

# Synthesis and Characterization of Certain Biodegradable Chitosan/Lactic Acid-based Polyester Blend Films

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## Abstract

Biodegradable blend films based on chitosan with poly(ethylene glycol lactate-co-ethylene glycol terephthalate), PEGLT and poly(butylene lactate-co-butylene succinate), PBLSA, were prepared by solution-mixing and film-casting method. The main objective of this investigation was the study and characterization of chitosan/lactic acid-based polyester blends which are useful as bio-packaging material for potential food applications. The first part of the investigation was related to the synthesis and characterization of polyesters, PEGLT and PBLSA by melt polycondensation method. The synthesized polyesters were characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and X-ray diffraction analysis. Then, the chitosan/polyester blend films were prepared using acetic acid-acetone solvent system. These blend films were also investigated for their miscibility using FTIR spectra and X-ray diffractogram. FTIR spectra showed that changes in the finger print region of the chitosan amide band in the blend were observed, indicating compatibility between hydrophobic chitosan with synthesized polyesters. Morphologies of these blend films were viewed using scanning electron microscopy.

**Keywords:** Biodegradable, chitosan, bio-packaging, melt polycondensation

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## INTRODUCTION

In the past decade, great efforts have been made to design and synthesize various PLLA-based biodegradable copolymers through combining biodegradable PLLA units with nondegradable polymers, especially aromatic polyesters [1, 2]. Chen *et al.* [3] reported the synthesis of biodegradable aliphatic/aromatic copolyesters (Mw in a range of 16,000–32,900) from terephthaloyl dichloride, bisphenol-A, 1,6-hexanediol and oligolactide. Initial experiments indicated the enhanced hydrolytic degradability and good biocompatibility because of the incorporation of PLLA. Du *et al.* [4] obtained moderate molecular weight biodegradable-cum-photoactive liquid crystalline copolyesters ( $\eta_{inh}$  in a range of 0.168–0.325 dL/g) from ferulic acid, 4-hydroxybenzoic acid and D,L-lactic acid. Increasing LA content and adjusting feed ratios could improve the solubility and biodegradability of the obtained copolyesters, while still retaining the liquid crystallinity. However, in most cases biodegradable copolyesters above are prepared based on dimethyl terephthalate or diacyl

dichloride as starting reactants and aromatic components. This process would produce toxic byproducts such as methanol or hydrochloride which had adverse effects on the environment.

Moreover, biodegradable behaviors of those copolyesters could not be satisfied and usually showed a slow degradation which limited their biomedical applications. Polylactide (polylactic acid) is a biodegradable aliphatic linear polyester which has many applications due to good processing abilities [5, 6]. Its monomer, lactic acid, is derived from agricultural products such as starch or sugar. In addition, PLA is proven as a biocompatible material with appreciable mechanical properties comparable to other commodity plastics. However, its low toughness has limited its use in certain applications. In order to improve the mechanical properties of PLA and retain its advantages of degradability, a copolymerization of lactic acid and other aromatic esters has been carried out. In many applications of the polymers, for example as biodegradable packing materials, the sorption and the diffusion of low molecular

components in the materials play an important role. Both chitosan and polylactide are biodegradable modern polymers from renewable resources.

Chitosan is a polysaccharide which belongs to the class of modern high-tech biopolymers that find applications in technology, medicine, agriculture and biotechnology [7]. Chitosan is a naturally occurring, bio-degradable, non-toxic, non-allergenic, odorless, biocompatible with living tissues, biodegradable biopolysaccharide derived from chitin, found in abundance in nature. Due to the basic character, it shows unique features such as bioactivity, biodegradability and biocompatibility, which distinguish it from other polysaccharides. These properties are a result of uniformly distributed amino groups in polyanhydro-glutamine chain. By physicochemical or chemical modification of chitosan, a number of different practically important polymer forms are produced [8, 9]. In many applications of the polymers, for example as biodegradable packaging materials, the sorption and the diffusion of low molecular components in the materials play an important role.

Chitosan has a potential as a packaging polymer and more particularly as an edible packaging. Indeed, this polymer has excellent oxygen and carbon dioxide barrier properties [10] and interesting bacteriostatic [11] and fungistatic properties [12]. Unfortunately, there are some limitations to the application of chitosan film for packaging, due to its high sensitivity to moisture. One strategy to overcome this drawback is to associate chitosan with a moisture resistant polymer, while maintaining the overall biodegradability of the product. Various biodegradable polymers, such as poly(vinyl alcohol) (PVA) [13], polyamide 6 [14], poly(3-hydroxybutyric acid) (PHB) [15] and poly( $\epsilon$ -caprolactone) (PCL) [16, 17], have been associated with chitosan to modify the hydrophilic properties of chitosan. PLA is a linear aliphatic thermoplastic polyester, produced from renewable resource and readily biodegradable [18]. Thanks to its mechanical properties comparable to those of polystyrene [19] and its good water vapor barrier [20], PLA could reasonably substitute conventional polymers in domains such as food packaging.

On the basis of the above-mentioned facts, it is obviously necessary to obtain a better understanding for these kinds of chitosan/polyester blends. The authors have synthesized two lactic acid-based polyesters. Using the synthesized polyesters, chitosan/polyester blend films were prepared by solution-mixing and film-casting method. Some results regarding the structure and morphology as well as the related properties of these blend films are presented here.

## EXPERIMENTAL

### Materials

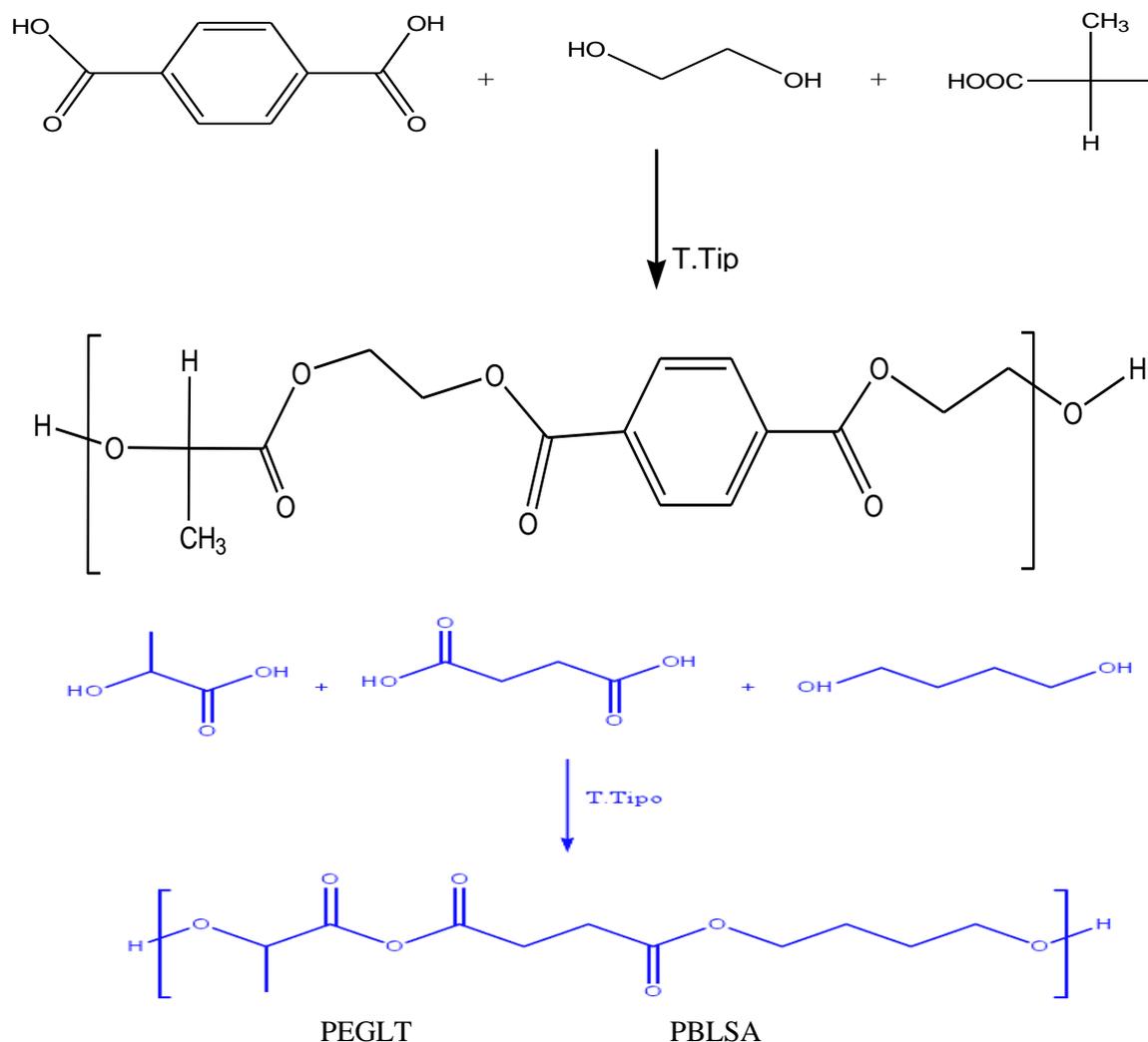
Lactic acid (Merck AR grade) and terephthalic acid (Lancaster AR grade) were recrystallized from deionized water and used. Chitosan (Merck AR grade) ethylene glycol (Lancaster, AR grade) and 1,4 butane diol (Merck AR grade) succinic acid (Lancaster AR grade) were dried with CaO overnight and then distilled under reduced pressure. Titanium tetra isopropoxide, used as catalyst, purchased from Lancaster was used as such. All the other materials and solvents used were of analytical grade.

### Synthesis

The copolyesters were synthesized by a two-step melt polycondensation method. The polycondensation flask was a three-neck flask equipped with a nitrogen inlet, a condenser and a thermometer. A magnetic stirrer was used to stir the reaction mixture. As an example, the synthesis of poly(ethylene glycol lactate-co-ethylene glycol terephthalate), PEGLT has been described. The reaction mixture was 0.1 mol lactic acid, 0.1 mol terephthalic acid and 0.2 mol ethylene glycol. The reaction mixture was purged with nitrogen and heated in an oil bath. The temperature of the reaction mixture was raised to 150 °C in 20 min. Then the temperature was gradually raised in 10 °C steps every minute to the fixed reaction temperature of 210 °C to remove water being the esterification byproduct. When water ceased to be generated, a predetermined amount of titanium tetra isopropoxide, TTiPO (0.1 mmol) catalyst was added to the reaction mixture. Subsequently, the pressure of the reaction system was gradually decreased and polycondensation was continued at 210 °C under a final reduced pressure lower than 0.5 mmHg. The reaction was terminated when the rotation of the mechanical stirrer was

stopped. The resulting crude copolyesters were dissolved in chloroform and then poured into excess of dry cold methanol to purify the polyester. The precipitated copolyesters were

dried in a desiccator for further characterization.



**Fig. 1:** Scheme of the Synthesis Reaction of Polyesters PEGLT and PBLSA.

### Preparation of Chitosan/Polyester Blends

Chitosan solution was prepared by dissolving chitosan in 1.0% (v/v) acetic acid aqueous solution with a 1.0 wt% chitosan concentration. In a typical experiment for preparing with PEGLT and PBLSA/chitosan thin film, 0.5 g of chitosan was first dissolved into 50 mL of 1.0% (v/v) acetic acid aqueous solution, and then, a certain amount of acetone was slowly added with vigorous stirring for 2 h, followed by adding 2% (w/v) PEGLT/PBLSA solution in acetone drop by drop with vigorous stirring for additional 2 h. Subsequently, this newly obtained gelatinous mixture was degassed under reduced pressure

and cast into teflon petri dish. The film with dish was then immersed into NaOH-CH<sub>3</sub>CH<sub>2</sub>OH aqueous solution (NaOH was dissolved on 80% ethanol aqueous solution with 0.5% NaOH) for 24 h. Finally, the solid-like film was exhaustively washed with distilled water until neutrality was achieved and dried slowly in air at room temperature for about 7 days.

### Characterization

#### *Inherent Viscosity*

The inherent viscosity of the synthesized polyester solutions in chloroform was

measured at 30 °C in a constant temperature bath using Ubbelohde Viscometer.

### Solubility Test

Solubility of random polyesters PEGLT and PBLSA was determined using various solvents qualitatively. It may be noted that the two polyester samples exhibit the similar solubility pattern despite their different compositions. Polyesters maintain a good solubility in acetone, CHCl<sub>3</sub>, THF, DMF and DMSO. The polyesters are insoluble in water, methanol and ethanol.

### Fourier-Transform Infrared (FTIR) Spectroscopy

IR spectra of the polyesters were recorded using a Perkin Elmer IR spectrometer in the range of 3800 cm<sup>-1</sup> to 480 cm<sup>-1</sup>. The samples were embedded in KBr pellets.

### <sup>1</sup>H NMR Spectra

<sup>1</sup>H NMR spectra were recorded on AV 3500 MHz spectrometer by using 7% wt of trifluoroacetic acid/CDCl<sub>3</sub> mixed solvent.

### <sup>13</sup>C NMR Spectra

<sup>13</sup>C NMR spectra were recorded on Jeol Model GS X at 300–600 MHz in deuterated chloroform as solvent.

### X-ray Diffraction Analysis

A Siemens D 500 diffractometer with CuKα filtered radiations was used for assessing the crystallinity of the polymers. The samples were scanned over the range of 2θ angle, from 5 ° to 50 °

### Scanning Electron Microscopy (SEM)

The morphologies of the chitosan/polyester blend films were examined by scanning electron microscopy (SEM).

## RESULTS AND DISCUSSION

### Inherent Viscosity and Solubility Studies

The inherent viscosity of the synthesized polyesters were measured in chloroform using Ubbelohde viscometer. The inherent viscosity and solubility of the polyesters are presented in Tables 1 and 2 respectively.

**Table 1:** Inherent Viscosity of Polyesters PEGLT and PBLT.

Polymer	Inherent viscosity $\eta_{inh}$ (dL/g)
PEGLT	0.82
PBLSA	0.9

The synthesized polyesters are soluble in CHCl<sub>3</sub>, acetone, DMSO but insoluble in alcohols and water.

**Table 2:** Solubility of Polyesters PEGLT and PBLSA.

S. No.	Polymer	Acetone	CHCl <sub>3</sub>	DMSO	Methanol	Ethanol	THF	DMF	Water
1	PEGLT	+++	+++	++	--	--	++	++	--
2	PBLSA	+++	+++	++	--	--	++	++	--

**Note:** +++ – Freely Soluble, ++ – Soluble, -- – Insoluble

### Fourier-Transform Infrared (FTIR) Spectroscopy

IR spectroscopy is a common technique for investigating the intermolecular and intramolecular interactions in polymer blends. Figures 2 and 3 present IR spectra of PEGLT, PBLSA, chitosan and two representative blend thin films: PEGLT/chitosan and PBLSA/chitosan. Several characteristic bands of PEGLT and PBLSA are located at 809 cm<sup>-1</sup> and 723 cm<sup>-1</sup> (CH bend); 1046 and

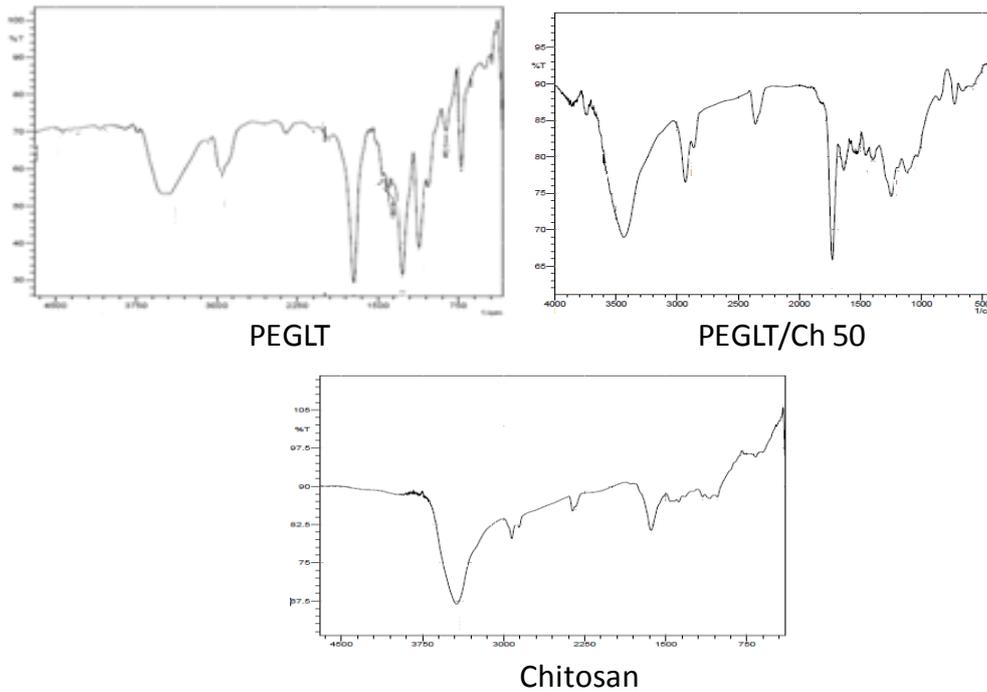
1116 cm<sup>-1</sup> (=C—O stretch) 1395 and 1394 cm<sup>-1</sup> (CH<sub>2</sub> wag); 1444 and 1427 cm<sup>-1</sup> (CH<sub>3</sub> bend); 1734 and 1725 cm<sup>-1</sup> (C=O stretch, ester group); 2963 and 2958 cm<sup>-1</sup> (CH stretch); 3078 (CH<sub>3</sub> stretch); 3613 and 3481 m<sup>-1</sup> (OH stretch, end group).

The main bands in the IR spectrum of chitosan can be seen as follows: a broad and strong overlapped band at around 3443 cm<sup>-1</sup> (OH and NH stretch); two weak bands at 2924 and

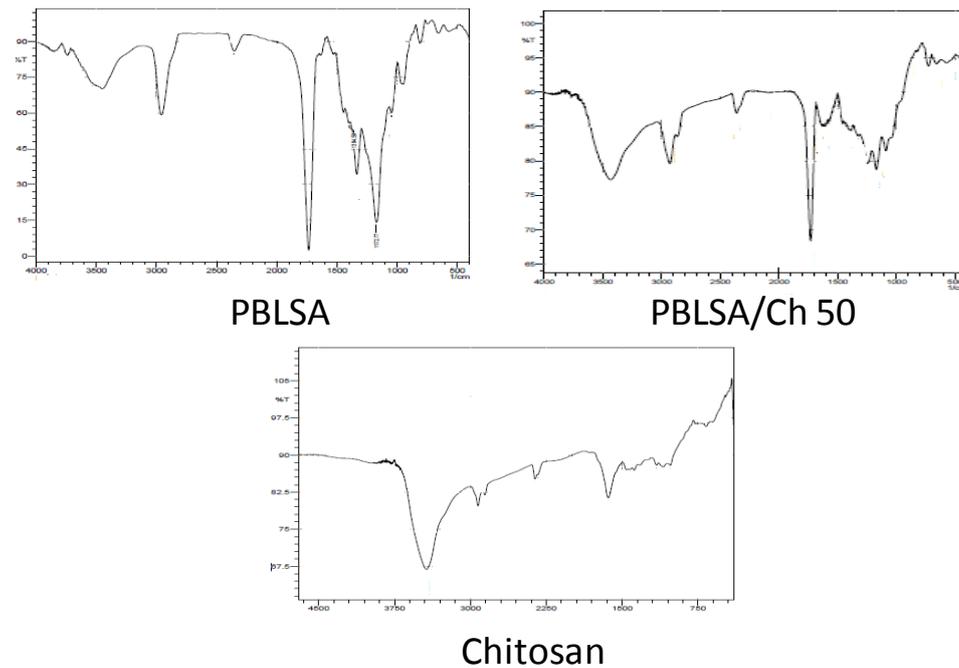
2857  $\text{S cm}^{-1}$  (CH stretch); two middle strong bands at 1639 and 1584  $\text{cm}^{-1}$  (amide I and amide II); 1160, 1094, and 1023  $\text{cm}^{-1}$  (saccharide structure) [21].

It can be observed from Figures 2 and 3 that a noticeable change occurs in the spectrum of PEGLT/chitosan and PBLSA/chitosan in

comparison with the spectrum of each component. The two original bands of the chitosan component at 1639 and 1584  $\text{cm}^{-1}$  for amide I and amide II are shifted to 1634 and 1557  $\text{cm}^{-1}$  for PEGLT/chitosan and 1615 and 1563  $\text{cm}^{-1}$  for PBLSA/chitosan a clearly measurable decrease in wavenumber for both peaks were recorded.



**Fig. 2:** IR Spectra of PEGLT, Chitosan/PEGLT Blend and Chitosan.

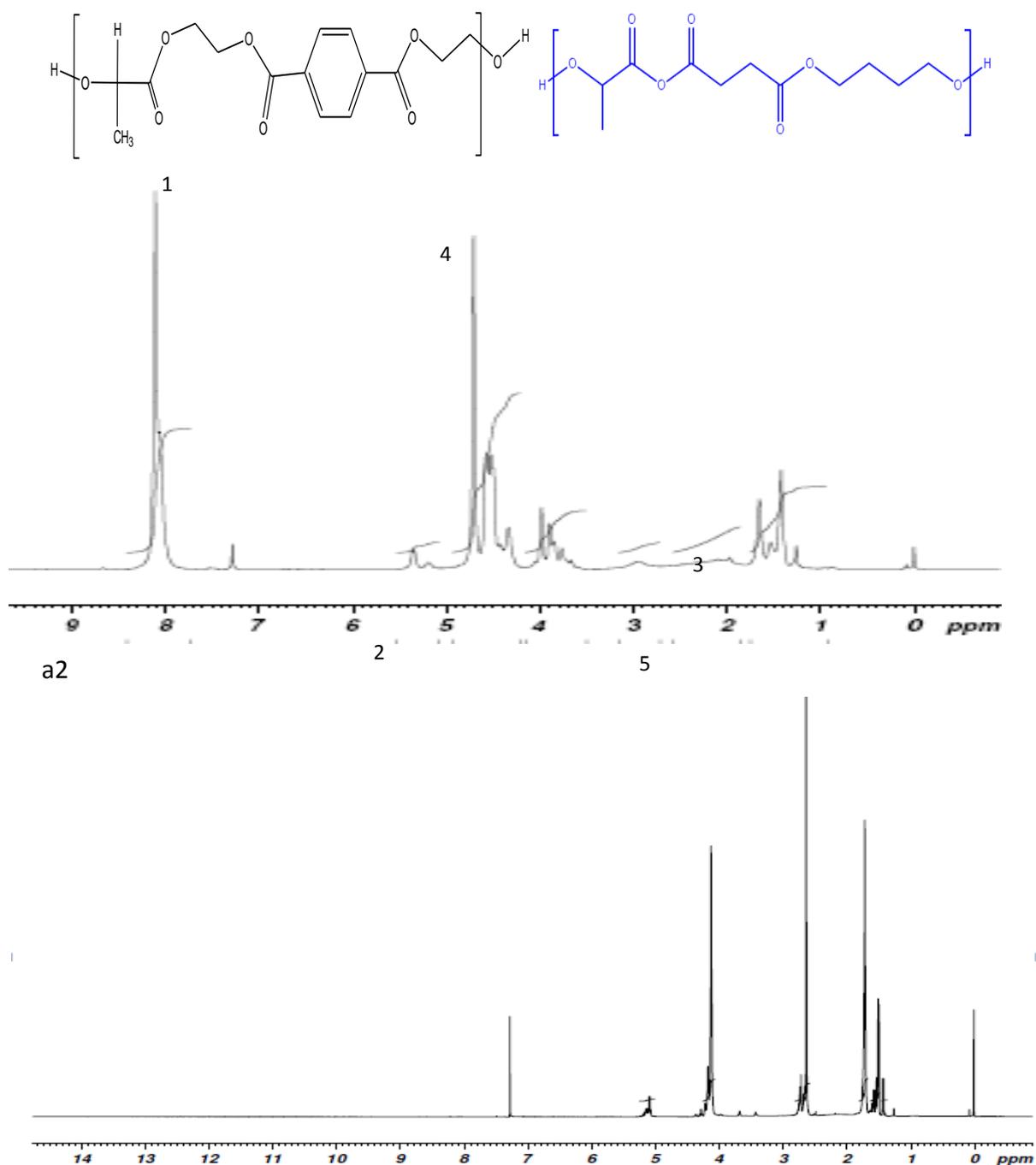


**Fig. 3:** IR Spectra of PBLSA, Chitosan/PBLSA Blend and Chitosan.

**<sup>1</sup>H NMR Spectroscopy**

The chemical shift values obtained from <sup>1</sup>H NMR spectra of the copolyesters are as follows. Aromatic protons of terephthalic group were observed at 8.1–8.08 ppm (singlet),

methylene protons of Diols (-CO-O-CH<sub>2</sub>) at 4.7–3.3 ppm (multiplet), methyl protons of LA at 1.9–1.2 ppm and methine protons of LA at 5.3–5.1 ppm.



**Fig. 4:** <sup>1</sup>H NMR Spectra of Polyesters PEGLT and PBLSA.

**<sup>13</sup>C NMR Spectroscopy**

The chemical shift values obtained from <sup>13</sup>C NMR spectra of the copolyesters are as follows. Aromatic group of terephthalic was observed at 134–129 ppm (multiplet),

methylene protons of Diols (-CO-O-CH<sub>2</sub>) at 20.39–25.4, 69.32–69.55 ppm (multiplet), methyl group of LA at 20–16 ppm (multiplet) and methine protons of LA at 69–62 ppm (multiplet).

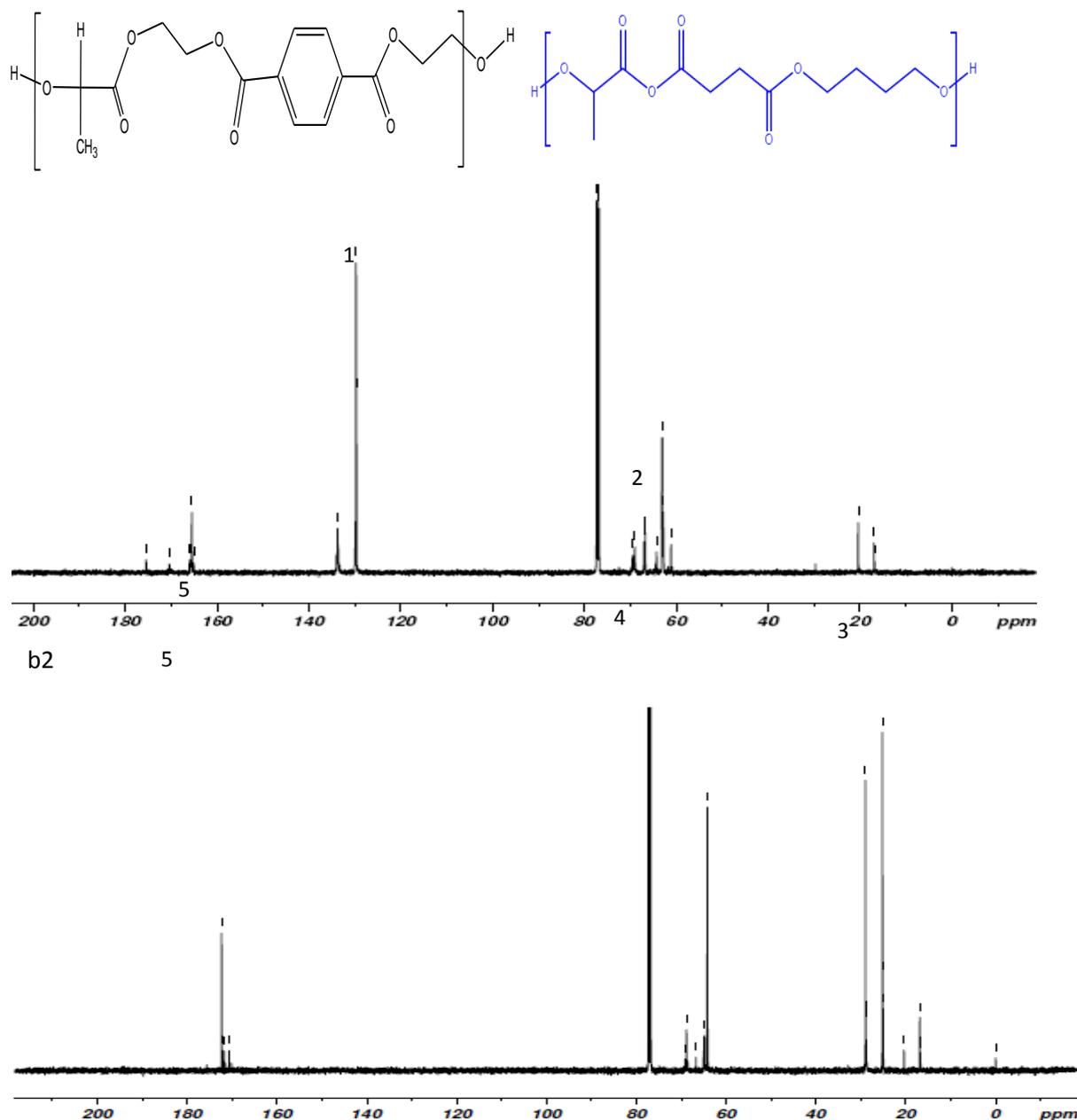


Fig. 5:  $^{13}\text{C}$  NMR Spectra of Polyesters PEGLT and PBLSA.

### X-ray Diffraction (XRD)

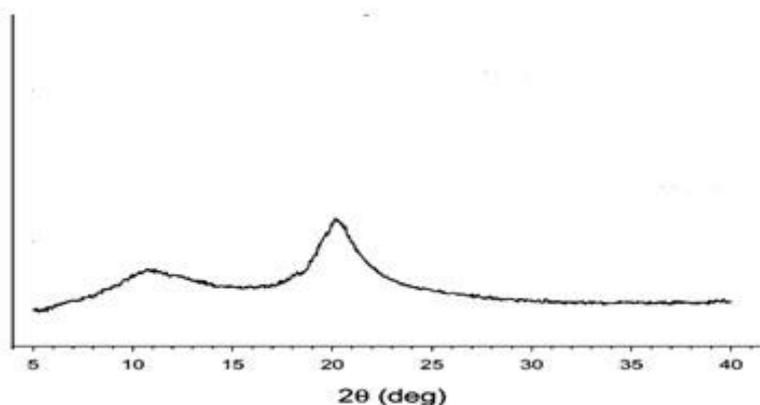
X-ray diffractogram of the polyesters, chitosan/polyester blend and chitosan are presented in Figures 6 and 7. Since both chitosan and PEGLT/PBLSA are semicrystalline polymers, their crystalline property will certainly affect the structure and property of blended thin films. The X-ray pattern of the pure chitosan membrane shows two characteristic peaks located at  $2\theta$  about  $10.2^\circ$  and  $20.2^\circ$ . It is known that chitosan always contains bound-water (5%) even when it has been extremely dried. The incorporation

of bound-water molecules into the crystal lattice, commonly termed hydrated crystals, generally gives rise to a more dominated polymorph which can be normally detected by a broad crystalline peak in the corresponding X-ray pattern, and therefore, the crystalline peak centered at around  $10.2^\circ$  is attributed to the hydrated crystalline structure of chitosan [22]. Another peak registered near  $20.2^\circ$  is reported to be the indication of the relatively regular crystal lattice (110, 040) of chitosan [23, 24]. The diffractogram of the pure PEGLT polymer consists of two main

diffractive peaks at angle  $2\theta$  of around  $16.2^\circ$  and  $17.8^\circ$ . The peak recorded at  $2\theta$  at  $16.2^\circ$  is recognized as the (200, 110) reflection of the crystals [25, 26] and the other peak that appeared at  $17.8^\circ$  corresponds to the (010) reflection [27].

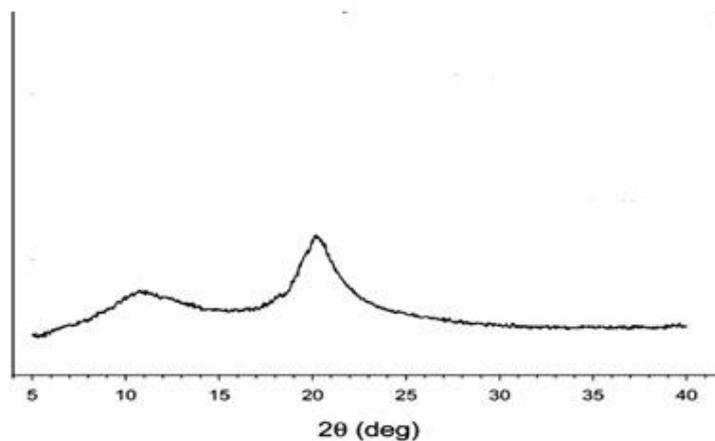
In the case of the chitosan/PBLSA blend film, although two crystalline peaks still remain, its crystallinity has been decreased by nearly half compared to that of pure chitosan. These results reveal that after the chitosan is effectively blended with PBLSA, the original crystalline structure of chitosan could have been partially destroyed or seriously modified, and as a consequence, the blend membranes obtain a partially miscible structure with amorphous domains due to the interactions between chitosan and PBLSA.

Some distinct changes in diffractogram of PEGLT/chitosan film are also observed. As shown in Figure 6, the original peak of chitosan component at  $10.2^\circ$  almost completely vanishes in X-ray pattern of the blend film. Although two crystalline peaks are recorded for the film, a narrow peak presumably matched with PEGLT has been shifted to around  $18^\circ$ , and another broad peak registered at about  $21.5^\circ$  differs from the original peaks of the PEGLT or chitosan component in both shape and position. The obtained results signify that two components, chitosan and PEGLT, have interacted with each other in a certain manner so that the original crystalline structures of each component have been disturbed or partially damaged to a different extent [28].



## Chitosan

*Fig. 6: X-ray Diffraction Patterns of Chitosan.*



## Chitosan

*Fig. 7: X-ray Diffraction Patterns of Chitosan.*

### Scanning Electron Microscope (SEM)

The morphology of the films of polyester and chitosan/polyester blend is examined through scanning electron microscopy (SEM). The

images of the polyester and chitosan/polyester blend are presented in Figures 8 and 9. The images show the phase separation in the blend films at microscopic level.

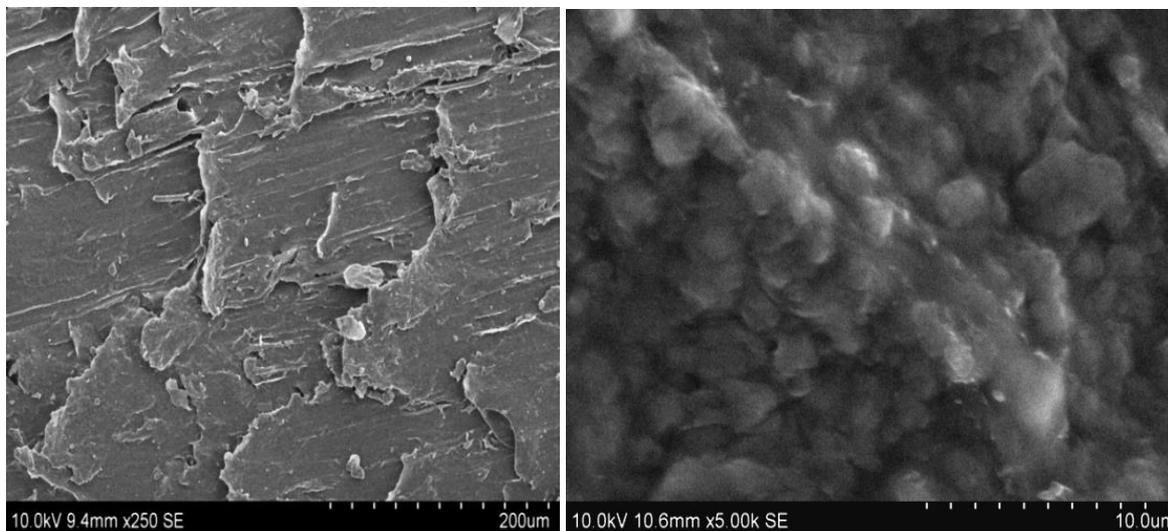


Fig. 8: SEM Images of PEGLT and Chitosan/PEGLT Blend.

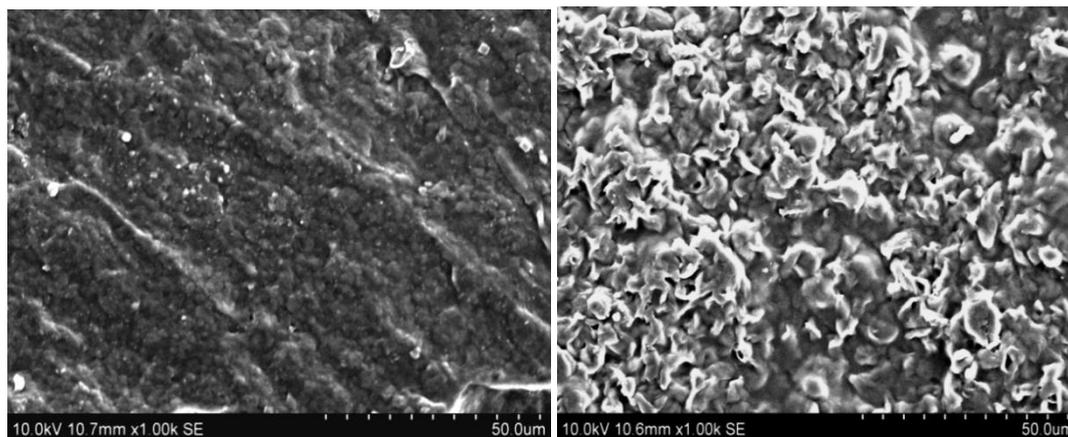


Fig. 9: SEM Images of PBLSA and Chitosan/PBLSA Blend.

### CONCLUSIONS

The random polyesters PEGLT and PBLSA were synthesized through an economical method of two-step melt polycondensation of lactic acid, terephthalic acid/succinic acid and 1,4 butane diol/ethylene glycol, in the presence of catalyst titanium tetra isopropoxide. The synthesized polyesters were characterized by means of solubility, viscosity measurements, FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectral analysis, X-ray diffraction and SEM. The synthesized polyesters are utilized for preparing chitosan/polyester blend films by solution-mixing and film-casting method. The blend films show a phase-separated morphology at a microscopic level. Although

phase separation at a microscopic level is observed, the results obtained from FTIR and X-ray diffractograms suggest that there exist pronounced interactions probably due to hydrogen binding components of the blend. The present investigation can be considered as a potentially interesting tool for the designing of a new bio-packaging material for food applications.

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