td>4.462</td>
<td>0.4459</td>
<td>0.9995</td>
<td>0.9995</td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>(3.387 \times 10^4)</td>
<td>10.440</td>
<td>0.5256</td>
<td>0.9985</td>
<td>0.9982</td>
</tr>
<tr>
<td>LD85/HD15/TS20</td>
<td>(3.237 \times 10^4)</td>
<td>5.683</td>
<td>0.4791</td>
<td>0.9992</td>
<td>0.9991</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>(4.014 \times 10^4)</td>
<td>5.525</td>
<td>0.4647</td>
<td>0.9997</td>
<td>0.9997</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>(5.530 \times 10^4)</td>
<td>14.350</td>
<td>0.4949</td>
<td>0.9993</td>
<td>0.9992</td>
</tr>
</tbody>
</table>

It is observed from Table 7 that the value of \(\lambda\) for HDPE is slightly higher than LDPE, and increasing the weigh percent of HDPE in the blends increases the \(\lambda\). In contrast, the increasing weight of TS causes to decrease in the value of \(\lambda\) which is similar to \(\lambda\) trend obtained from the generalized Maxwell model.

The value of \(\eta_0\) is higher for HDPE than that of LDPE and increasing the content of HDPE and TS in the blend increases the value of zero shear viscosity. At the zero rate of shear, the chains are in the entanglement state in which the zero viscosity is calculated in this case. Entanglement between polymer chains is the main factor of viscosity dependence on molecular weight. The higher molecular weight of HDPE causes a higher zero shear viscosity and with increasing the weight percentage of HDPE in the blends, an increase in \(\eta_0\) is observed \(^{38,46}\).

The exponent of \(c\) is dependent on molecular weight distribution and approaches an upper limit of unity for a monodisperse linear polymer \(^{44}\). As can be seen, the value of \((n)\) was increased with increment of HDPE/LDPE ratio from 0.41 to 0.52 and decreased from 0.52 to 0.47 with TS weigh percent in the melts.

The flow curves of the viscosity plotted against the shear rate in logarithmic scales of polymers at various temperatures are approximately equivalent to parallel straight lines. A relationship of straight
lines on a logarithmic scale indicates that the viscosity and shear rate can be described by a power-law Eq. 4. This equation is the most common model used to express shear thinning behavior. The equation is as follows:

\[ \eta = m \dot{\gamma}^{n-1} \]

where \( \eta \) is the viscosity, \( \dot{\gamma} \) is the shear rate, \( m \) is the consistency index, and \( n \) is the power-law melt index. This relationship has poor performance in fitting in with data at shear rates close to zero (Newtonian region).

Table 8 shows the Power law model parameters for polyethylene film samples and LDPE/HDPE/TS film blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n )</th>
<th>( m ) [pa.s^n]</th>
<th>R-square</th>
<th>Adj-Rsq</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>0.5046</td>
<td>9191</td>
<td>0.9987</td>
<td>0.9984</td>
</tr>
<tr>
<td>HD</td>
<td>0.4342</td>
<td>( 3.575 \times 10^4 )</td>
<td>0.9988</td>
<td>0.9985</td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>0.4847</td>
<td>( 1.123 \times 10^4 )</td>
<td>0.9992</td>
<td>0.9991</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>0.4495</td>
<td>9636</td>
<td>0.9995</td>
<td>0.9994</td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>0.4483</td>
<td>( 1.144 \times 10^4 )</td>
<td>0.9993</td>
<td>0.9992</td>
</tr>
<tr>
<td>LD85/HD15/TS20</td>
<td>0.4432</td>
<td>( 1.227 \times 10^4 )</td>
<td>0.9992</td>
<td>0.9991</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>0.4435</td>
<td>( 1.482 \times 10^4 )</td>
<td>0.9992</td>
<td>0.9990</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>0.4629</td>
<td>( 1.338 \times 10^4 )</td>
<td>0.9991</td>
<td>0.9989</td>
</tr>
</tbody>
</table>

According to Table 8, the value of \( m \) for HDPE is higher than LDPE, and the addition of HDPE to the mixture has resulted in an increase in \( m \) (The value of \( m \) for sample LD90/HD10/TS15 is approximately equal to the LDPE). Increasing TS to the mixture has increased the value of \( m \) (The presence of glycerol in starch as a plasticizer increases macromolecular mobility and decreased the rheological properties).

The value of \( n \) for the HDPE is lower than that of LDPE. The power law exponent \( n \) of various polyethylene (PE) grades, is between 0.3 to 0.6, and depends on molecular weight and long-chain
branching $^{34,49}$. Linear narrow molecular weight distribution polymers are more viscous (less shear thinning) than their with broad distribution of the same average molecular weight $^{42}$. A low melt index means a high molecular weight with a greater sensitivity to shear. The higher molecular weight in HDPE dominates the broad molecular weight distribution of LDPE and has shown more shear thinning behaviour.

### 3.6 Degradability

#### 3.6.1 Weight Loss

Table 9 is related to the percentage of mass loss for LDPE film and LDPE/HDPE/TS film blends for 3 months in the environment (observing Fig. 12 for a better comparison).

<table>
<thead>
<tr>
<th>sample</th>
<th>first month</th>
<th>second month</th>
<th>Third month</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>0.099±0.021</td>
<td>0.165±0.014</td>
<td>0.264±0.021</td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>0.741±0.063</td>
<td>1.363±0.057</td>
<td>2.757±0.110</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>0.604±0.120</td>
<td>0.957±0.250</td>
<td>2.493±0.055</td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>0.249±0.041</td>
<td>0.249±0.080</td>
<td>0.999±0.060</td>
</tr>
<tr>
<td>LD85/HD15/TS20</td>
<td>0.509±0.098</td>
<td>0.401±0.014</td>
<td>2.330±0.180</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>0.274±0.051</td>
<td>0.397±0.057</td>
<td>2.199±0.301</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>0.394±0.073</td>
<td>0.505±0.089</td>
<td>2.286±0.140</td>
</tr>
</tbody>
</table>

Table 10 is related to the percentage of mass loss for LDPE film and LDPE/HDPE/TS film blends for 3 months in the soil (observing Fig. 13 for a better comparison).
Table 10
Data of weight loss (%) in the soil for the LDPE/HDPE/TS film blends.

<table>
<thead>
<tr>
<th>sample</th>
<th>first month</th>
<th>second month</th>
<th>Third month</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>0.193±0.021</td>
<td>0.358±0.035</td>
<td>0.496±0.028</td>
</tr>
<tr>
<td>LD95/HD5/TS15</td>
<td>4.923±0.159</td>
<td>5.563±0.154</td>
<td>5.507±0.159</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>2.736±0.854</td>
<td>4.173±0.090</td>
<td>4.645±0.128</td>
</tr>
<tr>
<td>LD85/HD15/TS15</td>
<td>3.619±0.120</td>
<td>4.187±0.170</td>
<td>4.542±0.210</td>
</tr>
<tr>
<td>LD85/HD15/TS20</td>
<td>3.571±0.110</td>
<td>4.729±0.090</td>
<td>4.922±0.086</td>
</tr>
<tr>
<td>LD85/HD15/TS25</td>
<td>2.403±0.210</td>
<td>3.990±0.100</td>
<td>4.060±0.953</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>3.356±0.570</td>
<td>5.563±0.230</td>
<td>6.115±0.080</td>
</tr>
</tbody>
</table>

According to the Fig. 12a and Fig. 13a increasing HDPE from 5 to 15 wt% in the matrix was reduced the degradability in the environment and soil. Among PEs, the density (or crystallinity) of PE affects photostability. PE with lower density has lower optical stability and has more degradability and thus the reduction of LDPE/HDPE ratio in the blends decreased the degradation rate. According to Fig. 12b and Fig. 13b, increasing starch loading has increased the degradation kinetics, especially in sample LD85/HD15/TS30. The higher starch content increases the degradation rate and thus increases the mass loss. This could be due to the hydrophilic nature of the starch. The starch is hydrophilic in nature and retains moisture that contributes to the degradation of the polymer.

Considering the desirable properties and good biodegradability of the sample LD90/HD10/TS15, it will be evaluated for FTIR and the rheological analysis of the degraded sample in comparison with the sample LDPE as well as the sample with the highest wt% of starch (LD85/HD15/TS30) and biodegradability.

### 3.6.2 Fourier transform infrared specimens after degradation

Figure 14 shows the Fourier transform infrared of degraded specimens in the soil and environment compared to the early specimen for LDPE, LD90/HD10/TS15, and LD85/HD15/TS30.

According to Fig. 14 some peaks have been appeared and removed in addition to the peaks introduced for the specimens in Section 3.1 due to degradation in the soil and environment, that as follows:
For the LDPE sample, peaks of 1601 cm\(^{-1}\) and 1036 cm\(^{-1}\) in the soil degradation analysis, as well as peaks of 1037 cm\(^{-1}\), 1629 cm\(^{-1}\), and 1711 cm\(^{-1}\) in the environment degradation analysis, have been appeared and no peaks removed.

For the LD90/HD10/TS15 sample, in environment degradation analysis, peaks of 2341 cm\(^{-1}\), 2359 cm\(^{-1}\), and 1715 cm\(^{-1}\) have been appeared and no peaks were removed. in soil degradation analysis, peaks of 2341 cm\(^{-1}\), 2359 cm\(^{-1}\), and 1601 cm\(^{-1}\) have been appeared and the peak of 1149 cm\(^{-1}\) removed.

For the LD85/HD15/TS30 sample, in environment degradation analysis, peaks of 2341 cm\(^{-1}\), 2359 cm\(^{-1}\), 1715 cm\(^{-1}\), and 1647 cm\(^{-1}\) have appeared and no peaks were not removed. in soil degradation analysis, the peaks of 1080 cm\(^{-1}\) and 1150 cm\(^{-1}\) have been removed and the peak of 3315 cm\(^{-1}\) has been drastically reduced and the peaks of 2341 cm\(^{-1}\), 2359 cm\(^{-1}\), 1723 cm\(^{-1}\) and 1652 cm\(^{-1}\) appeared.

To introduce the peaks that appeared, the peaks at 2341 cm\(^{-1}\) and 2359 cm\(^{-1}\) are related to the formation of CO\(_2\), which has appeared in specimens that contain starch and regarding degradation of PE in the presence of microorganisms\(^{51}\). accentuated peaks at 1081,1158 cm\(^{-1}\) representing the C-O stretching\(^{20}\), the peak of 1600 cm\(^{-1}\) is attributed to the aromatic ring due to the presence of additives Irganox and Weston399\(^{52}\). the bands in the region of 1000–1100 cm\(^{-1}\) is representing the C-O stretching vibrations (C-O-C, C-O-H) that the degradation of polyolen by oxidation has been leading to the formation of carbonyl or ketone and hydroxyl\(^{53}\). The peak of 1640 cm\(^{-1}\) corresponds to (-C = C-)\(^{54}\), it can also be attributed to the O-H bending of water absorption\(^{55}\).

To monitor the degradation rate in polyethylene, the carbonyl index is used, which is the ratio of the carbonyl peak area (1705–1740 cm\(^{-1}\)) divided by the methylene peak area (1471–1485 cm\(^{-1}\))\(^{56}\). The reason for division by methylene peak area is to eliminate the effect of film thickness.

Table 11
The carbonyl index of degraded specimens in the environment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>peak area (1705–1740 cm(^{-1}))</th>
<th>peak area (1471–1485 cm(^{-1}))</th>
<th>carbonyl index</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>.45</td>
<td>1.14</td>
<td>.40</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>.75</td>
<td>.76</td>
<td>.98</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>.60</td>
<td>.70</td>
<td>.85</td>
</tr>
</tbody>
</table>

According to Table 11, the carbonyl index of sample LD90/HD10/TS15 is higher than the sample with 30wt% TS and LDPE sample.

3.6.3 Rheology of specimens after degradation
Figure 15 depicted the storage modulus and loss modulus versus angular frequency for LDPE, LD90/HD10/TS15 and LD85/HD15/TS30 films. A slight increase of storage modulus and loss modulus can be seen for the specimens degraded in the soil compared to the early specimen, but for the degraded specimens in the environment, a high decrease of storage modulus and loss modulus can be seen.

Table 12 shows the relaxation time and modulus for the samples degraded in the soil.

Table 12: Gc and $\lambda$ of degraded specimens in the soil.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\omega_c$ [rad/s]</th>
<th>$\lambda$ [s]</th>
<th>$G_c$ [Pa]</th>
<th>% Change $G_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>7.0632</td>
<td>0.1415</td>
<td>1.8034 x 10^4</td>
<td></td>
</tr>
<tr>
<td>LD-soil</td>
<td>7.9149</td>
<td>0.1263</td>
<td>1.9712 x 10^4</td>
<td>9.3</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>7.0490</td>
<td>0.1419</td>
<td>1.5969 x 10^4</td>
<td></td>
</tr>
<tr>
<td>LD90/HD10/TS15-soil</td>
<td>6.4421</td>
<td>0.1455</td>
<td>1.9049 x 10^4</td>
<td>19.2</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>5.4485</td>
<td>0.1835</td>
<td>1.9821 x 10^4</td>
<td></td>
</tr>
<tr>
<td>LD85/HD15/TS30-soil</td>
<td>6/9263</td>
<td>0.1353</td>
<td>2.5609 x 10^4</td>
<td>29.2</td>
</tr>
</tbody>
</table>

In the samples degraded in the environment, the storage modulus and loss modulus does not have a crossover point in the range of angular frequency analysis and the amount of loss modulus is greater than the storage modulus which indicates the viscous behavior of the samples. The effect of photo-irradiation on LDPE and its blends is mainly chain scission which leads to a decrease in the molecular weight of the samples. As a result, the samples do not show elastic behavior. According to Table 12 for LDPE and LD85/HD15/TS30 films, it can be seen that the relaxation time was reduced and the modulus was increased. In the LD90/HD10/TS15 film an increase in modulus and no decrease in relaxation time was observed.

Figure 16 shows the complex viscosity versus angular frequency of degraded specimens in the soil and environment compared to the early specimens. A slight increase and a sharp decrease in complex viscosity data are observed for degraded samples in the soil and environment compared to the early specimens, respectively.

Table 13 shows the Power-law model parameters for degraded specimens in the soil and environment compared to the early specimen for (a) LDPE, (b) LD90/HD10/TS15 and (c) LD85/HD15/TS30 films.
Table 13
Power-law model parameters of degraded specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>m [pa.s^n]</th>
<th>%Change</th>
<th>n</th>
<th>R-square</th>
<th>Adj-Rsq</th>
<th>%Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>9191</td>
<td></td>
<td>0.5046</td>
<td>0.9987</td>
<td>0.9984</td>
<td></td>
</tr>
<tr>
<td>LD-soil</td>
<td>$1.053 \times 10^4$</td>
<td>14.5</td>
<td>0.4754</td>
<td>0.9985</td>
<td>0.9982</td>
<td></td>
</tr>
<tr>
<td>LD-Environment</td>
<td>454.5</td>
<td></td>
<td>0.6537</td>
<td>0.9986</td>
<td>0.9984</td>
<td>29</td>
</tr>
<tr>
<td>LD90/HD10/TS15</td>
<td>9636</td>
<td></td>
<td>0.4497</td>
<td>0.9995</td>
<td>0.9994</td>
<td></td>
</tr>
<tr>
<td>LD90/HD10/TS15-soil</td>
<td>$1.126 \times 10^4$</td>
<td>17</td>
<td>0.4667</td>
<td>0.9987</td>
<td>0.9985</td>
<td></td>
</tr>
<tr>
<td>LD90/HD10/TS15-Environment</td>
<td>504.7</td>
<td></td>
<td>0.6616</td>
<td>0.9962</td>
<td>0.9955</td>
<td>47</td>
</tr>
<tr>
<td>LD85/HD15/TS30</td>
<td>$1.302 \times 10^4$</td>
<td></td>
<td>0.4587</td>
<td>0.9992</td>
<td>0.9991</td>
<td></td>
</tr>
<tr>
<td>LD85/HD15/TS30-soil</td>
<td>$1.452 \times 10^4$</td>
<td>11.5</td>
<td>0.4671</td>
<td>0.9988</td>
<td>0.9987</td>
<td></td>
</tr>
<tr>
<td>LD85/HD15/TS30-Environment</td>
<td>1068</td>
<td></td>
<td>0.6275</td>
<td>0.9986</td>
<td>0.9984</td>
<td>37</td>
</tr>
</tbody>
</table>

For values of $n$, except for the LDPE sample degraded in the soil, as seen, an increase in the value of $n$ was observed for all composites degraded in the soil and environment, which is higher for the samples degraded in the environment. This increase is due to the decrease in the dependency of viscosity on the shear rate which can be attributed to the reduction of molecular weight and chain-breaking due to degradation. For the values of $m$, a slight rise and a significant reduction are observed for degraded samples in the soil and environment, respectively. The change of $n$ is proportional to the carbonyl index changes in the Table 11.

4 Conclusions

The biodegradable polymer blends were produced by melt blending of synthetic LDPE, HDPE and the starch biopolymer for packing applications. The effects of starch content in the presence of a different weight percentage of HDPE on the LDPE film properties were investigated in detail. According to the analyzes that were taken, Fourier transform infrared (FTIR) spectra and SEM micrographs confirmed the immiscibility of LDPE/HDPE matrix with TS in the blend. In addition, the SEM micrographs showed a fairly good dispersion of TS (at low wt%) in the blend. DSC analysis showed the immiscibility of LDPE
and HDPE at LD85/HD15 ratio, as well as an increase in crystallinity with increasing HDPE and a
decrease in crystallinity with increasing TS loading. In the analysis of oxygen permeability, the increase of
weight percentage of TS has increased the permeability, but blending LDPE with HDPE could reduce the
oxygen permeability (12.5%) when with the LDPE film. The water absorption of the samples decreased to
some extent with increasing HDPE and the absorption increased with increasing TS. Storage and loss
moduli of samples as well as their complex viscosity with different amounts of HDPE and TS were used
to estimate the relaxation time spectra and zero shear viscosity. By adding HDPE into the matrix in the
presence of TS, rheological properties close to LDPE were obtained and the abovementioned results
indicated that blending LDPE with HDPE could successfully overcome the drawbacks of TS. Finally, it
was found that oxidation of PE was occurred in the degraded samples in the soil and environment, due to
formation of oxygen containing groups which was observed in our FTIR results. Hydroperoxides which
are formed during oxidative degradation of PE could initiate free radical chain scission of the PE chains
which was proved through rheological analysis for the degraded samples in the environment.

Declarations

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Author Contributions

M. Zeraatpisheh carried out the experiments, wrote the main manuscript and prepared all Figures and
Tables in consultation with S. Hassanajili. Both Authors discussed the results and contributed to the final
manuscript. S. Hassanajili reviewed the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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Figures

Figure 1
FTIR spectra for the LDPE/HDPE/TS blend films.

Figure 2

DSC thermograms for the LDPE/HDPE/TS blend films.
Figure 3

Scanning electron microscopy (SEM) micrographs of the tensile fracture surface of (a) LDPE (b) LD95/HD5/TS15 (c) LD90/HD10/TS15 (d) LD85/HD15/TS15 (e) LD85/HD15/TS20 (f) LD85/HD15/TS25 (g) LD85/HD15/TS30.
Figure 4

Percentage of water uptake for the LDPE/HDPE/TS film blends with immersion time with weekly intervals as (a) increase the percentage of HDPE and (b) increase the percentage of TS.

Figure 5

Storage moduli $G'$ and loss moduli $G''$ versus the shear rate at $T = 190^\circ C$ for increasing the percentage of HDPE of the LDPE/HDPE/TS film blends.
Figure 6

Storage moduli $G'$ and loss moduli $G''$ versus the shear rate at $T = 190^\circ C$ for increasing the percentage of TS of the LDPE/HDPE/TS film blends.

Figure 7
Values of $G_c$ and $\lambda$ resulting from the intersection point with increasing the percentage of HDPE for the LDPE/HDPE/TS film blends.

**Figure 8**

Values of $G_c$ and $\lambda$ resulting from the intersection point with increasing the percentage of TS for the LDPE/HDPE/TS film blends.
Figure 9

Values of $\lambda$ and $G$ resulting from the Maxwell model with increasing the percentage of HDPE for the LDPE/HDPE/TS film blends.

Figure 10
Values of $\lambda$ and $G$ resulting from the Maxwell model with increasing the percentage of TS for the LDPE/HDPE/TS film blends.

**Figure 11**

Complex viscosity versus the shear rate at $T = 190\,^\circ$C with increasing the percentage of (a) HDPE and (b) TS for the LDPE/HDPE/TS film blends.

**Figure 12**

The weight loss (%) in the environment with increasing the percentage of (a) HDPE and (b) TS for the LDPE/HDPE/TS film blends.
Figure 13

The weight loss (%) in the soil with increasing wt% of (a) HDPE and (b) TS for the LDPE/HDPE/TS film blends.
Figure 14

FTIR spectra of degraded specimens in the soil and environment compared to the early specimen: (a) LDPE, (b) LD90/HD10/TS15 and (c) LD85/HD15/TS30.
**Figure 15**

Storage and loss modulus of degraded specimens in the soil and environment compared to the early specimen: (a) LDPE, (b) LD90/HD10/TS15 and (c) LD85/HD15/TS30.
Figure 16

Complex viscosity of degraded specimens in the soil and environment compared to the early specimen: (a) LDPE, (b) LD90/HD10/TS15 and (c) LD85/HD15/TS30.