

Enhancement of properties and biodegradability of polybutylene succinate by epoxidized palm oil

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Abstract

In this study, epoxidized palm oil (EPO) was employed as a modifier for polybutylene succinate (EPO) using chloroform as a solvent by solution casting process. Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups of PBS and PBS/EPO blends. Thermal stability and morphological properties of the blends were investigated by thermogravimetric analyzer (TGA) and scanning electron microscope (SEM) technique, respectively. Biodegradation of this blend was also studied. The FTIR spectra indicated that there are some molecular interactions by intermolecular hydrogen bond between PBS and EPO. The PBS/EPO blend showed high thermal stability and significant improvement of biodegradation compare to pure PBS. Morphological results of PBS/EPO blends showed that EPO was good miscible with PBS.

Keywords: biodegradable polymers; epoxidized palm oil; polybutylene succinate

1. Introduction

Recently, biodegradable polymers have attracted much attention as substitutes for petrochemicals-based polymers due to its benefits for both health and environmental protection [1, 2]. Accordingly, many efforts have been made by materials scientists and engineers to discover, develop and modify of biodegradable polymers derived from renewable resources [3]. Polybutylene succinate (PBS) is one of the biodegradable thermoplastic polyesters which can prepared from butanediol and succinic acid produced by fermentation process [4, 5]. In addition to its applications in textile industry and medical fields, PBS is a promising candidate to produce disposable packaging. However, low molecular weight and low stiffness and high cost restrict its applications [6]. Many studies have been conducted to enhance the properties by blending of biodegradable polymers with other polymers or using low molecular weight plasticizers [7–13]. The morphologies and phase behaviors of polylactic acid /PBS blend have been investigated by Park *et al* [14], while the structures and properties of this blend were studied by Yokohara *et al* [15]. Jin *et al* reported that physical, thermal properties and biodegradation of PBS were evaluated by modification it with peroxide [16].

In this study, epoxidized palm oil (EPO) was used to improve properties and biodegradation of PBS. EPO is produced from esters of glycerol in palm oil containing different of saturated and unsaturated fatty acids. It offers many advantages in chemical industries field because it is derived from renewable, biodegradable and abundant raw materials [9, 17, 18]. The literature review in research reveals there is no information for modification of PBS with EPO.

2. Materials and methods

2.1 Materials

Epoxidized palm oil was provided by Advanced Oleochemical Technology Division (AOTD), Malaysia. PBS and chloroform were purchased through local suppliers from Nagoya, Japan and Merck, Germany, respectively.

2.2 Preparation of PBS/EPO blends

The required amounts of PBS and EPO were dissolved in 10 ml chloroform separately. The EPO solution was then transferred into the PBS solution with a dropper and continuous stirring. After all the EPO solution was transferred into the PBS solution, the resultant mixture was then stirred for 1 hour. After that, the mixture was refluxed for 2 hours. The PBS/EPO blend was poured into a Petri dish and left to dry. The amount of PBS to EPO used in this study is listed in Table 1.

Sample	Weight of PBS (g)	Weight of EPO (g)
1	1.00	0.00
2	0.90	0.10
3	0.85	0.15
4	0.80	0.20
5	0.75	0.25
6	0.55	0.45

Table 1. The amount of the PBS/EPO blends
1. táblázat A PBS/EPO keverékek összetétele

2.3 Fourier-transform infrared (FTIR) spectroscopy

The FTIR spectra of the blends samples were recorded by the FTIR spectrophotometer (Perkin Elmer FT-IR-Spectrum BX, USA) using KBr disc technique.

2.4 Scanning electron microscopy (SEM)

The morphology of tensile fracture surface of the blend was observed by scanning electron microscope (SEM) at room temperature. A JEOL (model JSM-6300F) SEM with field emission gun and accelerating voltage of 5 kV was used. A gold coating of a few nanometres in thickness was coated on tensile fracture surfaces.

2.5 Thermogravimetric analyzer (TGA)

The thermal stability of the samples was studied by using Perkin Elmer model TGA 7 Thermogravimetric analyzer was used to measure the weight loss of the samples. The samples were heated from 30 to 800 °C with the heating rate of 10 °C min⁻¹ under nitrogen atmosphere at the flow rate of 20 ml min⁻¹.

2.6 Biodegradation test

The biodegradability of the PBS, PBS /EPO blend and the PCL/CS-OMMT nanocomposite was determined as per ASTM D5338-92. A mixture of mature compost (200 g, wet weight) and the plastics (5%, on a dry basis) were introduced and incubated at 58 °C. The moisture content of the compost was maintained at 65%. CO₂ produced from the compost was absorbed by a 0.4 N potassium hydroxide and 2 N barium chloride mixture solution, and was quantified by titrating the solution with 0.2 N HCl.

3. Results ad discussion

According to our recent paper [19], the PBS/EPO blend at the weight ratio of 55/45 has redox property. Therefore, this ratio was used in the subsequent experiments.

The FTIR spectra of PBS and PBS/EPO blend are shown in Figs. 1 and 2. The peaks located at 2.947 and 1.714 cm⁻¹ of PBS were assigned to the stretching vibration of -CH₂ and vibration of -C=O bonds, respectively; while in the blend material these peaks were found in the neutralized regions of 2.926 and 1.718 cm⁻¹. This result is in agreement with previous results that show the peaks of infrared were shifted due to the interaction between polylactic acid and EPO in this blend [9]. The FTIR result indicates that there are some molecular interactions between PBS and EPO. It was believed that hydrogen bonding could be formed between the ester group of PBS and the oxirane group of EPO.

The interaction between PBS and EPO may also be attributed to the possible hydrogen bonding that occurs between the oxirane group in EPO and the small amount of terminal hydroxyl groups in the PBS main chain. A proposed possible site for interaction between PBS and EPO is shown in Fig. 3. FTIR spectrum of the neat PBS supports this claim which shows a peak at 3.433 cm⁻¹ (hydroxyl group stretching). It was observed this characteristic peak in the neutralized regions of 3.431cm⁻¹ with decrease in the relative strength of this peak due to incorporation of EPO in the PBS.

Thermogravimetric analysis was used to study the thermal stability of PBS/EPO blends by measuring their thermal decomposition temperature at the onset and end of weight loss. Higher decomposition temperature means better thermal

stability for the blends. The thermal decomposition temperature at the onset and end of weight loss for PBS/EPO blends was shown in Fig. 2. With the addition of EPO, the thermal stability of PBS component was increased. For example, the onset of PBS increased from 330 to 350 °C and the end of decomposition process increased from 430 to 480 °C (Fig. 4). It is clear that the increase of thermal stability of PBS came from the effect of EPO.

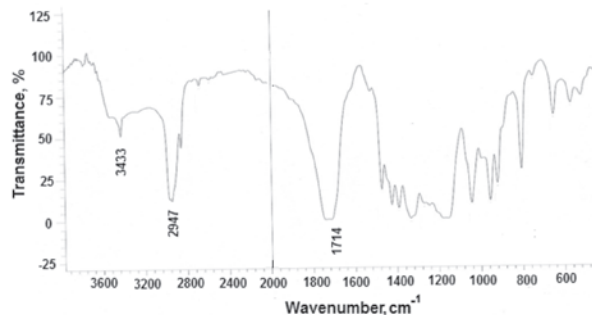


Fig. 1 The FTIR spectrum of EPO
1. ábra Epoxidált pálmaolaj FTIR spektruma

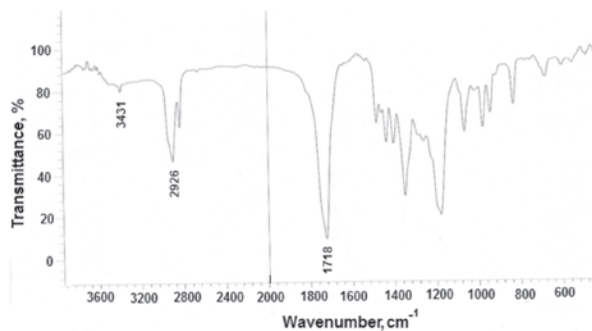


Fig. 2 The FTIR spectrum of PBS/EPO blend
2. ábra PBS/EPO keverék FTIR spektruma

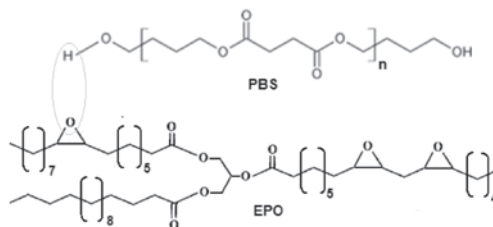


Fig. 3. Proposed chemical interactions (intramolecular hydrogen bonding) between PBS and EPO
3. ábra Feltételezett kémiai kölcsönhatások (molekulaközi hidrogénkötések) a PBS és EPO között

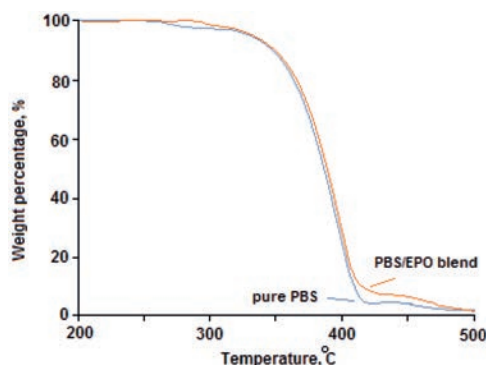


Fig. 4 Thermograms of PBS/EPO blends
4. ábra PBS/EPO keverékek termogramjai

The biodegradation of PBS and PBS/EPO blend was studied by the weight loss in the compost. The weight change of the PBS/EPO blend in the compost at 58 °C is shown in Fig. 5. The biodegradability of neat PBS blend increases with increasing of incubation time after blending with EPO. It is clearly seen that the biodegradability is significantly enhanced after 60 days (4.90% weight loss).

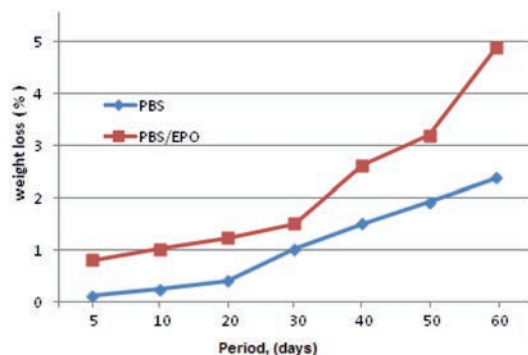


Fig. 5 Weight loss of pure PBS and PBS/EPO blend
5. ábra Tiszta PBS és PBS/EPO keverék tömegvesztetése

Phase morphology of the neat PBS and PBS/EPO blends were assessed by SEM. The SEM image of the neat PBS and PBS/EPO blend are shown in Fig. 6. SEM of PBS/EPO blends micrographs show very good compatible morphologies without the edge, cavity, and holes resulting from poor interfacial adhesion. It is possible that the good adhesion of these blends is due to molecular interactions between PBS and EPO that could create hydrogen bonds.

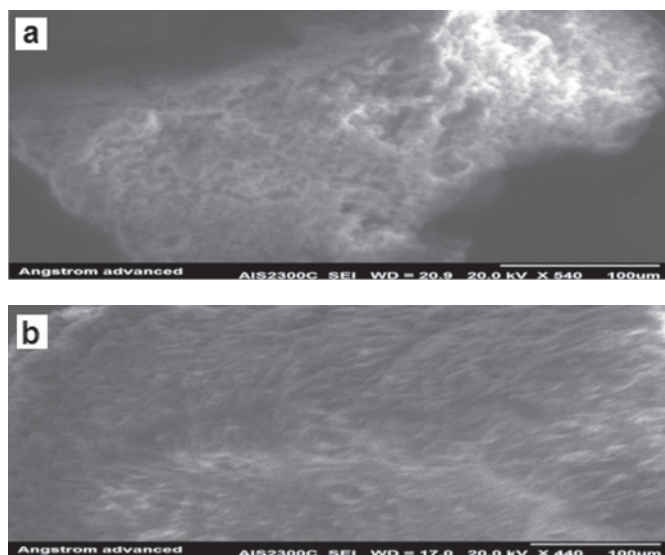


Fig. 6 SEM micrographs of fracture surfaces of pure PBS and PBS/EPO blend
6. ábra Törésfelületek SEM felvételei tiszta PBS és PBS/EPO keverék esetén

4. Conclusion

The modification of EPO by new renewable, biodegradable and abundant raw materials (EPO) via solution casting process using chloroform as a solvent was reported. The results indicate that improved biodegradability could be achieved by incorporation of EPO. FTIR spectroscopy shows some molecular interactions by intermolecular hydrogen bond between PBS and EPO. In addition to high thermal stability properties was observed for

PBS/EPO blends compare to pure PBS, SEM micrographs of PBS/EPO blends show good compatible.

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Polibutilén-szukcinát tulajdonságainak és biológiai lebomlókéességének javítása epoxidált pálmaolajjal

A szerzők bemutatják az epoxidált pálmaolaj (EPO) hatását polibutilén-szukcinátra (PBS), kloroform oldószer felhasználásával. A vizsgált keverékek funkciós csoportjait Fourier-transzformációs infravörös spektroszkópiával (FTIR) határozták meg, míg a termikus stabilitást és a morfológiai jellemzőket termogravimetriai (TGA) eljárással és pásztázó elektronmikroszkópos (SEM) vizsgálattal ellenőrizték. Az FTIR spektrumok igazolták az EPO és PBS összetevők között kialakuló molekulaközi hidrogénkötések meglétét. A létrehozott elegyek termikus stabilitása jó, és a biológiai lebomlókéességük számottevően jobb, mint a kezeletlen PBS komponensé. A morfológiai vizsgálatok igazolták, hogy az EPO és PBS összetevők jól elegyednek egymással.

Kulcsszavak: biológiailag lebomó polimerek; epoxidált pálmaolaj; polibutilén-szukcinát



The European Polymer Federation (EPF) is an umbrella organization of national polymer groups in Europe.

The goal of EPF is to coordinate, inform about and support the development of polymer science in Europe.

Currently EPF has 24 full members and 5 associate members from 27 countries.

Major activities of EPF is the organization of congresses, conferences, workshops and summer schools.

The EPF is guided by its chairlady, general secretary, executive committee and general assembly.

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