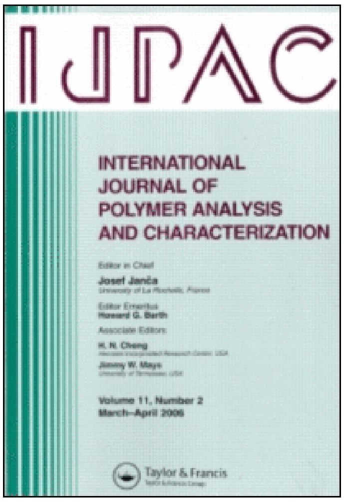

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Miscibility Study of Chitosan/Poly(Vinyl Pyrrolidone) Blends in Dilute Solution

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Abstract: Miscibility of chitosan (CHI) with two poly(vinyl pyrrolidone) samples (PVP-1 and PVP-2) of different molecular weights was studied in dilute solution by viscometry. Blends with chitosan weight fraction in the range 0.10–0.90 were studied at 30°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. CHI ($M_v = 3.3 \times 10^5$) and PVP-1 ($M_v = 2.5 \times 10^4$) were found to be miscible at a blend composition of CHI/PVP 0.90/0.10. PVP-2 ($M_v = 1.1 \times 10^6$) and CHI were miscible in the full range of blend compositions studied. The existence of favorable secondary interaction between CHI and PVP leading to miscibility was demonstrated by FTIR spectroscopy.

Keywords: Miscibility; Compatibility; Viscometry; Chitin; Chitosan; Poly(vinyl pyrrolidone)

INTRODUCTION

Viscometric analysis of polymer-polymer miscibility in dilute solution is based upon the Huggins equation, which reflects the relationship between

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specific viscosity η_{sp} and polymer concentration c, as follows:

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

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

$$b = k_H[\eta]^2 \quad (2)$$

Krigbaum and Wall[1] adapted the Huggins equation to a ternary system, namely, a mixture of two polymers in a common solvent. 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.[1] Cragg and Bigelow[2] 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.[3] proposed a new parameter α, which reflects the interaction of unlike polymer molecules provided that strong specific interactions between polymers that 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 our previous works.[4]

Chitosan, a biocompatible and biodegradable polymer derived from chitin, presents exceptional chemical and biological qualities that can be used in different areas from health care to agriculture and dyes for fabrics. It is an anticholesterolemic agent and a metal chelating agent.[5] It is obtained by deacetylating chitin for the molecule to be soluble in most diluted acids. As a result of deacetylation, amine groups that give the molecule the cationic character in acid solutions replace amide groups of chitin. This is especially interesting since the majority of polysaccharides are usually neutral or negatively charged. Chitosan exists in an extended conformation in solution, and in the absence of a counterion it exhibits characteristic solution properties of a polyelectrolyte, which deviate from the classical Huggins equation.[6] To approximate the solution behavior of chitosan to that of a nonionic polymer, acetic acid/sodium acetate buffer solution was chosen as the solvent in this study. The presence of acetate ions partially screens the repulsion force between the cationic centers of the polymer backbone.[7]

Poly(vinyl pyrrolidone), PVP, having a high capacity for complex formation in addition to good stabilizing and solubilizing capacity,

Table I. Summary of miscibility parameter equations

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

insensitivity to pH, and good biological compatibility, has become one of the most frequently used specialty polymers. Today, PVP is widely used in the pharmaceutical industry. PVP is available in several viscosity grades, ranging from very low to very high molecular weight, giving this family of products great flexibility across a wide range of industries. PVP polymers are film formers, protective colloid and suspending agents, dye-receptive agents, binders, stabilizers, detoxicants, and complexing agents.[9]

Since both chitosan and PVP have a wide range of applications in the pharmaceutical and cosmetic industries, mixtures of these polymers may be included in drug or cosmetics formulations either in solution or in the solid state. This study aimed at investigating the miscibility of these two polymers in solution.

EXPERIMENTAL SECTION

Chemicals

Chitosan (CHI) of molecular weight 3.3×10^5 was a product of Primex. PVP-1 and PVP-2 were products of BASF with molecular weights 2.5×10^4 and 1.1×10^6 respectively as given by the producer. All polymer samples were used as received and all molecular weights are viscosity average values. 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

An Ubbelohde viscometer was used for dilute solution viscosity measurements. Viscosity measurements were carried out in a constant-temperature water bath, kept at $30 \pm 0.1^\circ C$ by an electronically controlled thermostat. Gooch crucibles (G4) were used to filter polymer solutions.

Method

Viscosity Measurements

Viscosity measurements of both homopolymers and blends were carried out in filtered acetic acid/sodium acetate buffer solutions at 30°C. CHI and blends were studied in a concentration range of 0.1–0.5 g/dL. PVP-1 was studied in the 1.0–2.0 g/dL concentration range while a lower concentration range of 0.5–1.0 g/dL was suitable for the higher molecular weight sample PVP-2. 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 a Mattson Satellite 5000 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Viscosity Measurements

Viscosity data for the solutions of CHI, PVP-1, and PVP-2 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.[8] For all blends and homopolymers studied, the Huggins coefficients fall within these ranges, confirming the reliability of our data. The Huggins coefficient values for PVP-1 and PVP-2 are 0.86 and 0.53 respectively. Hence, the low molecular weight PVP sample, PVP-1 with a molecular weight of 2.5×10^4, acts as a rigid chain close to the theta state, while PVP-2, which has a much higher molecular weight (1.1×10^6), is more like a coil rather than a rigid chain under the conditions studied. CHI is a rigid polymer approaching the coil conformation as interpreted from a k_H value of 0.58.

Table II. Dilute solution viscosity data for CHI, PVP, and CHI/PVP blends at 30°C in 0.1 M CH_3COOH/0.2 M CH_3COONa

	PVP-1			PVP-2		
Sample	[η] dL/g	b	k_H	[η] dL/g	b	k_H
CHI	4.72	13.0	0.58	4.72	13.0	0.58
PVP	0.20	0.03	0.86	0.96	0.49	0.53
CHI/PVP (0.10/0.90)	0.74	0.26	0.47	1.42	1.12	0.56
CHI/PVP (0.25/0.75)	1.47	0.95	0.44	2.15	2.24	0.48
CHI/PVP (0.50/0.50)	2.55	3.16	0.49	3.15	5.44	0.55
CHI/PVP (0.75/0.25)	3.53	6.53	0.52	3.90	8.25	0.54
CHI/PVP (0.90/0.10)	4.58	12.6	0.60	4.41	12.4	0.64

Composition and Molecular Weight Dependence of Miscibility Parameters

Mixtures of PVP and CHI were studied at 30°C at compositions of 0.90, 0.75, 0.50, 0.25, and 0.10 with respect to weight fraction of PVP-1 and PVP-2. The miscibility parameter values, Δk and α, calculated for the blends studied are summarized in Table III. For the low molecular weight PVP sample, PVP-1, miscibility with CHI is observed at a low PVP fraction (CHI/PVP: 0.90/0.10). When the fraction of CHI in the blend is 0.90, CHI whose molecular weight is higher than that of PVP-1 and whose chain conformation approaches a coil more than that of PVP-1 may act as a pseudo-solvent for the low molecular weight PVP by entangling around the short, rigid PVP chains. The viscosity behavior of the miscible blend is determined by chitosan as reflected by a k_H value of 0.60. As the fraction of PVP in the mixture increases and the fraction of CHI decreases, the possibility of this entanglement, which leads to miscibility, decreases. Hence, immiscibility is observed for blend compositions of CHI/PVP of 0.25/0.75, 0.50/0.50, and 0.75/0.25. The high molecular weight PVP sample, PVP-2, is miscible with CHI at any composition. Having a higher molecular weight than PVP-1, PVP-2 approaches a coil conformation in the solution studied. It may be expected that both CHI and PVP may entangle around each other depending on the blend composition, leading to miscibility at all compositions. Dipole-dipole interactions between the carbonyl oxygen of the pyrrolidone ring and the hydrogen atoms of alcohol, amine, or amide groups of chitosan pyranose ring should be responsible for miscibility observed for blends of these two polymers at the molecular level.

Table III. Miscibility parameters for CHI/PVP blends at 30°

	PVP-1		PVP-2	
Sample	Δk	α	Δk	α
CHI/PVP (0.10/0.90)	−0.11	−0.18	0.18	2.14
	Immiscible		Miscible	
CHI/PVP (0.25/0.75)	−0.35	−0.17	0.12	−0.08
	Immiscible		Miscible	
CHI/PVP (0.50/0.50)	−0.90	−0.10	0.36	0.0
	Immiscible		Miscible	
CHI/PVP (0.75/0.250)	−2.9	−0.06	0.0	0.0
	Immiscible		Miscible	
CHI/PVP (0.90/0.10)	12.0	0.02	1.8	0.06
	Miscible		Miscible	

It seems that in addition to favorable secondary interactions between the polymers, blend composition and polymer conformation are important parameters affecting miscibility in solution. In a previous study of ours on the miscibility of chitosan with poly(ethylene oxide), PEO, miscibility between the two polymers was observed under the conditions when soft, flexible PEO chains could orient themselves around the more rigid CHI chains.[5] In the present study, a similar phenomenon has been observed. CHI and PVP are miscible in solution when the blend composition is in favor of orientation of one polymer along the other.

Concentration Dependence of Δb Parameter

Miscibility parameters Δb calculated for the blends studied are plotted against total blend concentration in Figures 1 and 2. The trend exhibited

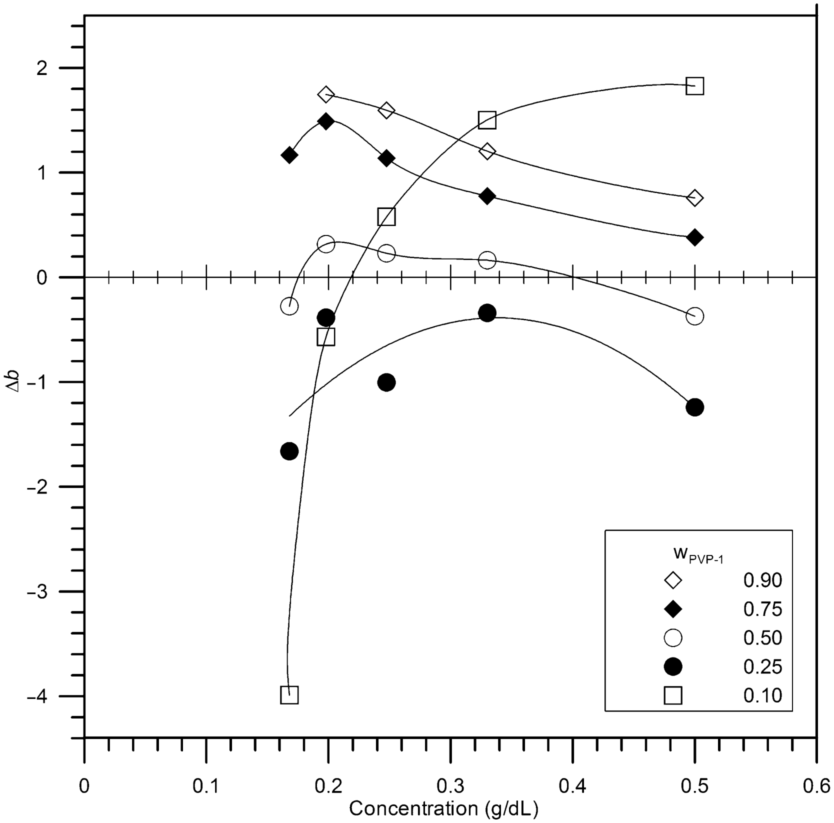

Figure 1. Concentration dependence of miscibility parameter Δ*b* for CHI/PVP-1 blends.

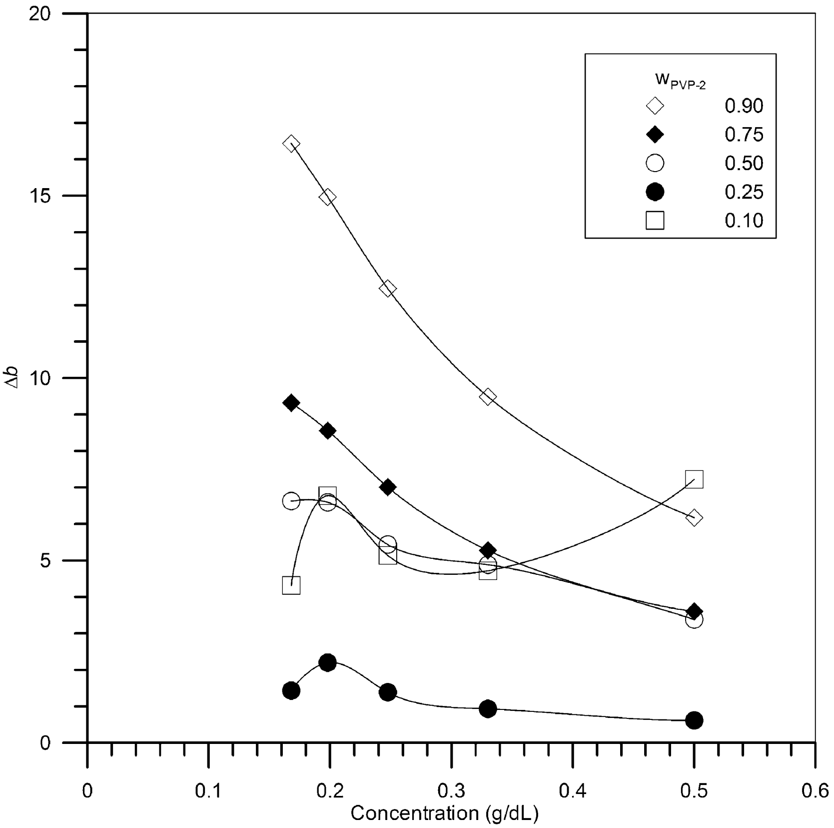

Figure 2. Concentration dependence of miscibility parameter Δ*b* for CHI/PVP-2 blends.

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.[10] For a given polymer mixture, a tendency towards positive values with increasing concentration would be interpreted as a tendency towards compatibility in the solid state.

In Figure 1, the relationship of Δ*b* values with total polymer concentration is shown for CHI/PVP-1 blends. For the miscible blend CHI/PVP-1:(0.90/0.10), the miscibility parameter Δ*b* takes negative values at low concentrations but reaches positive values at higher concentrations, indicating ultimate miscibility for this mixture. For the other four blends, which have been characterized as immiscible according to their Δ*k* values, even though Δ*b* starts at positive values at low concentrations, it exhibits a tendency towards negative values with increasing total polymer concentration. Except for CHI/PVP-1:(0.90/0.10), CHI/PVP-1 blends are all immiscible according to the negative trend of Δb versus concentration plots.

For the CHI/PVP-2 blends, all of which were assigned to be miscible according to their Δk and α values, Δb is well above zero at all concentrations. However, in all graphs except for the one that represents the behavior of CHI/PVP-2: (0.90/0.10), Δb values decrease with increasing concentration, raising the question whether these blends might have limited miscibility in the semidilute regime or in the solid state.

FTIR Analysis of Molecular Interactions between CHI and PVP

The FTIR spectra of CHI, the blend CHI/PVP: 0.85/0.15, and PVP-2 taken in the solid state are compared to each other in Figure 3. Favorable interactions between CHI and PVP are reflected in the shifts for the peaks representing the carbonyl groups of PVP and CHI and also the amine group of CHI. It is observed in the spectra that the stretching vibration of C=O group is at 1659 cm^{-1} for PVP and at 1649 cm^{-1} for CHI, whereas it is at 1642 cm^{-1} for the blend. It can also be observed that −N−H stretching for CHI is at 1596 cm^{-1}, whereas it is at 1573 cm^{-1} in the spectrum of the blend. Two new small shoulders appear at 3282 and 3179 cm^{-1}, which may be attributed to the dipole-dipole interactions between hydroxyl groups of CHI and carbonyl group of PVP.

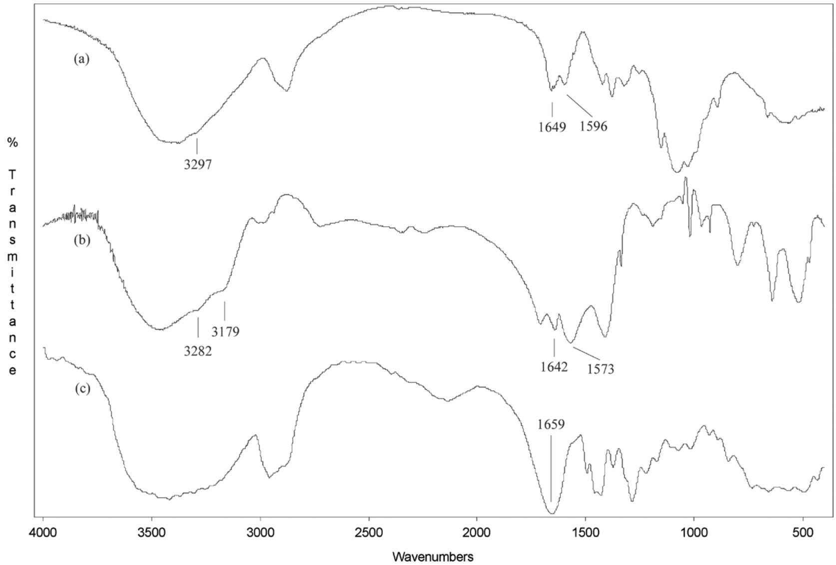

Figure 3. FTIR spectra of (a) CHI, (b) CHI/PVP-2 (0.85/0.15), and (c) PVP-2.

There are a few reports in literature on molecular interactions between CHI and PVP. Miscibility of water-soluble chitosan of degree of deacetylation 47% with PVP of molecular weight 2.5×10^4 was studied using solid-state nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) analyses. Films were cast from water solutions of the mixed polymers. There is a shift in T_g value of PVP from 149 to 190°C as the chitosan content in the mixture increases from 0 to 70%, indicating miscibility. However, ^{13}C-NMR cross-polarization/magnetic angle spinning (CP/MAS) does not give clear evidence of any specific intermolecular interaction for the CHI/PVP blends studied.[11]

The glass transition temperature T_g of chitosan of degree of deacetylation 96%, which had not been identified before, was determined to be 203°C by Sakurai et al.[12] Blended films prepared from chitosan and PVP ($M = 90\,000$) solution showed an increase in T_g value with an increase in the weight fraction of chitosan, indicating miscibility at the molecular level.

CONCLUSIONS

Chitosan of molecular weight 3.3×10^5 and low molecular weight poly (vinyl pyrrolidone) with a molecular weight of 2.5×10^4 show limited miscibility in solution at 30°C. The blends are miscible at a blend composition of CHI/PVP:0. 90/0.10. CHI and high molecular weight PVP with 1.1×10^6 molecular weight are miscible with each other at all compositions in solution at 30°C. Favorable interactions between CHI and PVP leading to miscibility can be interpreted from a comparison of FTIR spectra of the homopolymers and the blend.

REFERENCES

[1] Krigbaum, W. R. and F. T. Wall. (1950). Viscosities of binary polymeric mixtures. *J. Polym. Sci.* **5**, 505–514.

[2] Cragg, L. H. and C. C. Bigelow. (1955). The viscosity slope constant k′-ternary systems: Polymer-polymer-solvent. *J. Polym. Sci.* **16**, 177–191.

[3] Sun, Z., W. Wang, and Z. Feng. (1992). Criterion of polymer-polymer miscibility determined by viscometry. *Eur. Polym. J.* **28**, 1259–1261.

[4] Yilmaz, E., N. Erdenizci, and O. Yilmaz. (2003). Miscibility of chitosan and poly(ethylene oxide) in dilute solution. *Int. J. Polym. Anal. Charact.* **8**, 327–338.

[5] Sandford, P. A. (1992). Chitosan—Commercial uses and potential applications. In *Chitin and Chitosan*, eds. G. Skajak-Braek, T. Anthonsen, and P. Sanford. London: Elsevier Applied Science, pp. 51–69.

[6] Anthonsen, M. W., K. M. Varum, and O. Smidsrod. (1993). Solution properties of chitosans: Conformation and chain stiffness of chitosans with different degrees of N-acetylation. *Carbohydr. Polym.* **22**, 193–201.

[7] Wang, W., S. Bo, S. Li, and W. Qin. (1991). Determination of the Mark-Houwink equation for chitosans with different degrees of deacetylations. *Int. J. Biol. Macromol.* **13**, 281–285.

[8] Bohdanecky, M. and J. Kovar. (1982). *Viscosity of Polymer Solutions*. Amsterdam: Elsevier.

[9] Barabas, E. S. (1990). N-vinyl amide polymers. In *Concise Encyclopedia of Polymer Science and Engineering*, ed. J. I. Kroschwitz. New York: John Wiley, pp. 1236–1241.

[10] Shih, K. S. and C. L. Beatty. (1990). Blends of polycarbonate and poly(hexamethylene sebacate). IV: Polymer blend intrinsic viscosity behavior and its relationship to solid-state blend compatibility. *Br. Polym. J.* **22**, 11–17.

[11] Nishio, Y. (1999). Water-soluble polymer blends with partially deacetylated chitin: A miscibility characterization. *J. Polym. Sci. Part B Polym. Phys.* **37**, 1533–1538.

[12] Sakurai, K., T. Maegawa, and T. Takahashi. (2000). Glass transition temperature of chitosan and miscibility of chitosan/poly(N-vinyl pyrrolidone) blends. *Polymer*. **41**, 7051–7056.