Chitosan/Poly(Amide-Imide) Blend Films: Studies on Thermal and Mechanical Stability, Morphology and Biodegradability

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ABSTRACT: A diacid monomer was synthesized by the condensation of L-tryptophan amino acid and pyromellitic dianhydride (PMDA). The diacid was utilized for the synthesis of three types of poly(amide-imide)s (PAIs) using three different kinds of diamines. The synthesized monomer and PAIs were characterized using FT-IR, ¹H-NMR and ¹³C-NMR spectroscopies and the PAIs were also used for the fabrication of chitosan (CS)/PAI blend films. XRD patterns of the PAIs, CS and CS/PAI blend films were also studied. Thermal stability of PAIs, CS and CS/PAI samples were studied using thermogravimetric analysis (TGA). The blend samples showed a higher thermal stability compared to the CS film, especially at higher temperatures. Morphology of the CS and blend CS/PAI films was studied before and after the biodegradation by SEM. The mechanical stability studies showed that blend CS/PAI films had a proper mechanical strength and their young's modulus increased compared to the pristine chitosan. The in vitro fungal colonization of diacid monomer, PAIs, pure CS and blend CS/PAI samples were performed using Aspergillus niger fungi. After biodegradation, the pure CS showed the highest weight loss of 21.2 wt % among the samples. The blend CS/PAI samples also showed higher weight losses compared to the pure PAIs.

KEYWORDS: Biodegradable; Chitosan; Poly(amide-imide); Polymer blend.

INTRODUCTION

Nowadays, there are ever-rising demands which encourage us for developing biodegradable and biocompatible polymer materials for addressing the problems which concern the worldwide environment and

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solid waste management. Biodegradation, the only degradation process which is able to completely remove a polymer or its degradation products from the environment, is an irreversible pathway in which at least one degradation

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phase is performed by biological agents [1-3]. Chitosan (CS), the second most abundant biopolymer in nature after cellulose, is a nontoxic, edible, and biodegradable polysaccharide derived from deacetylation of chitin. Chitin, as a waste product of the seafood processing industry, is abundantly found in the exoskeleton of crustaceans such as the crabs, shrimps and prawns, the insect's cuticle and the cell walls of most fungi [4-6]. Chitosan as a biodegradable and biocompatible natural biopolymer with low immunogenicity and multifunctionality is vastly a subject of attention in great spectra of studies such as food packing, biomedical applications, including drug delivery, tissue engineering and using for antimicrobial strategies like wound healing [1, 7-12]. However, the various applications of CS are frequently confined because of some drawbacks like insolubility in water and poor processability. As reported in many studies, various research works such as addition of nano-fillers, carbon nanotubes, clay, silica and graphene to CS [10, 13, 14], Grafting polymers onto CS [15], blending CS with polymers [16] etc. have been performed for modifying and adapting the thermal, mechanical and electrical properties of CS. There are some factors such as polymer structure, molecular weight, morphology and chemical treatments influencing the biodegradation process [3, 17-20]. In recent decades, among many bioanalogous polymers, the optically active poly(amide-imides) PAIs containing L-amino acids with different functional groups within their structures, have been considered as an interesting area for researchers [21-26]. Amino acids as chiral and naturally occurring compounds can be utilized for organic synthesis, food, drug and polymer industries. As the amino acids interact with biological systems, their application in these materials develops the biocompatibility and biodegradability [27-29]. Optically active polymers containing characteristic structures of amino acids, are thermally stable and processable compounds which have found several applications in enantiomer separation, chiral stationary phases in HPLC techniques and asymmetric catalysis in enantioselective synthesis [30-33]. In recent decade, several studies have found PAIs comprising amino acid groups as biodegradable and biocompatible polymers by investigating their bio activity in culture media and in soil [23, 34-36]. Synthesis of eco-friendly PAIs is an important field in the macromolecular science. Ionic liquids which have amazing properties such as chemical and thermal stability, low vapor pressure and high specific solvent abilities, have been also utilized as 'green solvents' and catalysts for the synthesis of PAIs in recent works [37-39].

As mentioned, CS and PAIs are two kinds of biodegradable and biocompatible polymers which have different applications owing to their characteristic properties. Till now, there is no report about blending CS and PAIs including amino acids in their structures. As PAIs have high thermal stability and processability, it is expected that blending PAIs possessing different properties with CS may lead to adapted properties which may be required in scientific works or industry. Moreover, PAIs commonly have a low filmability and weak mechanical strength compared to CS and it can be expected that blending PAIs with CS may improve some properties such as filmability and mechanical strength. As a highly biodegradable polymer, CS may also increase and biodegradability of PAIs which are currently utilized for different purposes in the industry. Here, we report the synthesis and characterization of a diacid monomer using L-tryptophane amino acid, and also the synthesis of three different PAIs via the mentioned monomer, using an ionic liquid as solvent and catalyst. The aim of this work is studying the morphology, thermal and mechanical stability and biodegradability of blend CS/PAI films in comparison with the pure PAIs and CS. In the present work, we synthesize novel polyamide-imides that have amino acid in the structure of diacid monomer. We report the synthesis and characterization of a diacid monomer using L-tryptophane amino acid, and also the synthesis of three different PAIs via the mentioned monomer, using an ionic liquid as solvent and catalyst. The aim of this work is studying the morphology, thermal and mechanical stability and biodegradability of blend CS/PAI films in comparison with the pure PAIs and CS. Synthetic procedures, PAI characterization and properties, as well as evaluation of in vitro biodegradation were given in the following sections.

EXPERIMENTAL SECTION

Materials

Pyromellitic dianhydride (PMDA), L-tryptophane, 4,4'-Biphenyldiamine (benzidine), 3,3'-Dimethyl-4,4'biphenyldiamine (O-toluidine), triphenyl phosphite,



Scheme 1: The synthesis route of diacid monomer. Synthesis of poly(amide-imide)s (PAI)s.

N-methyl-2-pyrrolidone (NMP) and glacial acetic acid were purchased from merck. Chitosan (medium molecular weight, 75-85% deacetylated) was prepared orbital india. 2,2-Bis[4-(4from company, aminophenoxy)phenyl] propane (BAPP) was purchased Aldrich. 1-butyl-3-methylimidazulium from sigma chloride was prepared according to the methods described elsewhere [40]. All other materials were used as received without further purification.

Synthesis of diacid monomer

First, 1.96 g (9.6 mmol) of L-tryptophane and 0.87 g (4.0 mmol) of PMDA were placed into a 100 ml roundbottomed flask, equipped with a condenser and magnetic heater-stirrer. Then, 40 ml of glacial acetic acid was added to the mixture and the solution was stirred at 80°C until the materials were completely dissolved. The temperature then was raised gradually and the reaction solution was refluxed at 120 °C for 48 h. Finally, the product was precipitated in methanol, washed with methanol, isopropyl alcohol and distilled water several times and dried at room temperature. Melting point (mp): 202-204°C, [αD 25]: 95.8°, (0.050 g in 10 mL DMSO) Elem. Anal. calcd. for C₃₂H₂₂N₄O₈ (590.14): C, 65.08%; H, 3.75%; N, 9.49%. Found: C, 58.28%; H, 3.20%; N, 13.77%. ¹H NMR (400 MHz, CDCl₃), ⁵(ppm): 3.5(d.d, 4H), 5.2(d, 2H), 6.8-8.3 (Ar, 12 H), 10.75 (S, NH). ¹³C NMR (75 MHz, CDCl₃), **b** (ppm): 170, 165, 137, 136, 127, 123, 121, 119, 118, 117, 112, 110, 52, 23. The synthesis route of diacid monomer is shown in Scheme 1.

Here, 1.77 g (3 mmol) of the synthesized diacid monomer was dissolved in a mixture solution, containing 3 g of 1-butyl-3-methylimidazulium chloride, 1 mL of triphenylphosphite and 3 ml of NMP, into a double necked round-bottomed flask, topped with a reflux condenser and equipped with nitrogen flow and magnetic heater-stirrer. After that, 0.662 g (3.6 mmol) of benzidine was added to the mixture and the solution was stirred at 120 °C for 12 h. the dark brown solution was precipitated in methanol after cooling down to the room temperature. The light brown deposits of the product were washed out many times with methanol, isopropanol and distilled water and then dried at room temperature. Two other kinds of PAIs containing 2,2-Bis[4-(4aminophenoxy)phenyl] propane (BAPP) and 3.3'-Dimethyl-4,4'-biphenyldiamine (O-toluidine) diamines were also synthesized using the same procedure. The molecular weight M_w of the poly(amide-imide) (PAI) was about 2.3 \times 10⁴ ($M_{\rm w}/M_{\rm n}$ = 1.96). The synthesis routes for PAIs are demonstrated in Scheme 2.

Film preparation

First of all, a 2.0 % (w/v) solution of chitosan was made by dissolving the medium molecular weight chitosan in a 2% v/v of acetic acid/water solution by constant continuous stirring at room temperature for 20 h. The chitosan film was prepared by casting the mentioned solution on a flat glass surface and drying in oven at 70 °C for 20 h. Three types of CS/PAI films were also prepared by blending a 7.5 wt % of PAIs into the chitosan matrix (w/w), by the following procedure; first, a homogenous solution of chitosan was prepared by dissolving the chitosan in a 2 % (v/v) solution of acetic acid/water, as mentioned formerly. After that, a solution of PAI in DMSO were prepared and added to the chitosan solution gradually. The mixture was then stirred at 80 °C for 4 days. The homogenous solution were then cast on a flat glass and dried in vacuum oven at 80 °C for 24 h. The films of pure PAIs were also prepared by casting an 8 W% of each PAI in DMSO on a flat glass and then drying in oven at 80 °C for 24 h.



Scheme 2: The synthesis route for PAIs via direct poly-condensation of diacid and diamines.

Measurements

Structure of the synthesized diacid monomer was confirmed using FT-IR, 1H NMR and 13C NMR spectroscopies. The synthesized PAIs were also characterized via FT-IR and ¹H NMR techniques. The FT-IR tests of the solid diacid and PAIs were performed on an ALPHA-Bruker FT-IR Spectrometer using KBr pellets and vibrational transition frequencies were reported in wave number (600-4000 cm⁻¹). The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker (400 MHz) using DMSO-d6 as spectrometer solvent and tetramethylsilane (TMS) as an internal standard. X-Ray Diffraction (XRD) was performed using XRD (INEL, Equinox 3000, France). ThermoGravimetric Analyses (TGA) for the pure chitosan and blend films were performed on a TGA/DSC-Mettler Toledo, when the samples were heated from room temperature to 600°C at a scanning rate of 10°C/min under Argon atmosphere. The mechanical properties measurements were performed by a mechanical tester Instron-5566 instrument. Samples were tested with gauge length of 20 mm at 25 °C and ambient humidity (about 45 % relative humidity) condition. The sample dimensions were 9×50 mm so that 20 mm of each sample was pulled between the pulling jaws at a constant speed of 5 mm/min. For achieving better results, each of the samples was tested 3 times. The surface and cross sectional morphologies of the films,

before and after the biodegradation Test were studied using a Seron AIS2300 Scanning Electron Microscope (SEM). The biodegradability measurements were performed vitro fungal colonization through in using Aspergillus niger fungi. A suspension of fungal spores with the population of 1×10^6 spore/ml under the aseptic conditions were placed on the Potato dextrose agar media containing 50 mg/l of chloramphenicol antibiotic and then it was incubated at 28 °C for 24 h until the fungus cultured on the surface of the medium. The sterilized and accurately weighed samples including the pills of diacid monomer and PAIs and also the film pieces $(1 \times 1 \text{ cm}^2)$ of pure chitosan and blend CS/PAI were then transferred into the Petri dishes containing the media cultured with Aspergillus niger and incubated at 28 °C for 30 days. Afterward, the fungal thalli were carefully removed from the samples and they were completely dried in vacuum oven and their weight losses were calculated to assure their biodegradability at the environment.

RESULTS AND DISCUSSION

Synthesis and characterization of diacid monomer

Scheme 1 shows a typical procedure for the synthesis of diacid monomer which was obtained through the condensation of 2 mol equiv. of L-tryptophane with 1 mol equiv. of PMDA in refluxing glacial acetic acid. The molecular structure of synthesized diacid monomer



Fig. 1: The FT-IR spectra of diacid monomer (a), PAI-1 (b), PAI-2 (c), PAI-3 (d).

was confirmed by FT-IR, ¹H NMR and ¹³C NMR spectroscopies. As it is outlined in Fig. 1, the FT-IR spectra showed absorption bands around 3418 cm⁻¹ (indole N-H), 3000-3500 (acid-OH), 1724 (imide, symmetric C=O stretching) and (acid C=O stretching and asymmetric imide C=O stretching) and 1381 cm⁻¹ (imide ring vibration, axial), confirming the formation of imidic bonds. The ¹H NMR spectra of diacid (Fig. 2) showed a singlet peak at 10.73 ppm which was attributed to the proton of indole N-H. The quartet peak appeared at 5.10-5.15 ppm was assigned to the proton of the chiral center. The peaks of aliphatic CH₂ were also appeared at about 3.38-3.62 ppm, which are overlapped with the peak of DMSO water. The peaks of aromatic region seemed between 6.85-8.14 ppm are also illustrated in the Fig. 2. The ¹³C NMR spectra of diacid are shown in Fig. 3. The peaks of acidic and imidic carbonyl are appeared at 169.8 and 165.3 ppm. Two peaks appeared at 53.2 and 24.1 ppm were attributed to the carbons of chiral center and aliphatic CH₂, respectively. The characteristic peaks of aromatic region are appeared between 109.4-136.3 ppm.

Synthesis and characterization of PAIs

Three types of poly(amide-imide)s were synthesized by direct polyamidation of diacid monomer with three different diamines. The synthesis route for PAIs is shown in Scheme 2. PAIs structures were characterized and



Fig. 2: The ¹H NMR spectra of diacid monomer.

confirmed using FT-IR and ¹H NMR spectroscopies. The FT-IR spectra of PAIs are shown in Fig. 1. As it can be seen, the FT-IR spectra of PAI-1 (with 4,4'-Biphenyldiamine) showed a series of strong absorption bonds at about 3385 cm⁻¹ (N-H stretching bonds of amide and benzimidazole), 1774 cm⁻¹ (imidic symmetric stretching of C=O), 1724 cm⁻¹ (amidic C=O stretching and asymmetric imide C=O stretching), 1380 cm⁻¹ (C-N of imidic bond), 1609 cm⁻¹ (C-N of indole), 2922 cm⁻¹ (aliphatic CH₂), 1501 cm⁻¹(C=C of aromatic rings), 724 and 814 cm⁻¹ (C-H bending of aromatic rings). As Fig. 4 shows, in the ¹H-NMR spectra of PAI-1, N-H protons of indole and amide groups are appeared at 10.71-10.74 and 9.99-10.10 ppm. The characteristic peak of chiral center proton was seen at 5.25 ppm. The peaks of aromatic protons were appeared in the range of 6.69-8.38 ppm. For PAI-2 a series of FT-IR and ¹H NMR characterizations almost similar to PAI-1 were observed. The FT-IR spectra (Fig. 1) showed absorption bands at 3300-3400 cm⁻¹ (N-H stretching of amide and indole groups), 2923 cm⁻¹ (stretching vibration of aliphatic C-H), 1776 and 1724 cm⁻¹(C=O stretching vibrations of imide and amide), 1494 cm⁻¹ (C=C stretching), 1377 cm⁻¹ (imidic C-N stretching), 727 and 812 cm⁻¹ (C-H bending of aromatic rings).

The ¹H NMR spectra of PAI-2 (Fig. 5) showed weak peaks appeared at 10.84 and 9.03 ppm which could be



Fig. 3: The ¹³C NMR spectra of diacid monomer.

assigned to the N–H protons of amide and imide groups. Protons of the aromatic region were appeared in the range of 6.68-8.40 ppm. The peak appeared at 5.06 ppm was attributed to the hydrogen of chiral center. The sharp peaks at 1.01and 1.04 ppm were due to the protons of methyl groups and the protons of aliphatic CH₂ were also appeared at the range of 2.02-2.25 ppm.

The structure of PAI-3 was also confirmed by FT-IR and ¹H NMR spectroscopy techniques. The FT-IR spectra (Fig. 1) showed characteristic peaks at 3300-3400 cm⁻¹ (amide and indole N–H stretching), 2933 and 2967 cm⁻¹ (stretching of aliphatic C-H bonds), 1774 cm⁻¹(imide symmetric C=O stretching), 1713 cm⁻¹ (amide C=O stretching and asymmetric C=O stretching of imide), 1371 cm⁻¹ (C–N vibration of imide ring), 730 and 822 cm⁻¹ (aromatic rings C–H bending). The ¹H NMR peaks for PAI-3 (Fig. 6) were also seemed at 10.49-10.87 ppm (amidic protons), 9.82 ppm (proton of indole N–H), 6.28-7.91 ppm (hydrogens of aromatic region), 5.07 ppm (H of chiral center), 1.226-1.525 ppm (protons of methyl groups) and 1.90-2.01 ppm (CH₂ protons). Some physical properties of the synthesized PAIs are gathered in Table 1.

XRD patterns

XRD patterns of the films of chitosan, pure PAIs and blend CS/PAI samples were studied and the results are shown in Fig. 7. The XRD pattern of chitosan exhibited broad diffraction peaks around $2\theta = 10.5^{\circ}$ and $2\theta = 21.1^{\circ}$ which are the typical peaks for chitosan. Pure PAI-1, PAI-2 and PAI-3 films showed broad peaks around $2\theta = 19.4^{\circ}$, $2\theta = 17.5$, 19.6 and 25.1° and $2\theta = 14.9^{\circ}$, 19.5° and 24.2° respectively, which shows the amorphous structure of the PAIs. The XRD patterns of CS/PAI blend films showed that the peaks of pure PAIs are mixed with the pure CS peak and the characteristic peaks of the pure PAIs disappeared and were not observed in the blend CS/PAIs film anymore. This can be due to the strong interactions such as intermolecular hydrogen bonding between PAIs and CS which have led to a good miscibility in the blend samples. Furthermore, in comparison with the typical peak of pure CS in $2\theta = 20.1^{\circ}$, the peaks of blend samples also showed a shift toward lower amounts of $2\theta = 20.1$, 20.4 and 20.2° for PAI-1, PAI-2 and PAI-3 respectively. These results also could be attributed to the strong interactions between CS and PAI polymeric chains.



Fig. 4: The 1H-NMR spectra of PAI-1.



Fig. 5: The 1H NMR spectra of PAI-2.

Morphology observations

It is currently known that the morphology of a polymeric material can perform a key role in the degradation procedure [3, 41]. Chitosan and chitosan/PAI films were successfully prepared via the solution-casting method. Surface and cross sectional Morphologies of the pure CS and CS/PAI sheets, before and after the biodegradation process were studied using Scanning Electron Microscopy (SEM). Fig. 8 shows the SEM images of the samples before the biodegradation.



Fig. 6: The 1H NMR spectra of PAI-3.



Fig. 7: XRD patterns of the CS film, pure PAI films and CS/PAI blend films.

As seen, all of the films showed a smooth, dense and homogeneous surface and without any pores or fractions. The cross sectional observations also revealed that PAIs are well-mixed in CS matrix, which this could be due to the strong hydrogen bonding between the plentiful oxygen and nitrogen containing functional groups existing in CS and PAIs structures which brings CS/PAI sheets dense structures with consistency and toughness. The cross sectional SEM images also exhibited that blending CS with PAIs has changed the morphology

			•	
sample	color	[α]D 25 a	Viscosity ninh(dL/g)a	Yield (%)
PAI-1	brown	-34.3	0.34	92%
PAI-2	Dark grey	-26.7	0.42	94%
PAI-3	Bright brown	-38.2	0.37	91%

Table 1: Some physical properties of PAIs

a) Measured at a concentration of 0.5 g/dL in DMF at $25^{\circ}C$.



Fig. 1: SEM micrographs from surface (left) and cross section (right) of pure CS (a, a'), CS/PAI-1 (b, b'), CS/PAI-2 (c, c') and CS/PAI-3 (d, d').



Fig. 9: TGA curves of pure PAIs.

observed in CS/PAI blend films compared to the pure chitosan. The pure CS showed smoother but somewhat rough, uneven and corrugated structure, while the blend samples showed more uniformity and toughness at all.

Thermal stability

The thermal stability of synthesized PAIs, CS and CS/PAI blend samples were evaluated using ThermoGravimetric Analysis (TGA). The TGA curves of synthesized PAIs are shown in Fig. 9.

According to the plots, all of PAIs showed high thermal stabilities with a tree step weight loss pattern. The high thermal stability of PAIs is due to the presence of strong linkages such as imide bond and indole rings in the polymer structure and also introduction of high rigid pyromellitoyl group within the backbone of PAIs [23, 42, 43]. The first weight loss before about 100-120 °C is due to the evaporation of water molecules engaged within the PAIs structures. As it can be seen, the first weight loss of PAI-3 is higher than the other PAIs which is due to availability of more oxygen groups in the backbone of PAI-3 compared to the other PAIs, which can engage more water molecules through formation of hydrogen bonds. The second weight loss observed about 230 °C in the curves could be attributed to the thermal degradation of indole groups existing at the PAI structures. The last weigh loss steps occurred at the temperatures upper than 430 °C were due to the decomposition of polymer



Fig. 10: TGA curves of pure CS and CS/PAI films.

backbone of PAIs. Thermal stabilities of the prepared films were also evaluated and the TGA curves are also depicted in Fig. 10.

As the curves show, the pure CS and also CS/PAI samples exhibited a two stage weigh loss pattern in their TGA plots. The first one is due to the loss of water molecules and the second one is attributed to the decomposition of chitosan structure which form the main component of the films. It was concluded that blending of PAIs with pure CS film can enhance the thermal stability of CS/PAI samples compared to the pure CS, particularly at the temperatures between 300-600 °C. This is due to the high thermal stability of PAIs existing in the blend samples and also hydrogen bonding between the functional groups of CS and PAI. Scheme 3 shows a schematic.

Representation of hydrogen bond formation between PAIs and CS polymeric chains. According to the polymer structures, it can be seen that there are plenty of functional groups which are capable of forming hydrogen bonds. As the PAI-3 contains more oxygen groups in its structure, in comparison with PAI-1 and PAI-2, it can perform a greater hydrogen bonding network with CS structure which can keep the polymeric chains together more strong, and consequently the sample CS/PAI-3 shows a higher thermal stability compared to the other CS/PAI blend samples.

The thermal properties data of the samples are collected in Table 2.

				,		
Sample $T_{5\%}$ (°C) ^a $T_{10\%}$ (°C	T (OC) a	^a 2 nd weight loss start (°C)	3 rd weight loss start (°C)	Residual weight (%) at		
	1 _{10%} (°C) "			400 (°C)	600 (°C)	
PAI-1	219	255	232	440	75.3	54.3
PAI-2	216	254	229	438	73.9	52.7
PAI-3	224	261	227	486	81.3	58.5
CS	238	281	279	_	50.2	42.6
CS/PAI-1	247	262	264	_	53.9	46.9
CS/PAI-2	241	258	263	_	51.1	44.9
CS/PAI-3	235	287	266	_	57.7	52.8

Table 2: Thermal stability data of the samples

a) Temperature at which 5 and 10% weight loss was recorded by TGA at a heating rate of 10 °C min⁻¹ in an Argon atmosphere



Scheme 3: A schematic representation of hydrogen bonding between the polymeric chains of Chitosan and PAIs (PAI-3).

Mechanical properties

The stress-strain curves of the samples are illustrated in Fig. 11. The mechanical properties of pure PAIs were not measured because their films were brittle. According to the stress-strain curves the pure chitosan showed the highest tensile stress of 116 MPa and elongation at break of 6.6 % among the samples. The blend CS/PAI films also showed high tensile stress values of 95.1-107.5 MPa. However, compared to the pure chitosan, the stress and strain values somewhat decreased in the blend samples, but the young's modulus values are increase in the blend films implying an increase in the elasticity of the blend samples. The measured mechanical properties of the samples are gathered in Table 3.

Biodegradation and weight loss

Biodegradability of the samples was determined by calculating the weight losses of samples through their exposure in vitro colonization via Aspergillus niger fungi at 28 °C for 30 days. It was seen that all of the samples showed fungal colonization. After removing the fungal thalli and drying the samples, their weight losses were accurately measured. As the weight loss data (Table 4) revealed, the samples showed different biodegradability trends. The synthesized diacid monomer showed a weight loss of 5.8 wt%, while the PAIs 1, 2 and 3 showed the weight losses of 3.7, 4.3 and 5.2 wt% respectively, implying the higher biodegradability of diacid monomer in comparison with the PAIs containing the same diacid

Sample

Weight loss (wt%)

Samples	Thickness (µm)	Stress (MPa)	Strain (%)	Young's modulus (GPa)
CS	62	116.1	6.6	3.43
CS/PAI-1	62	95.1	4.3	4.31
CS/PAI-2	58	101.2	3.9	4.22
CS/PAI-3	60	107.5	3.4	4.29

Table 4: Weight loss data of the samples after biodegradation process.

PAI-3

5.2

PAI-2

4.3

PAI-1

3.7

Table 3: Mechanical properties of the pure CS and CS/PAI blend films.

20 - 90 - 80 -	CS CS/PAI-1 CS/PAI-2 CS/PAI-3	M			
90 - 80 -	CS/PAI-2 CS/PAI-3	M			
80 -	,	/ / X /			
		////////			
50 -					
10		/			
20 -					
۰L	2	4			8
	40 20 0 0		u_{0}	u_{0}	u_{0}

Diacid monomer

5.8

Fig. 11: Stress-Strain curves of the pure CS and CS/PAI blend films pure PAIs were not measured because their films.

monomer in their structures. This can be attributed to the formation of strong amidic bonds in the PAIs structures. PAI-3 showed the highest biodegradation among the PAIs which this can be due to the soft segments of loose etheric bonds existing in the structure of PAI-3 which can increase the biodegradability of the structure. Based on the several scientific works mentioned previously, it could be expected that the pure chitosan has a high biodegradability trend, and in this work, the pure CS film with a weight loss of 21.2 wt% showed the highest biodegradability among all of the samples. The blend CS/PAI samples with 7.5% (w/w) of PAIs also showed higher biodegradations in comparison with the pure PAIs due to the presence of a great percentage of CS in the blend samples. However, they showed lower weight losses compared to the pure chitosan film.

The morphology changes of the film samples after he biodegradation test through fungal colonization vere studied by SEM images. Fig. 12 shows the fungal olonization on the surfaces of the film pieces ncluding the and before removing the fungal thalli. The SEM images clearly showed the spores of fungi nd growth of fungal mycelium on the samples, mplying the tendency of the samples for biodegradation. The SEM images after removing he fungal thalli from the films (Fig. 13) revealed he changes in the morphology of the samples.

CS/ PAI-1

14.6

CS

21.2

CS/PAI-2

14.1

CS/PAI-3

16.1

The solid structures of the films collapsed and their mooth and flat surfaces changed to the moldy, rough, orous and cracked morphologies after the growth of the olony. As a result of digestion by the enzymes secreted from the fungi, the films exhibited different morphology types through 30 days of biodegradation. As CS structure is the main component of each blend film (92.5 wt% of CS and 7.5 wt% of PAI), it may be expected that the blend samples should exhibit similar biodegradability and morphology to the pristine CS, but it was revealed that the introduction of PAIs into the CS matrix reduces the biodegradation and changes the morphology of the blend samples in comparison with the pristine CS. The blend samples containing PAIs 1, 2 and 3 showed weigh losses of 14.6, 14.1 and 16.1 wt%, which their weight loss ratios to the pristine CS is about 68.8, 66.5 and 75.9%, respectively. Since all of the pure PAIs exhibited lower biodegradability compared to the pure CS, it was deduced that homogeneously dispersed PAIs within the chitosan matrix can influence the biodegradability of the blend films through changing their morphology and also the chemical nature and biological activity of CS/PAI films. However, all of the blend samples showed higher



Figure 12: SEM images from surface of pure CS (a), CS/PAI-1 (b), CS/PAI-2 (c) and CS/PAI-3 (d) films, after 30 days of fungal colonization.



Figure 13: Surface view of pure CS (a), CS/PAI-1 (b), CS/PAI-2 (c) and CS/PAI-3 (d) films, after removing the fungal thalli (after 30 days).

biodegradability trends compared to the pure PAIs, which can recommend us the utilization of CS for enhancing the biodegradability of PAIs.

CONCLUSIONS

Poly(amide-imide)s (PAIs) containing amino acid in their structures and chitosan are known as two kinds of polymers with biodegradability activity. In current work, a new diacid monomer was synthesized using Ltryptophane amino acid, and then three types of Poly(amide-imide)s were successfully synthesized using the mentioned monomer. The synthesized PAIs were used for the fabrication of CS/PAI films and studying their thermal and mechanical stability, morphology and biodegradability properties [44]. The thermal stability data showed that PAIs can increase the thermal stability of the blend CS/PAI films, because of the high thermal stability nature of PAIs and also formation of hydrogen bonds between the rich oxygen and nitrogen containing functional groups of CS and PAIs [45]. In the mechanical properties test, although the tensile strength and elongation at break of the CS/PAI blend films somewhat decreased, all the samples generally showed good mechanical stabilities and the young's modulus increased in blend CS/PAI films. Moreover, it was deduced that some drawbacks of the brittle pure PAIs such as low filmability and weak mechanical properties can be improved by blending them with CS homogenously. The SEM images also revealed that replacing a 7.5 wt% of PAI within chitosan can change the morphology of the blend CS/PAI sheets compared to the pristine CS film. All of the films showed different morphologies with dense and homogeneous structures and smooth surfaces without any holes, divisions and segments. The XRD patterns also confirmed that PAIs are mixed with CS matrix successfully and they are combined homogeneously with strong interactions between CS and PAIs chains. The biodegradation test was carried out using Aspergillus niger fungi during 30 days of in vitro fungal colonization. The results showed that the diacid monomer containing L-tryptophane amino acid in its structure has a biodegradation activity. Moreover, all of the PAIs also showed biodegradation activity. The morphology observations of the prepared films after colonization, revealed the growth of fungal colonies on all of the film samples. After removing the fungal thalli,

the films which were metabolized by the A. niger fungi showed different types of morphology. The pure chitosan film showed the highest weight loss (21.2 wt %) and the blend samples showed relatively high weight losses compared to the pure PAIs. however, the biodegradability somewhat decreased in blend samples compared to the pristine CS. It was deduced that PAIs homogeneously existed in the combination of blend films can change the morphology and chemical properties of CS/PAI samples which leads to lower biodegradability activity in comparison with the pure chitosan. However, the CS/PAI blend samples also showed relatively high biodegradability trends, and they still hold the promise for being used as biodegradable polymers. It was revealed that CS and PAI have a good compatibility and PAIs can also increase the processability of CS in organic solvents because of the existence of several functional groups capable of forming hydrogen bonds in both PAI and CS structures. The results of this work also mentioned the blending of chitosan for enhancing the biodegradability of PAIs which have several applications in different areas of science and technology. As the whole things which are mentioned above these composites could be a good item for fresh-keeping or other fields as a kind of green and biodegradable packaging material, so it is important because of growing many export markets which have waste disposal restrictions for packaging materials. In the near future, almost all product packaging will be manufactured from biodegradable polymers and composites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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