

Mechanical Properties of Biodegradable PLA/PCL Blend Films Prepared with A-Tocopherol

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Manuscript Received online 10/28/2020, Accepted 11/12/2020

Biodegradable blends of PLA and PCL were prepared by solution-blending method based on the complementary mechanical properties between both rigid PLA and ductile PCL. PLA/PCL blend films was prepared using different mass fraction of each component. We then evaluated the addition of α -tocopherol (α -Toc) as antioxidant agent in the blends. The mechanical properties of PLA/PCL biodegradable films were investigated by adding α -Toc in the range of 1.5-3.5 wt.%. Based on this, α -Toc was added to improve the mechanical and barrier properties of the PLA/PCL blend films. With the increase of PCL ratio in PLA/PCL blends, the modulus of elasticity decreased and the elongation at break increased. In addition, it was observed that the opacity of the film increased with increasing PCL ratio. With the addition of α -Toc to PLA-%20/PCL-%80 blend, the elongation at break increased compared to that of this film prepared without α -Toc. However, with the increase of α -Toc percentage in the PLA/PCL films, the elongation at break decreased and the Young's modulus increased. The best mechanical properties for flexible packaging film were seen with the film to which α -Toc was added at 1.5 wt.%. As a result, biodegradable PLA/PCL blend films with desired mechanical properties for packaging film can be obtained by adding PCL to PLA matrix containing with α -Toc as antioxidant additive.

Keywords: PLA, PCL, biodegradable films, α -tocopherol, mechanical properties

Introduction

With the increasing use of petroleum-derived polymers, the variety of products in the packaging industry has also increased with the aim of providing for desired mechanical properties. The wide use of conventional petroleum-based polymers and their environmental impact due to their inconvenient disposal are already alarming, but one alternative could be the promising route of development and use of biodegradable polymers as raw materials for packaging.

Poly(lactic acid) (PLA) and poly(ϵ -caprolactone) (PCL) are two well-known

biodegradable polyesters with interesting and complementary properties^{1,2}. PLA is a semi crystalline thermoplastic that can be obtained from renewable resources such as corn starch¹. PLA can be used in a wide range of applications in different fields because of its great tensile strength and high modulus³. However, PLA is very brittle and this can limit some of its applications³. In order to use of PLA as flexible packaging material, it is necessary to add different additives or to blend flexible polymers such as PCL, which presents high flexibility, low melting point and good compatibility with other polymers. For this purpose additions should be made that can

bring flexibility to the same time, but do not decrease the strength.

In particular, the materials used in the food packaging industry are not desired to cause health problems and they are intended to be environmentally friendly. For this, the materials preferred to improve the mechanical properties of food packaging films should also be selected for the purpose. As if it is preferred to add an antioxidant material to the prepared packaging film in order to improve its mechanical properties and it is successful, both the mechanical properties of the film will improve and its shelf life will be extended.

Referring to previous studies, it has been shown that the introducing of α -tocopherol (α -Toc) increases the strength of PLA blends, and it can be used for food packaging⁴⁻⁶. Also, the use of α -Toc which has antioxidant properties, in the packaging films can help to extend the life of the food during its release².

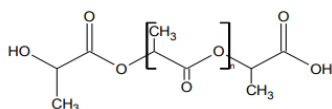


Fig. 1. Chemical structure of PLA.

In previous studies, it was observed that α -Toc was added separately to PLA and different polymers, however there is no triple combination study by adding of α -Toc as an antioxidant additive for PLA/PCL/ α -Toc film has ever been found. In this study, the purpose of using α -Toc is to gain antioxidant properties and improve the mechanical properties of the PLA/PCL film.

Experimental

Materials:

Poly(L-lactic acid) (PLA) (Ingeo 4043D) granule was purchased in granular form from NatureWorks LLC (USA). Poly(ϵ -

caprolactone) (PCL) Capa™ 6500 (PCL65) and Capa™ 6800 (PCL68) was purchased from Perstorp (Sweden) in granular form with mean molecular weight of $5 \times 10^4 \text{ g mol}^{-1}$ and $8 \times 10^4 \text{ g mol}^{-1}$. Chloroform (CHCl_3) with a density of 1.489 g/mL used as polymer solvent was purchased from Lab-Scan Analytical Sciences Ltd. DL-alpha tocopherol acetate (Toc) (>99% pure) was purchased from BASF (USA). All chemicals were used as received without any further purification process.

Films Preparation:

To prepare the PLA/PCL films, polymers was added by 8 wt. % of the solvent, respectively. Chloroform was used as a solvent for polymer solutions. Desired amounts of polymers was weighed and chloroform was added to the polymers. This solution was mixed with a magnetic stirrer for 24 h at room temperature. After mixing period, the solution was cast onto the glass plate (25x25 cm) and removed with hood waiting for 24 h at room temperature. Glass plates were dried at 60 °C under vacuum for 24 h. Finally, films separated from the glass plate by immersing pure water bath and dried at room temperature. The concentrations of PLA/PCL prepared films are listed in Table 1.

In addition, the PLA/PCL films containing with the 80 wt.% content of PCL were prepared by the addition of α -Toc in the range of 1.5, 2.5, 3.5 wt.% (based on the polymer weight) as antioxidant additive under the same conditions.

α -Toc concentration was chosen according to the studies in the literature⁷, which indicated that the most efficient results were obtained up to 3-3.5% amount of α -Toc. The weight percentages of α -Toc mixed with PLA/PCL68 films are listed in Table 2.



Fig. 2. Pictures of T1, T2 and T3 films (Prepared with α -Toc %1.5, 2.5, 3.5).

Table 1. Composition of PLA/PCL films (wt. %).

Sample	PLA	PCL65	PCL68
P1	100	-	-
P2	-	100	-
P3	50	50	-
P4	80	20	-
P5	20	80	-
P6	-	-	100
P7	80	-	20
P8	70	-	30
P9	50	-	50
P10	30	-	70
P11	20	-	80

Table 2. Composition of P11/ α -Toc films.

Sample	α -Toc (wt. %)
T1	1.5
T2	2.5
T3	3.5

Characterization:

Mechanical properties (Tensile strength, elongation at break and Young's modulus) were assessed with a Universal Test Machine (Zwick, Z0500, Germany) according to ASTM D 882-02. Film samples were cut into strips with dimensions of 2.54 × 50 cm and preserved at 23 °C and 50% relative humidity for 24 h before testing. The specimens were tested at a crosshead speed of 500 mm min⁻¹.

The thickness of the samples was determined by digital micrometer (Digimatic

Micrometer QuantuMike-IP65, Mitutoyo, Japan).

Results and discussion

The primary purpose of the experiments; it is to obtain flexible packaging film by blending of PLA and PCL biodegradable polymers. Because of the biodegradable PLA shows a hard and brittle structure, the use of PCL polymer, which is known to have flexibility, was preferred in order to give flexibility to the packaging film. In this context, blends of two different molecular weights PCL (PCL65: 60000 g/mol, PCL6800: 68000 g/mol) and PLA in different compositions were formed into a film.

Table 3 demonstrates the effect of both PCL65 and PCL68 on the tensile strength, elongation at break and Young's modulus of the PLA/PCL films. According to the experiment results; in terms of flexibility, it has been observed that PCL68 gives higher results in combination with PLA compared to PCL65.

In the table where PLA-20/PCL68-80 ratio seemed the most efficient, the elongation at break gave a high value such as 422.5%. Based on this, it can be concluded that it is more appropriate to prefer PCL68 in the compositions formed with PLA for the next steps. The Young's modulus and tensile strength were expected to decrease with higher PCL.

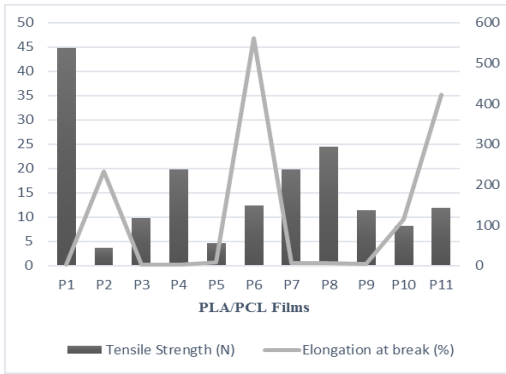


Fig. 3. Tensile strength and elongation at break of PLA/PCL films.

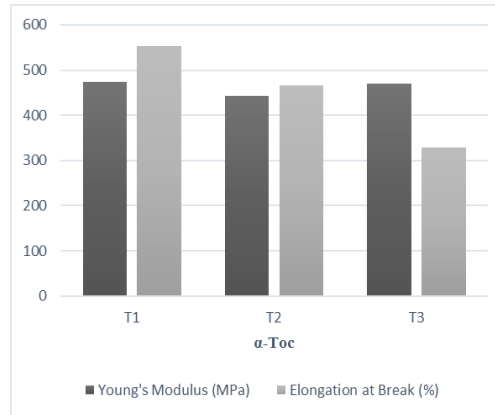


Fig. 3. Young's Modulus and elongation at break of PLA-20/PCL68-80 films with α -Toc (T1: 1.5%, T2: 2.5%, T3: 3.5%).

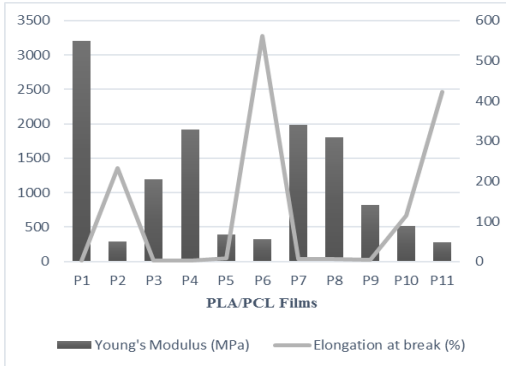


Fig. 4. Young's Modulus and elongation at break of PLA/PCL films.

In addition, in order to gain a different perspective on the study, α -Toc component, which is known to be released into the food during its use and delaying its degradation, was used when it is placed in food packaging materials. Table 4 displays the effect of α -Toc on the tensile strength, elongation at break and Young's modulus of the PLA/PCL68 films in the ratio of 20/80 wt.%.

Table 3. Mechanical properties of PLA/PCL films.

Sample	Tensile Strength (N)	Elongation at break (%)	Young's Modulus (MPa)	Thickness (micron)
P1	44.86	2.62	3208.34	23
P2	3.63	232.85	286.96	10
P3	9.74	1.44	1192.39	20
P4	19.79	2.96	1915.70	16
P5	4.71	8.21	388.79	12
P6	12.41	561.99	324.02	18
P7	19.75	5.86	1979.63	16
P8	24.53	6.08	1807.22	22
P9	11.37	4.31	823.25	23
P10	8.20	115.33	512.21	18
P11	11.86	422.45	274.87	30

Test speed: 500 mm/min

The elongation at break values of PLA-20/PCL68-80 films containing 1.5% (T1), 2.5% (T2) and 3.5% (T3) α -Toc were 553.51%,

467.06%, 328.51%, respectively. The elongation at break of the film prepared without adding tocopherol with the same PLA/PCL

ratio was 422.5%. Although α -Toc reduced flexibility, the film which was contained α -Toc it showed better mechanical properties than without contained α -Toc. Based on this, by

adding a certain amount of tocopherol to the packaging film, while providing antioxidant properties to the food packaging film, its mechanical properties can also be improved.

Table 4. Mechanical properties of PLA-20/PCL68-80 films prepared with α -Toc.

Sample	Tensile Strength (N)	Elongation at Break (%)	Young's Modulus (MPa)	Thickness (micron)
T1	13.47	553.51	473.23	21
T2	12.70	467.06	442.86	19
T3	12.76	328.51	469.94	22

Test speed: 500 mm/min

Conclusions

PLA/PCL biodegradable films were prepared by using PLA (4043D), PCL65 (CAPA™6500) and PCL68 (CAPA™6800) polymers with α -Toc as an antioxidant additive.

Biodegradable films were obtained by solvent-casting method. Mechanical tests are made according to ASTM D882 standards. The highest elongation at break of 422.45% was obtained for the PLA-20/PCL68-80 (P11) blend film. In prepared with PLA/PCL blends; PCL68 showed better mechanical properties as compared to that of PCL65. As the rate of adding α -Toc to the film increased, the elongation at break decreased and the Young's modulus increased. However, the best mechanical properties for flexible packaging film were seen with the film to which α -Toc was added at 1.5%. Continuing this study, after examining the antioxidant and thermal properties, α -Toc percentage will be determined.

Acknowledgements

The authors would like to thank to Elif Global Packaging Turkey for their support for the mechanical testing of films.

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