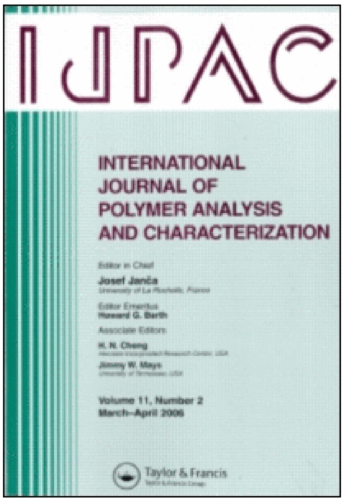

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Miscibility of Chitosan and Poly(Ethylene Oxide) in Dilute Solution

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Miscibility of Chitosan and Poly(Ethylene Oxide) in Dilute Solution

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Miscibility of chitosan (CHI) with poly(ethylene oxide) (PEO) was studied in dilute solution by viscometry. Blends with CHI/PEO compositions of 0.1/0.9, 0.2/0.8, and 0.3/0.7 were studied at 25°, 30°, and 35°C, in a buffer solution of 0.1 M acetic acid/0.2 M sodium acetate. Starting with the classical Huggins equation, the results of the viscosity behavior of each parent polymer and their blends were interpreted in terms of miscibility parameters, Δk, α, *and* Δb. *Miscibility between CHI and PEO was found to increase with weight fraction of PEO and polymer concentration. The existence of H-bonding interaction between CHI and PEO was demonstrated by FTIR spectroscopy.*

Keywords: Miscibility; Compatibility; Viscometry; Chitin; Chitosan; Poly(ethylene oxide)

Chitin is a natural polysaccharide, which originates from the outer shells of crustaceans. Chitin can be deacetylated to obtain chitosan, as shown in Scheme 1. Owing to its biocompatibility; nontoxicity; gel, film, and fiber-forming properties; metal, protein, and fat-binding abilities; and cationic character in solution, it has found various applications as a biomedical material as well as in hair treatment and skin care,

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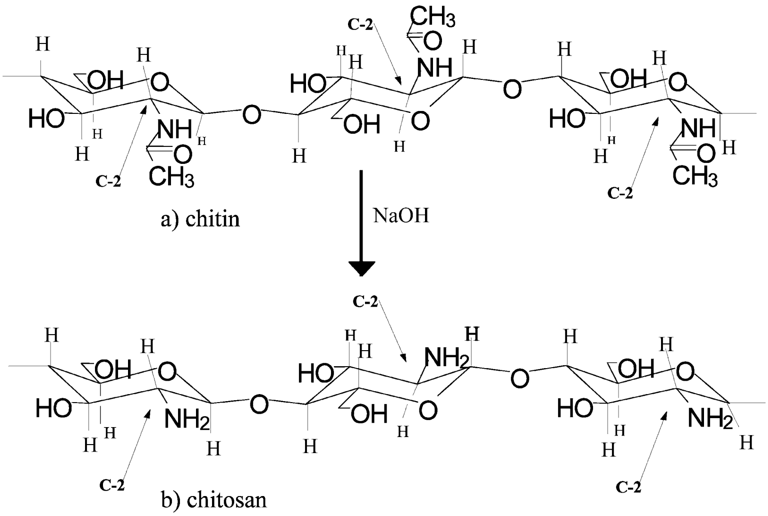

SCHEME 1

agriculture, the food industry, and wastewater treatment[1]. Recently, it has been proposed as a medical iron chelator[2].

Poly(ethylene oxide) (PEO) is a biodegradable, hydrophilic polymer. While poly(ethylene glycol) (PEG) oligomers have found uses in ceramic, cosmetic, pharmaceutical, and lubricant formulations, high-molecular-weight polymeric derivatives of PEO are used in detergents, cosmetic formulations, contact lens solutions, and dental adhesives due to their water solubility, rheological properties, low toxicity, thermo-plasticity, and flocculation ability[3].

The aim of this work is to study the miscibility of chitosan and PEO in dilute aqueous solution by viscometry. These two polymers have many common properties such as being biocompatible and biodegradable, having adhesive and flocculent properties, and being soluble in aqueous solutions. Studying molecular interactions between these two polymers is of technological importance especially for biomedical, pharmaceutical, and cosmetic applications. Dilute solution viscometry has been chosen as the most suitable technique since it provides information on miscibility at the molecular level, and it is easy, fast, and inexpensive when compared to other blend characterization techniques in bulk.

Viscometric analysis of polymer-polymer miscibility in dilute solution is based upon the Huggins equation, which reflects the relationship between specific viscosity, η_{sp}, and polymer concentration, c, as follows:

$$\eta_{sp} = [\eta]c + bc^2 \tag{1}$$

where c is the concentration and $[\eta]$ is the intrinsic viscosity, which is a measure of the effective hydrodynamic volume of the isolated polymer. Parameter b, which reflects the binary interactions between polymer segments, is related to the Huggins coefficient, k_H, by the equation

$$b = k_H[\eta]^2 \tag{2}$$

Krigbaum and Wall cited in Rudin et al.[4] adapted the Huggins equation to a ternary system, namely a mixture of two polymers in a common solvent as given below:

$$\eta_{sp,m} = [\eta]_m c_m + b_m {c_m}^2 \tag{3}$$

where

$$b_m = {w_1}^2 b_{11} + 2w_1w_2b_{12} + {w_2}^2 b_{22} \tag{4}$$

w_1 and w_2 are the weight fractions of polymers 1 and 2 respectively, and

$$b_m = k_m[\eta] \tag{5}$$

$$b_{11} = k_1{[\eta]_1}^2 \tag{6}$$

$$b_{22} = k_2{[\eta]_2}^2 \tag{7}$$

$$b_{12} = k_{12}[\eta]_1[\eta]_2 \tag{8}$$

$$[\eta]_m = w_1[\eta]_1 + w_2[\eta]_2 \tag{9}$$

A miscibility parameter, Δb, based on the specific viscosity, $\eta_{sp,m}$, of a polymer mixture was proposed by these authors. For miscible polymer pairs, Δb values are positive[4]. Cragg and Bigelow cited in Rudin et al.[4] studied the molecular interactions in a polymer mixture in solution and suggested a miscibility parameter, Δk, whose positive values would indicate favorable interactions of unlike polymer chains in solution and, hence, miscibility. Sun et al.[5] proposed a new parameter, α, which reflects the interaction of unlike polymer molecules provided that strong specific interactions between polymers, which would encourage aggregation, are absent and the solution is sufficiently dilute. If there are attractive thermodynamic interactions among molecules, then α is positive and vice versa.

The equations used to calculate all three of the above-mentioned miscibility parameters are summarized in Table I. A more detailed analysis of these equations can be found in a previous work of ours[6].

TABLE I A summary of miscibility parameter equations

$\Delta k = (k_{12})_{\text{exp}} - (k_{12})_{\text{theo}}$ where:	$\alpha = k_{\text{m}} - k_{\text{m1}}$ when: $k_{\text{m}} = (k_{\text{m}})_{\text{exp}}$	$\Delta b = (b_{12})_{\text{exp}} - (b_{12})_{\text{theo}}$ where:
$(k_{12})_{\text{exp}} = b_{\text{m}} - (w_1{}^2\ b_{11} + w_2{}^2 b_{22})/2w_1 w_2 [\eta]_1 [\eta]_2$ $(k_{12})_{\text{theo}} = (k_1 k_2)^{1/2}$	$k_{\text{m1}} = (k_{\text{m}})_{\text{theo}}$ $(k_{\text{m}})_{\text{theo}} = (w_1{}^2\ \text{b}_{11} + 2w_1 w_2 b_{12} + w_2{}^2 b_{22})^2\ (w_1[\eta]_1 + w_2[\eta]_2)^2$	$(b_{12})_{\text{exp}} = (\eta_{\text{sp}} - [\eta]_1 c_1 - [\eta]_2 c_2 - b_{11} c_1{}^2 - b_{22} c_2{}^2) / 2b_{12} c_1 c_2$ $(b_{12})_{\text{theo}} = \sqrt{b}_{11}\ b_{22}$ or $(b_{12})_{\text{theo}} = (b_{11} + b_{22})/2$
criterion: $\Delta k > 0$ miscible	criterion: $\alpha > 0$ miscible	criterion: $\Delta b > 0$ miscible

EXPERIMENTAL

Chemicals and their Purification

Chitin was a product of Sigma and was used as supplied. PEO was a product of BDH with a molecular weight of 1.0×10^5; it was used as received. A buffer solution of 0.1 M CH_3COOH/0.2 M CH_3COONa was used as the solvent. Both the acid and the salt were products of Merck and used without further purification.

Apparatus

Ubbelohde viscometers were used for dilute solution viscosity measurements at different temperatures. Viscosity measurements were carried out in constant-temperature water baths, kept constant within ±0.1°C by an electronically controlled thermostat. Aldrich (type 31655) syringe mountable filter holders with 25 mm diameter were used together with Aldrich S & S PTFE (Teflon) membrane filters with 25 mm diameter and 0.45 μm maximum pore size.

Method

Preparation and Characterization of Chitosan

Chitin was dispersed in 50% w/w NaOH solution and refluxed at 107°C for 3 h. The mixture was cooled to room temperature, filtered by suction filtration, and washed with water several times until the filtrate was neutral. The chitosan sample obtained was dried in an oven at 60°C. The degree of deacetylation (DD) of chitosan was determined by titration of its hydrobromide salt with 0.1 M NaOH solution[7]. The degree of deacetylation was calculated to be 60%.

Viscosity average molecular weight of chitosan was determined at 30°C in 0.1 M acetic acid/0.2 M sodium acetate buffer solution and was calculated to be 8.5×10^5 by using the K and α constants proposed by Wang et al.[8] as given below:

$$[\eta] = 1.04 \times 10^{-4}\ \mathrm{M}^{1.12} (\mathrm{mL/g}).$$

Viscosity Measurements

Viscosity measurements of both homopolymers and blends were carried out in the filtered acetic acid/sodium acetate buffer solution at 25°, 30°, and 35°C. PEO and the blends were studied in a concentration range of 0.1–1.0 g/dL. Chitosan was studied in the 0.01–0.1 g/dL concentration range. Average flow times were determined for at least five concentrations for each sample. Plots of reduced viscosity values against concentration were linear for all samples, with correlation coefficients of 0.99.

FTIR Analysis

The homopolymers and the blend samples were regenerated from acetic acid/sodium acetate buffer solution by solvent evaporation and dried at 40°C. Fourier transform infrared (FTIR) spectra of KBr pellets of the samples were taken by the Mattson Satellite 5000 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Viscosity Measurements

Dilute solutions of weak organic acids are suitable solvents for chitosan, owing to the protonation of the free amine groups on the polysaccharide backbone. However, the polycation formed exists in an extended rigid-rod conformation in solution and exhibits characteristic polyelectrolyte solution properties, which deviate from the classical Huggins equation. To overcome this difficulty, an acetic acid/sodium acetate buffer solution was chosen as the solvent. In a buffer solution, the polyelectrolyte approaches a random-coil conformation due to the screening effect of the counter ions on the cationic centers of the polymer backbone[9]. PEO, however, is known to be a flexible uncharged polymer,

TABLE II Dilute solution viscosity data for CHI, PEO, and CHI/PEO blends, at 25°, 30°, and 35°C

	T = 25°C			T = 30°C			T = 35°C		
Sample	[η]dL/g	b	k_H	[η]dL/g	b	k_H	[η]dL/g	b	k_H
CHI	4.61	14.8	0.695	4.97	16.2	0.657	6.44	20.9	0.504
PEO	0.805	0.271	0.418	0.879	0.281	0.364	0.749	0.215	0.561
CHI/PEO (0.1/0.9)	1.08	0.728	0.624	1.16	0.782	0.580	1.20	0.943	0.651
CHI/PEO (0.2/0.8)	1.29	1.15	0.685	1.31	1.081	0.625	1.73	1.42	0.477
CHI/PEO (0.3/0.7)	1.69	1.92	0.488	1.47	0.919	0.428	2.07	2.27	0.528

which obeys the classical Huggins equation. Viscosity data for the solutions of CHI, PEO, and their mixtures are given in Table II. Theoretically, the Huggins coefficient, k_H, of a flexible polymer is around 0.5 for theta solvents and 0.3 for good solvents. This value, however, varies around 0.69 and 0.88 for a rigid polymer in good and theta solvents, respectively[9]. At all temperatures studied, the Huggins coefficients of all samples fall within these ranges, confirming the reliability of our data.

Composition and Temperature Dependence of Miscibility Parameters

Mixtures of PEO and CHI were studied at 25°, 30°, and 35°C at compositions 0.9, 0.8, and 0.7 with respect to weight fraction of PEO. The miscibility parameter values, Δk and α, calculated for the blends studied are summarized in Table III. As can be followed from the table, the two different miscibility parameter values do not always agree with each other. In some cases, α values tend to indicate miscibility while Δk values indicate immiscibility. In cases where this contradiction is observed the blend has been assigned as immiscible according to the Δk parameter. The justification for this decision is that, in a system composed of polar polymers such as CHI and PEO, strong specific interactions among both like and unlike polymer chains are present and applicability of the α parameter to such systems is limited[5]. Positive α and Δk values and hence miscibility have been reported for CHI/PEG blends in literature[10].

For the systems studied, miscibility of CHI and PEO increases with the weight fraction of PEO in the blend samples at all temperatures studied. CHI/PEO (0.1/0.9) blend shows miscibility at all temperatures according

TABLE III Miscibility parameters for CHI/PEO blends at 25°, 30°, and 35°C

	T = 25°C		T = 30°C		T = 35°C	
Sample	Δk	α	Δk	α	Δk	α
CHI/PEO (0.1/0.9)	0.24	0.12	0.095	0.12	0.31	0.22
	Miscible		Miscible		Miscible	
CHI/PEO (0.2/0.8)	−0.028	0.12	−0.31	0.10	0.053	0.019
	Immiscible		Immiscible		Miscible	
CHI/PEO (0.3/0.7)	−0.18	0.068	−0.86	−0.13	−0.24	0.052
	Immiscible		Immiscible		Immiscible	

to Δk and α values. The blend CHI/PEO (0.2/0.8) is immiscible at 25° and 30°C and miscible at 35°C. CHI and PEO mixed in a ratio of 0.3/0.7 are not miscible with each other at any temperature studied. Specific interactions like dipole-dipole interaction or H-bonding should be responsible for the miscibility observed between CHI and PEO in solution. It can be proposed that favorable interactions occur between amide or amine nitrogen on the chitosan backbone and hydroxyl and etheric oxygen of PEO. Under the conditions where miscibility is exhibited between PEO and CHI, H-bonding interaction between the two polymers should be strong enough to overcome the intra- and intermolecular H-bonding among CHI chains themselves. As the weight fraction of PEO in the blend decreases, the probability for a CHI chain to establish H-bonding interaction with a chain of its own kind increases, since PEO chains become less available in the medium. Consequently, immiscibility between the two polymers is observed. A study of the rheological behavior of aqueous solutions of CHI/PEO mixtures suggested that rigid chitosan chains determine the rheological behavior of the CHI/PEO blends. As a result of H-bonding between the molecules of chitosan, water, and PEO with molecular weight less than 1×10^6, the soft polyether chains can be oriented along the rigid chitosan macromolecules[11]. The Huggins coefficient values given in Table II for the CHI/PEO blends studied suggest that a similar mechanism is involved in dilute solution as well. The CHI/PEO blends with 0.1/0.9 and 0.2/0.8 composition have k_H values of the order of 0.6, closer to that of CHI rather than that of PEO, indicating that PEO chains are oriented around rigid chitosan chains. The immiscible CHI/PEO blend with 0.3/0.7 composition has k_H values closer to that of PEO under the same conditions, showing the lack of any favorable interaction with or orientation around chitosan, in contrast to the other two blends.

Miscibility between CHI and PEO appears to be independent of temperature within the narrow temperature range studied, although a slight increase in miscibility parameter values is observed at 35°C.

Concentration Dependence of Δ*b* Parameter

Miscibility parameters Δ*b* calculated for the three blends studied have been plotted against total blend concentration at the three temperatures studied in Figures 1–3 for the samples CHI/PEO: 0.1/0.9, 0.2/0.8, and 0.3/0.7 respectively. The trend exhibited by Δ*b* values with respect to concentration may be taken as an indication of compatibility in the semidilute regime or even in the solid state[12]. For a given polymer mixture, a tendency toward positive values with increasing concentration would be interpreted as a tendency toward compatibility in the solid state.

The CHI/PEO (0.1/0.9) blend has positive Δ*b* values at 25° and 35°C but negative Δ*b* values at 30°C. The other two blends studied have negative Δ*b* values at all three temperatures, except for the second blend with 0.2/0.8 CHI/PEO ratio at 35°C. One common feature of the curves

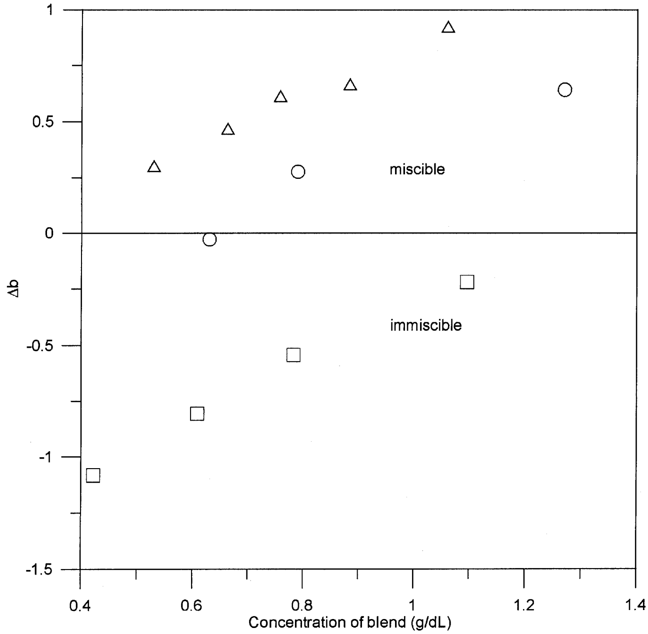

FIGURE 1 Concentration dependence of miscibility parameter Δ*b* for CHI/PEO (0.1/0.9) at (○) 25°C, (□) 30°C, and (Δ) 35°C.

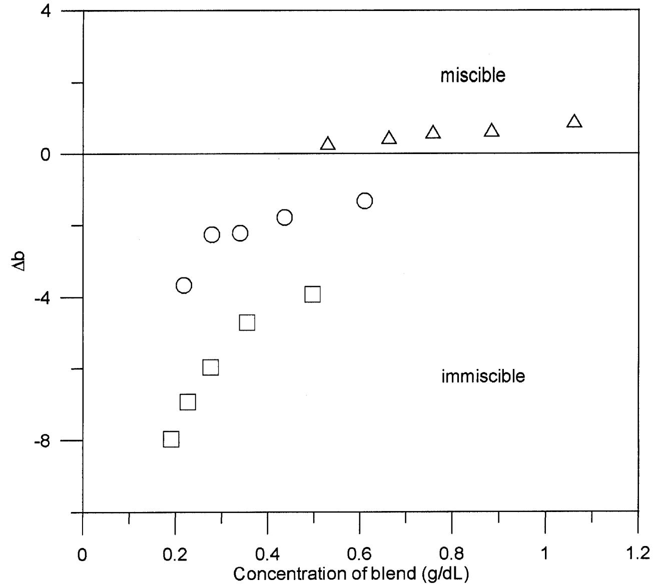

FIGURE 2 Concentration dependence of miscibility parameter Δb for CHI/PEO (0.2/0.8) at (○) 25°C, (□) 30°C, and (Δ) 35°C.

in the immiscible region is that they all have a tendency toward positive Δb values with increasing concentration. This could be taken as an indication of miscibility of these two polymers at higher concentrations or in the solid state at all three temperatures studied.

FTIR Analysis of Molecular Interactions between CHI and PEO

The FTIR spectra of PEO, the blend CHI/PEO: 0.3/0.7, and CHI taken in the solid state are compared to each other in Figures 4(a), (b), and (c) respectively. In the spectrum of PEO, -O-H stretching at 3448 cm^{-1}; -C-H stretching of methylene groups at 2891 cm^{-1}; and -C-H stretching, bending, and rocking vibrations at 1467, 1360, and 961 cm^{-1}, respectively; and -C-O bands at 1148, 1100, and 1063 cm^{-1} are observed. In the chitosan spectrum, absorption bands characterizing hydroxyl, amide I and II, and the pyranose group are observed at 3451, 1640, 1583, and 1153–1021 respectively. The spectrum of the blend displays characteristic absorption bands of PEO and CHI with two exceptions:

1. Amide II band of chitosan at 1583 shifts to 1563 cm^{-1}. This shift toward lower energy reveals that there is a favorable interaction

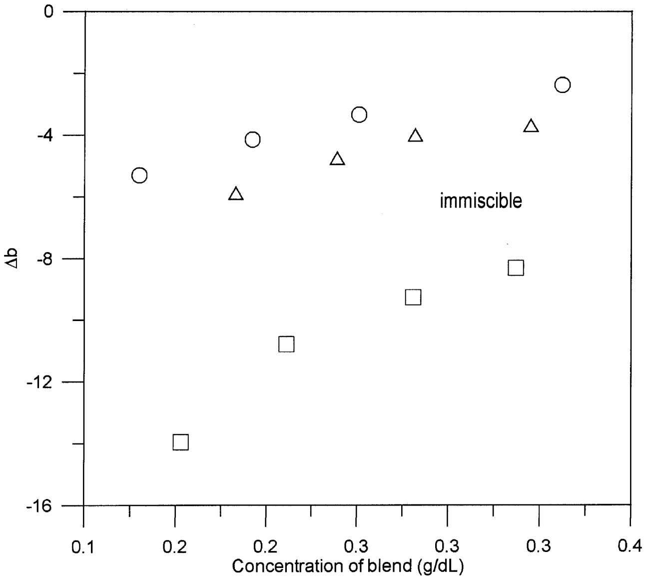

FIGURE 3 Concentration dependence of miscibility parameter Δ*b* for CHI/PEO (0.3/0.7) at (○) 25°C, (□) 30°C, and (Δ) 35°C.

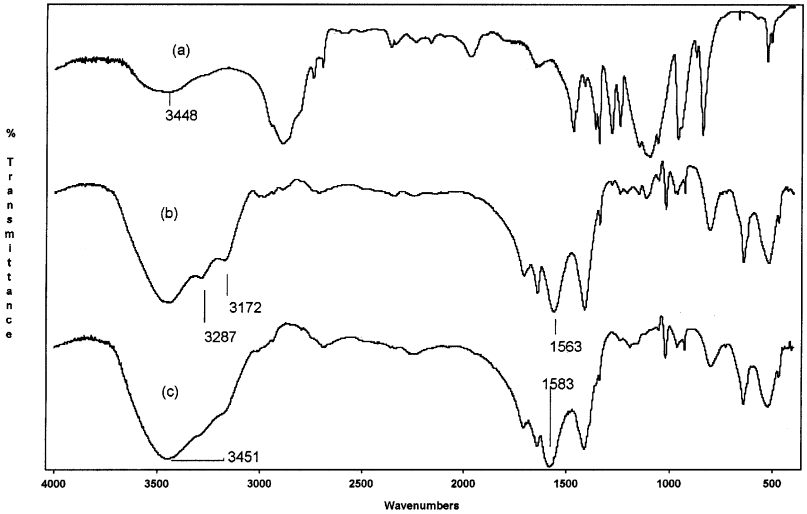

FIGURE 4 FTIR spectra of (a) PEO, (b) CHI/PEO (0.3/0.7), and (c) CHI.

between PEO and CHI through the amide group of CHI and free hydroxyl groups of PEO.

2. Two new small peaks appear at 3287 and 3172 cm^{-1}. These may be attributed to the H-bonding interaction between hydroxyl groups of CHI and PEO chains.

A report on the compatibility and morphology of CHI/PEO blend films is available in the literature[13]. Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) analyses of the blend films showed that CHI and PEO are compatible when volume fraction of chitosan in the mixture is less than 50%.

CONCLUSIONS

Chitosan and poly(ethylene oxide) are miscible at a CHI/PEO blend ratio of 0.1/0.9 at 25°, 30° and 35°C, in dilute acidic solution. A blend of CHI and PEO with a composition of 0.2/0.8 CHI/PEO is immiscible at 25° and 30°C but miscible at 35°C in solution. A blend with CHI/PEO: 0.3/0.7 is immiscible in solution at all three temperatures studied, but miscible in the solid state as predicted by solution properties and supported by FTIR analysis. Miscibility of PEO and CHI determined in terms of Δb parameter has a tendency to increase with increasing polymer concentration, which may be extrapolated to compatibility in the solid state. FTIR analysis indicated that H-bonding interaction exists between the two polymers.

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