Grafting of Poly(3-hydroxyalkanoate) and Linoleic Acid onto Chitosan

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ABSTRACT: Poly(3-hydroxy octanoate) (PHO), poly(3-hydroxy butyrate-*co*-3-hydroxyvalerate) (PHBV), and linoleic acid were grafted onto chitosan via condensation reactions between carboxylic acids and amine groups. Unreacted PHAs and linoleic acid were eliminated via chloroform extraction and for elimination of unreacted chitosan were used 2 wt % of HOAc solution. The pure chitosan graft copolymers were isolated and then characterized by FTIR, ^{13}C-NMR (in solid state), DSC, and TGA. Microbial polyester percentage grafted onto chitosan backbone was varying from 7 to 52 wt % as a function of molecular weight of PHAs, namely as a function of steric effect. Solubility tests were also performed. Graft copolymers were soluble, partially soluble or insoluble in 2 wt % of HOAc depending on the amount of free primary amine groups on chitosan backbone or degree of grafting percent. Thermal analysis of PHO-*g*-Chitosan graft copolymers indicated that the plastizer effect of PHO by means that they showed melting transitions T_ms at 80, 100, and 113°C or a broad T_ms between 60.5–124.5°C and 75–125°C while pure chitosan showed a sharp T_m at 123°C. In comparison of the solubility and thermal properties of graft copolymers, linoleic acid derivatives of chitosan were used. Thus, the grafting of poly(3-hydroxyalkanoate) and linoleic acid onto chitosan decrease the thermal stability of chitosan backbone. J Appl Polym Sci 103: 81–89, 2007

Key words: chitosan; poly(3-hydroxy butyrate-*co*-3-hydroxyvalerate) (PHBV); poly(3-hydroxy octanoate) (PHO); graft copolymers

INTRODUCTION

Chitin is the second most abundant natural biopolymer after cellulose found in the shells of crustacean, e.g., crab and shrimp, and cuticles of insects and also in the cell walls of some fungi and microorganisms. Although chitin is structurally similar to cellulose, much less attention has been paid to chitin than cellulose, primarily due to its inertness. Fully or partially deacetylation of chitin yields chitosan, which is relatively reactive and soluble in acidic solutions. When the degree of N-acetylation is less than 50 wt %, the chitin becomes soluble in aqueous acidic solutions and is named chitosan. Chitosan has some advantages due to its nontoxicity and biodegradability without damaging the environment. It is a biocompatible material that breaks down slowly to harmless products (amino sugars) that are absorbed completely in body. Several biomedical applications of chitosan, such as artificial kidney membrane, artificial skin, absorbable sutures, hypocholesterolemic agents, drug delivery systems, and supports for immobilized enzymes and several food applications, such as antimicrobial agents, edible film industry, additives, nutritional quality, recovery of solid materials from food processing wastes, purification of water, have already been reported.[1,2]

Chemical modifications of chitosan by grafting method are important to prepare multifunctional materials in different fields of application and to improve its chemical, physical, and mechanical properties. Many studies were reported in the literature about grafting on to chitosan such as grafting of 4-vinylpyridine,[3] mono(2-methacryloyl oxyethyl)acid phosphate,[4] poly (ethyleneglycol),[5] L-lactic acid (CL),[6] 4-(6-methacryloxy-hexyloxy)-4′-nitrobiphenyl,[7] polyurethane,[8] acrylonitrile and methylmethacrylate.[9]

Poly(3-hydroxyalkanoate)s (PHA)s are highly crystalline, optically active materials that are elaborated by a wide variety of microorganisms. PHAs have many medical and industrial applications because of their biocompatibility, biodegradability, and permeability.[10] However their some physical, mechanical, and thermal properties have limited some applications, e.g., their actual use as plastics has so far been hampered by their thermal instability.[11,12] This prompted researchers to explore chemical modifications of PHAs and thus to obtain new materials with improved properties by crosslinking, graft copolymerization, and functionalization methods.[13,15]

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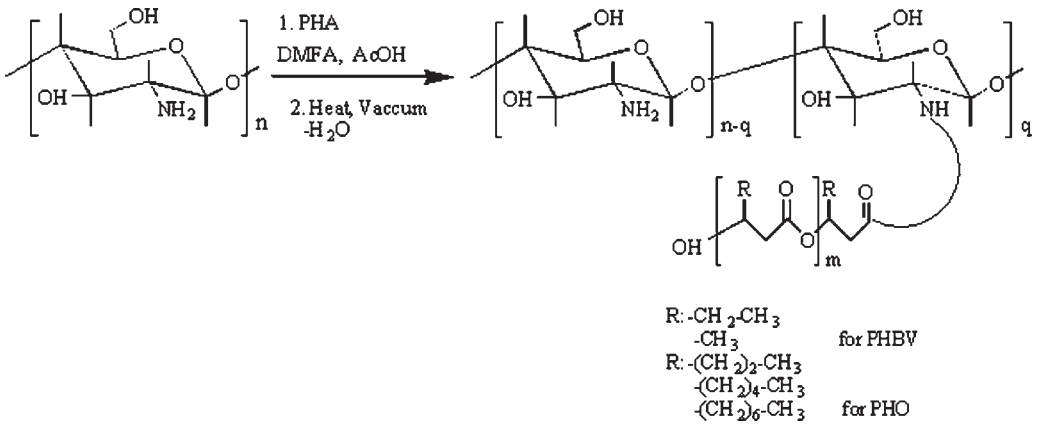


Scheme 1

Chitosan and PHAs are biodegradable and biocompatible polymers having different thermal and solubility characteristics. This study refers to the grafting reactions of chitosan and PHAs to combine their advantage and to minimize or to annihilate their disadvantage. Additionally the linoleic acid derivatives of chitosan have been mentioned to compare the solubility and thermal properties.

EXPERIMENTAL

Materials

Chitosan (CS) (low molecular weight) was supplied by Aldrich and used without further purification. Poly(3-hydroxy butyrate-*co*-valerate) (PHBV) was obtained from 4-pentenoic acid as a sole carbon source by Alcaligenes Eutrophus[16] and partially depolymerized prior to use by heating under reflux condenser with 1,2-diclorobenzene to facilitate solubility and subsequent modifications. Thus, PHBVs with low molecular weight (M_n = 14,664 and M_n = 77,338) were prepared by heating for 6 and 2.5 h under reflux condenser, respectively. Poly(3-hydroxy octanoate) (PHO) (M_n = 56,860) was obtained from Division of Life Science, Gyeongsang National University, Chinju, S. Korea, and used without any purification. PHO was partially depolymerized by heating for 3 h under reflux condenser to obtain PHO with M_n = 19,064. Linoleic acid was obtained from Fluka and used as a received. Glacial acetic acid was supplied by Merck. *N*,*N*-Dimethylformamide (DMFA) was supplied by Carlo Erba. Both were used without purification.

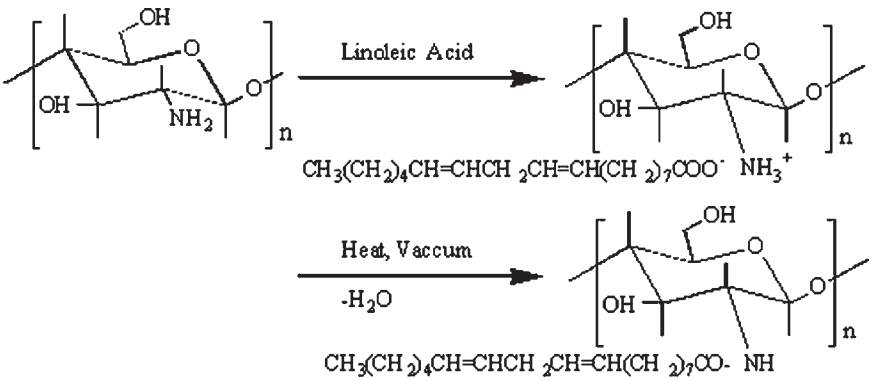
Synthesis of chitosan-g-PHBV and chitosan-*g*-PHO graft copolymers

Appropriate amounts of chitosan were dissolved in 2 wt % acetic acid (25 mL) and the solution was stirred overnight at room temperature. PHAs were dissolved in DMFA and the solution was also stirred overnight at ~35°C. A viscous solution of chitosan was gradually added to a solution of PHAs with stirring at 35°C for ~15 min. The obtained reaction mixture was stirred for

TABLE I
Synthesis of Chitosan Graft Copolymers

Run no.	Chitosan (g)	PHBV (M_n = 14,664) (g)	PHBV (M_n = 77,338) (g)	Linoleic acid (%)	PHO (M_n = 56,860) (g)	PHO (M_n = 19,064) (g)	Polym. time	Yield (g)[a]
V	0.50	1.00	–	–	–	–	4 h 15 min	0.91
VI	1.00	1.00	–	–	–	–	5 h	1.88
VII	1.00	0.50	–	–	–	–	4 h	1.47
XIV	1.00	–	0.50	–	–	–	4 h	0.81
VIII	0.50	–	–	47[b]	–	–	4 h	0.61
IX	0.50	–	–	38[c]	–	–	4 h	0.81
X	0.50	–	–	47[d]	–	–	5 h	0.82
XI	0.50	–	–	–	1.00	–	4 h	0.62
XII	1.00	–	–	–	1.00	–	4 h	1.07
XIII	1.00	–	–	–	0.50	–	4 h	1.02
XV	0.52	–	–	–	–	1.22	4 h	0.84

[a] The weight of pure product.
[b] Chitosan and linoleic acid aqueous solution were stirred 30 min at 90°C before heating under vacuum.
[c] Chitosan and linoleic acid aqueous solution were stirred 1 day at 40°C before heating under vacuum.
[d] Chitosan and linoleic acid aqueous solution were stirred 2 day at 40°C before heating under vacuum.



Scheme 2

an additional 1 h at 35°C and then the solvent was partially evaporated. After that the new viscous product was heated at 90°C in silicon oil bath under vacuum for a given time. Commonly, the obtained products were dry and an undivided form. Grafting reactions of PHBV and PHO were drawn in Scheme 1. The results and conditions of polymerizations were collected in the Table I.

Linoleic acid derivative of chitosan

Chitosan (0.5 g) was dissolved in aqueous solution of linoleic acid (38 and 47 wt %) at 40°C for a given time with continuous stirring. Reaction mixture was heated under vacuum at 90–95°C in silicon oil bath for a given time. Scheme 2 shows the reaction between linoleic acid and chitosan. And the detailed conditions and results for derivation reactions were also summarized in Table I.

Solubility Tests

The grafted products and homopolymers were tested for solubility in water, 2 wt % acetic acid (HOAc), chloroform ($CHCl_3$), and dimethylsulfoxide (DMSO). The results were summarized in Table II. The procedure for the purifications of products was determined according to this solubility test.

Measurements of swelling ratio of polymers

Swelling ratio (SR) of chitosan-*g*-PHBV and linoleic acid derivatives of chitosan were measured gravimetrically. The weighted polymers were placed in 2 wt % AcOH solutions for 2 days at room temperature. Swollen polymers removed from 2 wt % AcOH solutions and weighted. The SR of polymers is defined as $SR = W_s/W_d$, where W_s is the weight of solvent in the swollen polymer and W_d is the dry weight of polymer.

Purification of graft copolymers and preparation of chitosan-*g*-PHO graft copolymer films

First, the obtained product was extracted with $CHCl_3$ to remove the unreacted PHBV, PHO, and linoleic acid for 24 h. Afterwards, to remove the unreacted chitosan, the product was extracted with 2 wt % acetic acid solution for 1 h. Finally, the product washed several times with methanol and dried under vacuum at 30°C for 24 h.

Chitosan-*g*-PHO graft copolymers were dissolved in 2 wt % acetic acid solution and stirred overnight. The solution was filtered, poured in to a petri dish and allowed solvent to evaporate at room temperature for a few days. The films were dried under atmospheric conditions.

Characterization

The Fourier transform infrared (FTIR) spectra were obtained from a PerkinElmer Spectrum One spectrome-

TABLE II
Solubility Tests of the Copolymers

Run no.	Polymer/ copolymer	H_2O	HOAc (2 wt %)	$CHCl_3$	DMSO
	Chitosan	−	+	−	−
	PHBV	−	−	+	−
	PHO	−	−	+	−
	Linoleic Acid	−	−	+	+
V	Chit.-*g*-PHBV[a]	−	−	−	−
VI	Chit.-*g*-PHBV	−	−	−	−
VII	Chit.-*g*-PHBV	−	−	−	−
XIV	Chit.-*g*-PHBV	−	+	−	−
VIII	Chit.-*g*-Lino.[b]	−	−	−	−
IX	Chit.-*g*-Lino.	−	−	−	−
X	Chit.-*g*-Lino	−	−	−	−
XI	Chit.-*g*-PHO[c]	−	+	−	−
XII	Chit.-*g*-PHO	−	+	−	−
XIII	Chit.-*g*-PHO	−	+	−	−
XV	Chit.-*g*-PHO	−	±	−	−

(+) soluble; (−) insoluble; (±) partially.

[a] Chit.-*g*-PHBV graft copolymers (run nos. V, VI, VII) partly swelled in water and highly swelled in 2 wt % HOAc.

[b] Chit.-*g*-lino grafts (run nos. VIII, IX, X) partly swelled in 2 wt % HOAc.

[c] Chit.-*g*-PHO graft copolymers (run nos. XI, XII, XIII) highly swelled in water.

TABLE III
Swelling Properties of the Polymers in 2 wt % AcOH

Run no	Weight of polymer (g)		
	Original	Swollen polymer	SR
V	0.11	2.35	20.36
VI	0.11	2.06	17.73
VII	0.11	2.51	21.82
VIII	0.07	0.79	10.28
IX	0.04	0.22	4.50
X	0.07	0.93	12.28

Swelling ratio (SR) of polymers is defined as SR = W_s/W_d, where W_s is the weight of solvent in the swollen polymer and W_d is the dry weight of polymer.

ter, and all samples were prepared as potassium bromide pellets.

The ^{13}C-NMR spectra of graft copolymers were recorded with a Varian UNITY Inova 500 MHz spectrometer in solid state.

Differential scanning calorimetry (DSC) was carried out on a Setaram DSC 141 with a heating rate 10°C/min under a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was performed on PerkinElmer Pyris 1 with scan rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Chitosan-*g*-PHBV and chitosan-*g*-PHO graft copolymers were prepared by polycondensation method under vacuum at 90°C (Scheme 1). The grafting reaction took place in DMFA and acetic acid solution. Acetic acid was used as a catalyst and the assistant agent for dissolution of chitosan. Grafting of linoleic acid on chitosan was also performed by condensation reaction under vacuum at 90–95°C without a catalyst (Scheme 2). Results and initial conditions of experiments were given in Table I.

Solubility properties and purification of polymers

The solubility of graft copolymers and homopolymers was tested in H_2O, 2 wt % HOAc, $CHCl_3$, and DMSO (Table II). Chitosan is soluble in diluted acidic solutions, such as lactic acid, acetic acid, linoleic acid, and HCl, but insoluble in $CHCl_3$ and DMSO. PHBV and PHO are soluble only in $CHCl_3$. Linoleic acid is soluble in $CHCl_3$ and DMSO.

Chitosan-*g*-PHBV (V, VI, VII) graft copolymers were insoluble even in 2 wt % HOAc and $CHCl_3$, which are known to dissolve chitosan and PHBV, respectively. However, they swelled partly in H_2O and highly in 2 wt % HOAc (Table III). Chitosan-*g*-PHBV (XIV) prepared by using PHBV with higher molecular weight was soluble in 2 wt % HOAc (compare Run Nos. V, VI, VII with XIV in Table I and Table II).

Chitosan-*g*-PHO (XI, XII, XIII) graft copolymers were exhibited excess swelling in H_2O, solubility in 2 wt % HOAc and insolubility in the other solvents. Chitosan-*g*-PHO (XV) graft copolymer prepared by using lower molecular weight PHO was partially soluble in 2 wt % HOAc (See Table I and Table II compare Run Nos. XI, XII, XIII with Run No XV).

The solubility of the graft copolymers in 2 wt % HOAc depends on the number of unreacted (free) NH_2 groups on the chitosan backbone, which provides solubility in acidic medium to chitosan, namely depends on grafting percentage. When grafting percentage increases in other words when the number of free NH_2 groups decreases, the solubility of the polymer decreases. The increase in the molecular weight of PHAs used in grafting reactions decreased the grafting percentage of PHAs because of steric effect. Thus soluble polymers were obtained because of free NH_2 groups.

TABLE IV
Results of Purification of Graft Copolymers via Extraction with Chloroform and Acetic Acid Solution, respectively

Run no.	Initial condition			Yield (g)	Soluble fractions (g)		PHA in copolymer[a] (wt %)
	Chitosan(g)	PHA (g) PHBV	PHA (g) PHO		In $CHCl_3$[b]	In 2 wt % of HOAc	
Chit.-*g*-PHBV (V)	0.50	1.00	–	0.91	0.57	Insoluble[c]	47.0
Chit.-*g*-PHBV (VI)	1.00	1.00	–	1.88	0.16	Insoluble[c]	45.0
Chit.-*g*-PHBV (VII)	1.00	0.50	–	1.47	0.04	Insoluble[c]	31.0
Chit.-*g*-PHBV (XIV)	1.00	0.50	–	0.81	0.32	Soluble	22.0
Chit.-*g*-PHO (XI)	0.50	–	1.00	0.62	0.87	Soluble	21.0
Chit.-*g*-PHO (XII)	1.00	–	1.00	1.07	0.92	Soluble	7.5
Chit.-*g*-PHO (XIII)	1.00	–	0.50	1.02	0.43	Soluble	7.0
Chit.-*g*-PHO (XV)	0.52	–	1.22	0.84	0.78	Partially soluble	52.0

[a] Calculated theoretically from initial weight of used PHA, weight of unreacted PHA ($CHCl_3$ phases) and yield as (Initial weight of PHA (g) − Unreacted PHA (g)/Yield (g) × 100.

[b] Soluble fraction in chloroform was the unreacted PHO and PHBV.

[c] In the case of Chit.-*g*-PHBV (Run Nos. V, VI, VII) there were approximately 2 wt % soluble part which was attributed to unreacted chitosan.

(Compare Run Nos. VII with XIV in Table I and Table IV). Decrease in the molecular weight of PHAs used in grafting reactions increased the grafting percentage of PHAs, and thus, solubility of the polymers was decreased as expected. (Compare Run Nos. XI with XV in Table I and Table IV).

Linoleic acid derivative of chitosan was insoluble in all solvents used but only partly swelled in 2 wt % HOAc (Table II and Table III Run No's VIII, IX, X). The aim of grafting linoleic acid on chitosan is to obtain a hydrophobic polymer by confining all NH_2 groups, and to compare the solubility properties and thermal properties of polymers.

The graft copolymers were purified in accordance with solubility test results and the amount of soluble parts were weighted (Table IV). Chloroform or 2 wt % HOAc could dissolve the unreacted homopolymers, so copolymers can be separated from prepared product

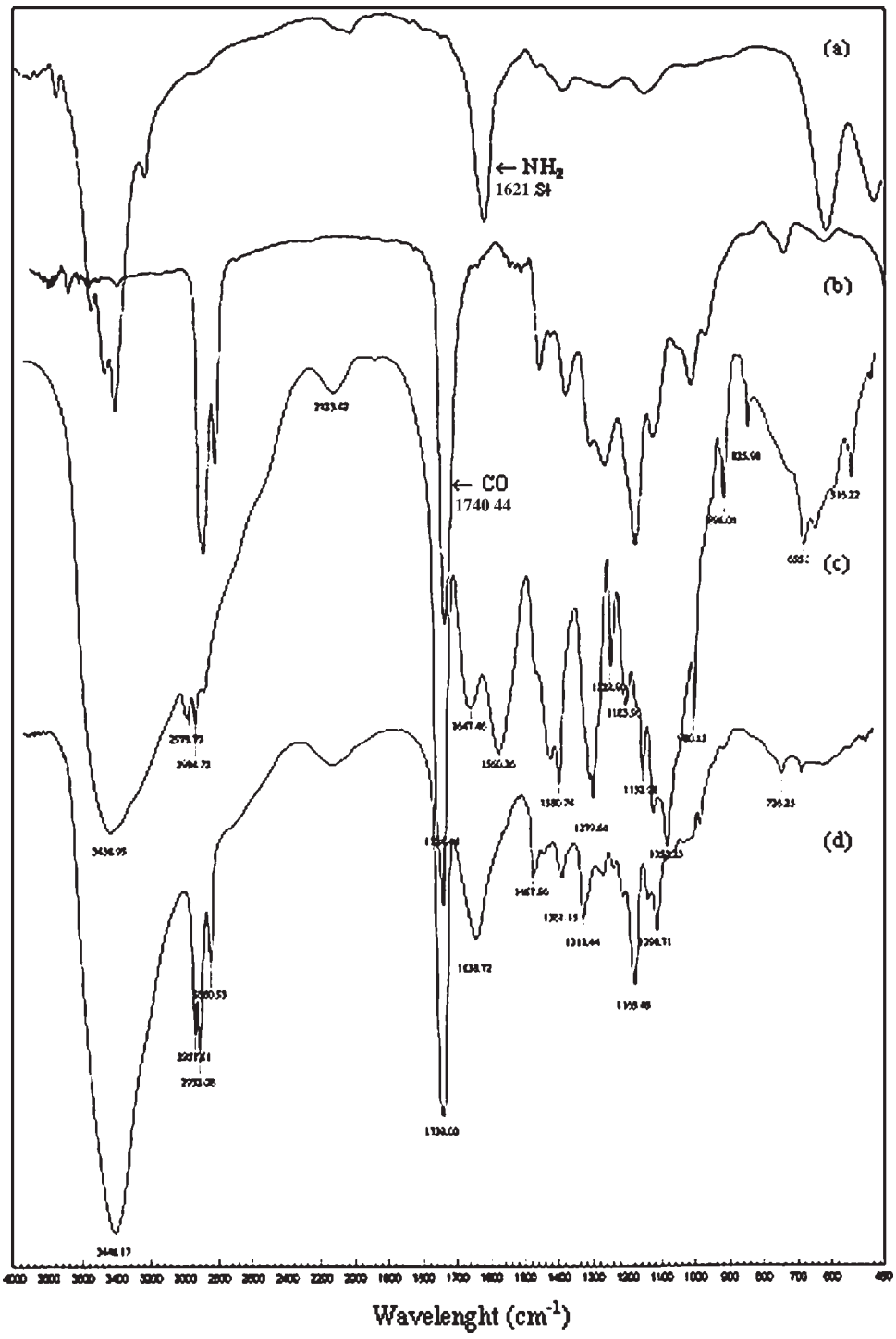


Figure 1 The FTIR spectra of (a) chitosan, (b) PHO, (c) chitosan-*g*-PHBV (Run No. VII), and (d) chitosan-*g*-PHO (Run No. XIII).

after extracting with $CHCl_3$ and 2 wt % HOAc, respectively. FTIR and GPC analysis of chloroform phases were demonstrated that they were unreacted PHBV or PHO. Furthermore, unimodal GPC spectra assumed that chloroform phase was free of soluble graft copolymer. It was also determined from GPC results that PHBV and PHO were not hydrolyzed during polymerization reactions. FTIR analysis of 2 wt % HOAc phases for run nos. V, VI and VII were also demonstrated that 2 wt % HOAc phases were unreacted chitosan. Percentage of microbial polyester in copolymer was varying between from 7 to 52 wt % as a function of molecular weight of PHAs, namely as a function of steric effect (Table IV).

FTIR analysis of graft copolymers

The FTIR spectra of chitosan, PHO, chitosan-*g*-PHBV, and chitosan-*g*-PHO were shown in Figure 1 (a,d), respectively. In the FTIR spectra of graft copolymers, compared with those of chitosan and PHO (or PHBV), additional peaks were determined. In the FTIR spectra of chitosan-*g*-PHBV, the peak at 1740.4 cm^{-1} represents the ester carbonyl groups from PHBV side chains of graft copolymers, the peaks at 1647.5 and 1560.4 cm^{-1} were attributed to the amide I band and amide II band, respectively. This confirms the successful formation of Chitosan-*g*-PHBV graft copolymer structure. In the FTIR spectra of chitosan-*g*-PHO, the peaks at 1739 cm^{-1} represents the ester carbonyl groups from PHO side chains and the peak at 1638.7 cm^{-1} represents amide II band, and especially this band demonstrates that the reactions of graft copolymerization are occurred.

NMR analysis of graft copolymers

Solid state ^{13}C-NMR analysis were performed to obtain clear spectrum because of the lack of complete solubility of graft copolymers. Figure 2 displays the ^{13}C-NMR spectra of chitosan-*g*-PHBV (a), chitosan-*g*-PHO (b), and chitosan-*g*-linoleic acid (c) copolymers. In these spectra, the peaks corresponding to chitosan were the broader resonance between 60 and 110 ppm at 102.8 ppm for C1, at 76.8 ppm for C3/C5 and at 60.8 ppm for C2/C6; the peaks corresponding to PHBV, PHO and linoleic acid side chains were the sharper resonance at 21.4 ppm for methyl, at 43 ppm for methylene, at 70 ppm for methine and at 170 ppm for carbonyl carbons of side chains.

Thermal characterization of graft copolymers

Thermal characterization of graft copolymers was performed by using DSC and TGA techniques. Thermal

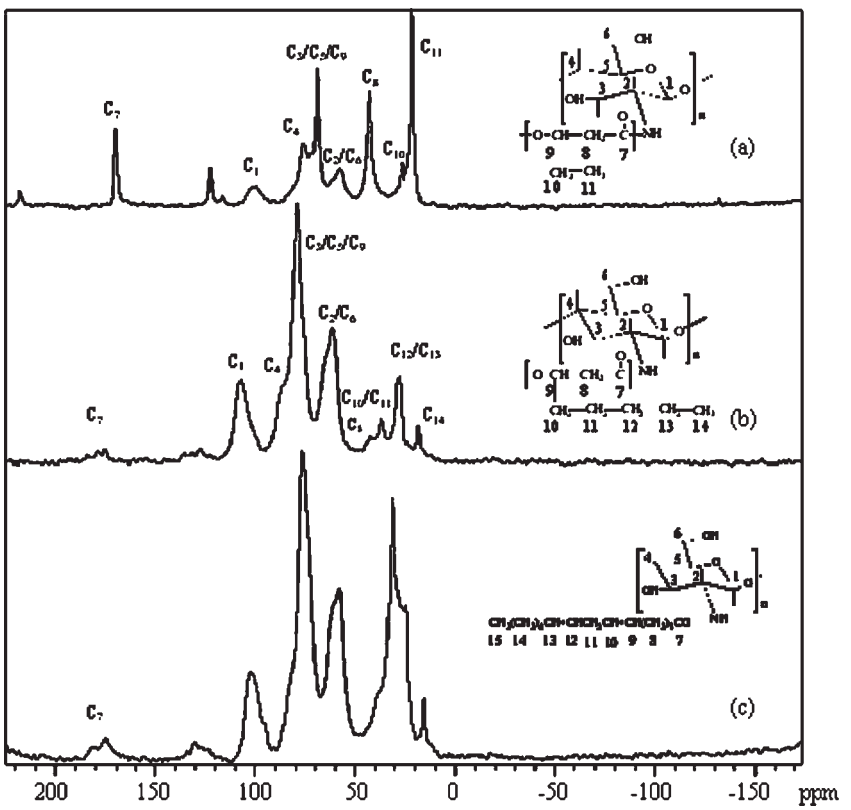


Figure 2 ^{13}C-NMR spectra of (a) chitosan-*g*-PHBV (Run No. V), (b) chitosan-*g*-PHO (Run No. XI), and (c) chitosan-*g*-linoleic acid (Run No. VIII).

TABLE V
Thermal Analysis of Graft Copolymers

Run no.	Polymer/ copolymer	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{m4} (°C)	T_d (°C)
	Chitosan	123	–	–	–	308
XI	Chit.-*g*-PHO	80	100	–	–	300
XI[a]	Chit.-*g*-PHO		61–125	–	288[b]	295
XII	Chit.-*g*-PHO	80	113	–	266[b]	290
XIII	Chit.-*g*-PHO		75–125	–	239[b]	295
V	Chit.-*g*-PHBV	131	144	–	251	–
VII	Chit.-*g*-PHBV	117	146	160	275	–

[a] Used different apparatus for DSC analysis
[b] Endothermic drift in the heat flow observed prior to exothermic peak initiation and due to formation of graft copolymer structure.

analysis results were summarized at Table V. Figure 3 shows DSC thermograms of chitosan and graft copolymers. In the DSC thermogram of chitosan the endothermic peak at 123°C is due to liberation of water contained in chitosan backbone because of free NH_2 groups and OH groups. The exothermic peak at around 308°C is due to thermal degradation of chitosan main chain.[7] The characteristics of DSC thermograms of chitosan-*g*-PHO are generally similar to that of chitosan, but in the case of graft copolymer it was shown that the endotherm at 123°C was shifted to at 100–113°C and a small additional shoulder at 80°C contributed to melting of PHO units and the decomposition peak temperature (exothermic peak) came down from around 308 to 290–300°C and intensity of these peaks decreased (compare (a) and (b) in Figure 3, see run no XI and XII in Table V). On the other hand, PHO homopolymer exhibits its melting at 61°C and glass transition at −36°C. The decrease at the decomposition peak temperature was attributed to the formation of graft copolymer structure. DSC thermograms of the other chitosan-*g*-PHO graft copolymers exhibited a broad melting transitions between 60.5 and 124.5°C for run no XI* and 75–125°C for run no XIII, which include melting of PHO and endotherm for chitosan. Furthermore, before exothermic peak initiation endothermic drift in the heat flow (indicated by an arrow in Figure 3 and indicated as T_{m4} for run no XI*, XII, XIII in Table V) was observed, which may originated from bulky side chains of grafts connected to chitosan.[9]

DSC thermogram of chitosan-*g*-PHBV graft copolymers exhibited three melting transitions at 117, 160, 274.8°C and a shoulder at 146°C [Fig. 3 (c)], while PHBV homopolymers shows T_ms at 130, 105, and 90°C. The exothermic decomposition peak corresponding to thermal degradation of chitosan main chain at 308°C nearly disappeared. These findings confirm the formation of graft copolymer structure.

When DSC thermogram of chitosan compared with that of linoleic acid derivatives of chitosan [Fig. 3 (d)], it was observed that the endotherm at 123°C was shifted to lower temperature (at 100°C) and occurring of split which might be due to heterogeneity of the structure namely there may be free NH_2 groups and capped NH_2

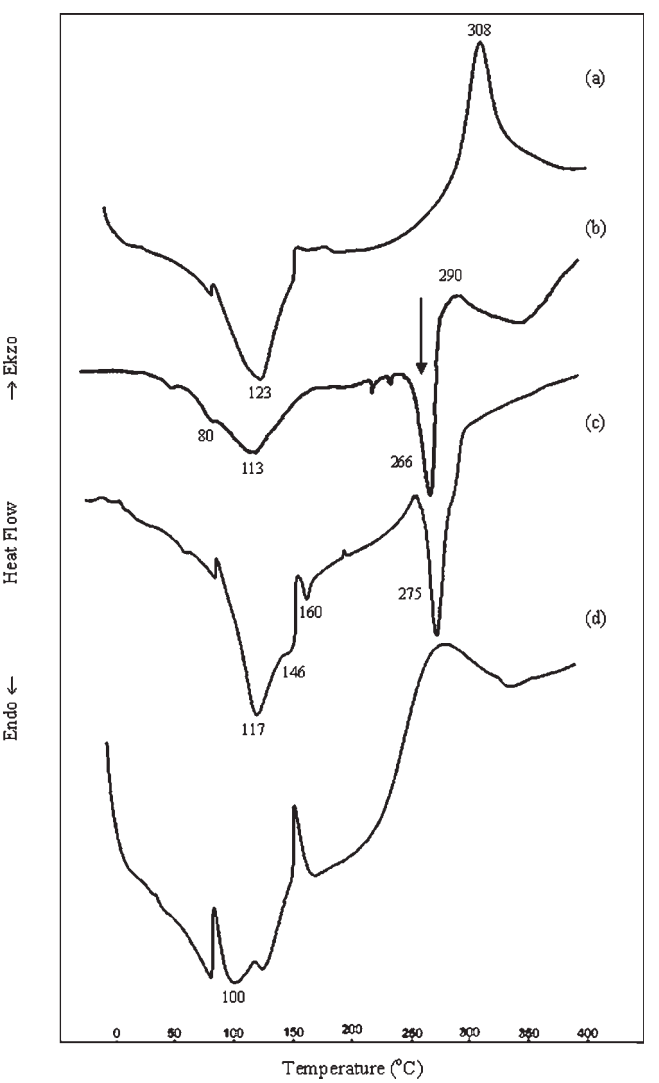


Figure 3 DSC thermograms of (a) chitosan, (b) chitosan-*g*-PHO (Run No. XII), (c) chitosan-*g*-PHBV (Run No. VII), and (d) chitosan-*g*-linoleic acid (Run No. VIII).

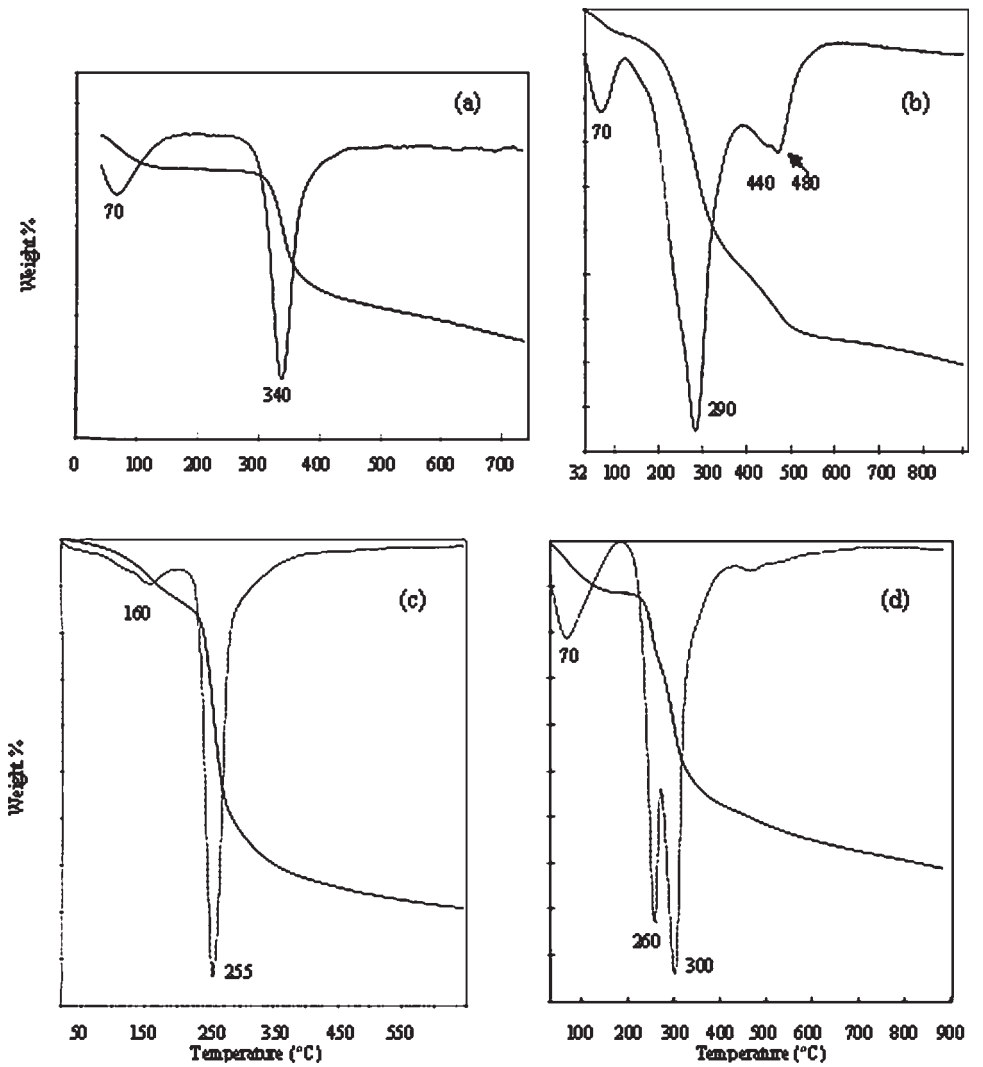


Figure 4 TGA thermograms of (a) chitosan, (b) chitosan-*g*-linoleic acid (Run No. X), (c) chitosan-*g*-PHBV (Run No. V), and (d) chitosan-*g*-PHO (Run No. XII).

groups with linoleic acid in chitosan backbone. It was also observed that the exothermic at 308°C was broader in the DSC thermogram of linoleic acid derivatives of chitosan.

TGA thermogram of chitosan exhibited one decomposition temperature (Td) at around 340°C and loss of water took place at around 70°C [Fig. 4 (a)]. TGA thermograms of linoleic acid derivatives of chitosan (Run Nos. VIII and IX in Table I) exhibited two main decomposition temperatures at around 280–290°C for chitosan backbone, at 465°C for linoleic acid grafts and a peak at around 70–100°C for the loss of water. On the other hand, in the case of run no X, it was observed that the decomposition of linoleic acid grafts occurred at two steps between 400 and 500°C [Fig. 4 (b)]. When Figures 4(a) and 4(b) were compared, in the case of linoleic acid derivatives of chitosan, multistep decomposition due to heterogeneity of the structure and decrease in thermal stability of chitosan backbone were observed. TGA thermograms of chitosan-*g*-PHBV graft copolymers exhibited only two decomposition temperatures at around 255–281°C, which is lower than that of chitosan and PHBV Td's and a small peak around 160°C while chitosan had a decomposition temperature at 340°C and a small peak at around 100°C for loss of water, and PHBV had a decomposition temperature at around 300°C and a small peak at around 150°C [Fig. 4 (c)]. It was also observed that the peak corresponding to loss of water at 100°C disappeared. This may explain the high grafting percentage of chitosan-*g*-PHBV graft copolymers. TGA thermogram of chitosan-*g*-PHO graft copolymers exhibited three decomposition temperatures at around 260°C for PHO, 300°C for chitosan, and 70°C for the loss of water while decomposition temperature of PHO was 300°C [Fig. 4 (d)]. TGA analyses demonstrated the formation of graft copolymers with the decreases at thermal stabilities in comparison to PHO, PHBV and chitosan.

CONCLUSIONS

Chitosan-*g*-PHBV and chitosan-*g*-PHO graft copolymers were synthesized and grafting of linoleic acid on chitosan were performed by condensation reaction under vacuum at 90–95°C. The graft copolymers were characterized by FTIR, ^{13}C-NMR (in solid state), DSC, and TGA. Solubility tests were also performed and graft copolymers exhibited different solubility behavior as a function of degree of substitution of NH_2 in other words as a function of grafting percent such as solubility, insolubility, or swelling in 2 wt % acetic acid and in water while chitosan does not swell in water. It was concluded that grafting percentage was affected by molecular weight and structure of grafted PHAs (steric effect) and finally solubility of polymers in the polymerization medium, so the solubility of chitosan-*g*-PHA graft copolymer could be controlled by arranging of grafting percentage. It has been planning to investigate applicability of these new materials in the medical applications, such as tissue engineering and drug delivery systems, by testing their antimicrobial activity and biocompatibility, because chitosan and PHA are natural polymers, and have many medical applications.

References

1. Singh, D. K.; Ray, A. R. J Macromol Sci Rev Macromol Chem Phys 2000, C40, 69.
2. Shahidi, F.; Arachchi, J. K. V.; Jeon, Y. Trends Food Sci Technol 1999, 10, 37.
3. Caner, H.; Hasipoglu, H.; Ylmaz, O.; Ylmaz, E. Eur Polym J 1998, 34, 493.
4. Jung, B.; Kim, C.; Choi, K.; Lee, Y. M.; Kim, J. J Appl Polym Sci 1999, 72, 1713.
5. Shantha, K. L.; Harding, D. R. K. Carbohydr Polym 2002, 48, 247.
6. Yao, F.; Chen, W.; Wang, H.; Liu, H.; Yao, K.; Sun, P.; Lin, H. Polymer 2003, 44, 6435.
7. Ding, W.; Lian, Q.; Samuels, R. J.; Polk, M. B. Polymer 2003, 44, 547.
8. Silva, S. S.; Menezes, S. M. C.; Garcia, R. B. Eur Polym J 2003, 39, 1515.
9. Prashanth, K. V.; Tharanathan, R. N. Carbohydr Polym 2003, 54, 343.
10. Lenz, R. W.; Marchessault R. H. Biomacromolecules 2005, 6, 1.
11. Grassie, N.; Murray, E. J.; Holmes, P. A. Polym Degrad Stab 1984, 6, 47.
12. Galeo, N.; Rozsa, C. Polym Int 1999, 48, 1202.
13. Hazer, B. In Biopolymers, Wiley-VCH: Weinheim, 2003; Vol. 10, Chapter 6, p 181.
14. Hazer, B. Curr Trends Polym Sci 2002, 7, 131.
15. Yalpani, M.; Marchessault, R. H.; Morin, F. G.; Monasterios, C. J Macromolecules 1991, 24, 6046.
16. Koçer, H.; Borcakli, M.; Demirel, S.; Hazer, B. Turk J Chem 2003, 27, 365.