New Chitin-Based Polymer Hybrids. 2. Improved Miscibility of Chitin Derivatives Having Monodisperse Poly(2-methyl-2-oxazoline) Side Chains with Poly(vinyl chloride) and Poly(vinyl alcohol)[1]

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ABSTRACT: A chitin derivative having monodisperse[1] poly(2-alkyl-2-oxazoline) side chains, i.e., chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**), was examined for miscibility with the commodity polymers poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA). The miscibility of the blends was investigated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) measurements. Graft copolymer **1** was compatible with PVC when the content of **1** in the blend was up to 40 wt %. Contact angle measurement against water of PVC/**1** blend surfaces indicated that the miscibility of the chitin backbone as well as poly(2-methyl-2-oxazoline) side chains in **1** with PVC was so good that the chitin segment would not migrate to the surfaces of the blends. DSC and FT-IR analyses revealed that graft copolymer **1** was miscible with PVA over the whole composition range.

Introduction

Hybridization of biopolymers including polysaccharides,[2−5] polypeptides,[6−9] and proteins[8] with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. Chitin is one of the naturally abundant polysaccharides present in the cuticles of crustaceans and the cell walls of some fungi and microorganisms. The blends of commodity polymers with chitin or chemically modified chitin are especially important from the view point of new material design and the effective utilization of chitin, which constitutes a very large biomass.

However, the insolubility of chitin in most common solvents has limited the study on blends of chitin compared with those of cellulose. Cellulose/poly(vinyl alcohol) (PVA),[2,3] cellulose/poly(vinylpyrrolidone),[4] and cellulose/poly(ethylene oxide)[3,5] blends have been reported as miscible pairs, whereas only a few investigations on the miscibility of chitin derivatives have been reported until now.[10−13] The poor solubility of chitin is caused by its rigid crystalline structure through intra- and intermolecular hydrogen bonds.[14] Chemical modification[15,16] and new solvents[17] have been investigated to improve the solubility. According to our strategy of modifying sugar-containing polymers by living polymerization,[18−20] we have already reported the synthesis of chitin derivatives having monodisperse poly(2-alkyl-2-oxazoline) side chains, i.e., chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**) and chitin-*graft*-poly(2-ethyl-2-oxazoline), by the reaction of ca. 50% deacetylated chitin with living poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline), respectively.[21,22] These chitin derivatives showed much improved solubilities in organic solvents, compared with chitin or deacetylated chitin.

Poly(2-alkyl-2-oxazoline)s, i.e., poly[(*N*-acylimino)ethylene]s, are produced by the ring-opening isomerization polymerization of 2-alkyl-2-oxazolines. Poly(2-methyl-2-oxazoline) is regarded as a polymer homologue of *N*,*N*-dimethylacetamide (DMAc), which is characterized as an aprotic polar solvent. Analogous to the case of DMAc, poly(2-methyl-2-oxazoline) has been shown to possess a strong affinity toward water[23, 24] and a high miscibility with various commodity polymers.[11,25−30] The miscibility of poly(2-alkyl-2-oxazoline)s has been studied with PVA,[11] polyamide (Nylon 6),[25−27] poly(vinyl chloride) (PVC),[28] poly(vinylidene fluoride),[28] polystyrene,[28] poly(acrylonitrile),[29] and poly(acrylic acid).[30]

The present article deals with the miscibility of chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**) with PVC and PVA, in which the poly(2-methyl-2-oxazoline) side chain is considered to be an effective compatibilizer. The binary blend system of PVA and graft copolymer **1** is a first example of miscible blends between a chitin derivative and a synthetic polymer in a whole range of their compositions to our knowledge.[11] Although we have already demonstrated the miscibility of graft copolymer **1** and PVC,[10] the miscibility was achieved within a limited range of blend composition, i.e., the content of graft copolymer **1** lower than 10 wt %. This paper reports improvements of the compatibility with PVC and the relationship between the chemical structure of **1** and its miscibility.

Experimental Section

Materials. Chitin from crab shells was purchased from Sigma Chemical Co (St. Louis). Partially deacetylated chitin with ca. 50% *N*-deacetylation was prepared by the method of Sannan et al.[31] Commercially available poly(vinyl chloride) (PVC, Wako pure chemical Co., Osaka, $M_n = 68\,000$) and poly(vinyl alcohol) (PVA, Nacalai Tesque, Inc., Kyoto, $M_n = 88\,000$, saponification value 99−100%) were used for the preparation of the blend films. It is known that the stereoregularity of a component polymer influences the compatibility of the blend.[32−34] The triad tacticity in PVC was determined by ^{1}H and ^{13}C NMR spectroscopy in dichloromethane-d_2 to be 32% syndiotactic, 20% isotactic, and 48% heterotactic.[35,36] ^{1}H NMR measurement of PVA in dimethyl sulfoxide-d_6 indicated that it had a triad syndiotacticity of 30%, isotacticity of 19%, and heterotacticity of 51%.[37,38] Dichloromethane and water used for preparation of films by the solvent cast method were purified by distillation.

Measurements. ^{1}H and ^{13}C NMR spectra were taken with a Bruker ARX 400 spectrometer operating at 400 MHz (^{1}H) and 100 MHz (^{13}C), respectively. Differential scanning calorimetry (DSC) analysis of dried films (9−13 mg) was carried

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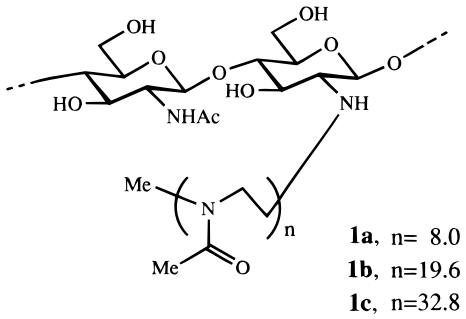

Figure 1. Structure of chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**).

Table 1. Characterization of Chitin-*graft*-poly(2-methyl-2-oxazoline) (1)

graft copolymer	chitin DA,[a] %	PMeOZO side chain n[b]	PMeOZO side chain M_w/M_n[c]	[PMeOZO]/[NH_2][d]	M_n[e] $\times 10^{-5}$
1a	55	8.0	1.1_3	0.96	5.1
1b	52	19.6	1.1_2	1.00	3.9
1c	52	32.8	1.1_8	0.45	9.8

[a] Degree of *N*-acetylation of deacetylated chitin, by ^{1}H-NMR in D_2O/CD_3COOD (95:5, v/v). [b] DP of the side chain, by ^{1}H-NMR in $CDCl_3$ at 27 °C. [c] By SEC in $CHCl_3$ (polystyrene standard). [d] Molar ratio of the poly(2-methyl-2-oxazoline) unit to the D-glucosamine unit of deacetylated chitin, by ^{1}H-NMR. [e] M_n of **1**, estimated by SEC in H_2O (pullulan standard).

out in a Perkin Elmer DSC-2 and Seiko DSC-100, 6100, and 6200. The instruments were calibrated with indium and tin. In order to provide the same thermal history for all samples, thermal data for the blends were obtained after one heating cycle to 110 °C followed by quenching to 40 °C in the differential scanning calorimeter. The DSC curves were recorded at a heating rate of 5 °C/min and showed good reproducibility in subsequent thermal scans. The glass transition temperature (T_g) was taken as the inflection point of the specific heat increment. IR spectra were recorded with a JASCO FT/IR-5MP spectrometer under nitrogen. The resolution was 4 cm^{-1}, and 100 signal-averaged scans were performed. The surfaces of the films were observed with a Hitachi S-4500 scanning electron microscope. The contact angles against water were measured at room temperature with a CAD type goniometer (Kyowa Co. CA-DT).

Preparation of Chitin-*graft*-poly(2-methyl-2-oxazoline) (1). Chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**) was prepared according to the previous paper.[21] The structure of the graft copolymer **1** used in this study is shown in Figure 1 and Table 1. The main chain of **1** consists of randomly linked D-glucosamine and *N*-acetyl-D-glucosamine repeating units. Poly(2-methyl-2-oxazoline) (PMeOZO) branches, which exhibit miscibility with poly(vinyl chloride) (PVC),[28] are attached to the 2-position of the D-glucosamine units of the main chain. The side chain length was regulated by living polymerization of 2-methyl-2-oxazoline in acetonitrile. The [PMeOZO]/[NH_2] values in Table 1 represent the reacted molar ratios of oxazoline polymer to D-glucosamine units in **1**, determined by ^{1}H NMR signal intensity. We have already reported the synthesis and solubility of a graft copolymer having shorter poly(2-methyl-2-oxazoline) segments (**1a**).[21] In this study, chitin derivatives having relatively longer side chains (**1b** and **1c**) were prepared both in 87% yield. In order to investigate the effect of polyoxazoline chain length, the weight fractions of polyoxazoline of **1b** and **1c** were set up to be almost same; thus, the [PMeOZO]/[NH_2] value of **1c** was lower than that of **1b**.

Preparation of PVC/Chitin-*graft*-poly(2-methyl-2-oxazoline) (1) Blend Films. According to the previous paper,[10] sample films of the PVC/graft copolymer **1** blend were prepared by casting from a dichloromethane solution. A mixture (100 mg) of PVC and **1** with the desired ratio was stirred at room temperature for 3 days. The solution was poured onto a Teflon dish (50 mm diameter) with a flat bottom, and the solvent was allowed to evaporate under atmospheric pressure at room temperature for 2 days. After drying further in vacuo at 50 °C for 3 days, the blend films were removed easily from the dish. The films were stored over P_2O_5 in a desiccator.

Table 2. Solubility Data of Chitin-*graft*-poly(2-methyl-2-oxazoline) (1)[a]

solvent	chitin	partially deacetylated chitin[b]	graft copolymer **1a**	graft copolymer **1b**	graft copolymer **1c**
water	−	+	+	+	
Me_2SO	−	±	+	+	+
DMF	−	±	±	+	±
DMAc	−	±	±	+	+
methanol	−	−	±	+	±
acetonitrile	−	−	±	±	±
chloroform	−	−	±	±	±
diethyl ether	−	−	−	−	−
n-hexane	−	−	−	−	−

[a] +, soluble; ±, partially soluble; −, insoluble; temp, rt; conc, 1 mg/mL. [b] Prepared according to ref 31. Degree of ***N***-acetylation determined by ^{1}H NMR to be 52%.

Preparation of PVA/Chitin-*graft*-poly(2-methyl-2-oxazoline) (1) Blend Films. A typical example is as follows. PVA (70 mg) was dissolved in 10 mL of water in an autoclave at 120 °C. After cooling at room temperature, 30 mg of graft copolymer **1** was added to the solution. The mixture was stirred for 12 h. The solution was placed on a Teflon laboratory dish (50 mm diameter) at 50 °C to remove the solvent. The films were further dried in vacuo at 50 °C for 3 days and stored in a previously described manner.

Results and Discussion

Solubility of Chitin-*graft*-poly(2-methyl-2-oxazoline) (1). Graft copolymer **1** was found to have improved solubility in some common solvents, compared with chitin or deacetylated chitin (Table 2). Chitin derivatives with relatively longer side chains (**1b** and **1c**) showed much better solubility than that with shorter poly(2-methyl-2-oxazoline) segments (**1a**). Graft copolymers **1b** and **1c** are soluble in *N*,*N*-dimethylformamide (DMF) and DMAc, while **1a** is partially soluble in these solvents. Particularly, graft copolymer **1b**, having a longer side chain linked to almost every D-glucosamine unit, is soluble even in methanol. The reason that **1c** is partially soluble in methanol is probably the lower polyoxazoline content of **1c** compared to that of **1b**.

Miscibility of PVC and Chitin-*graft*-poly(2-methyl-2-oxazoline) (1). We have already reported that graft copolymer **1a**, having shorter poly(2-methyl-2-oxazoline) segments, showed miscibility with PVC in the blend composition range of **1a** lower than 10 wt %.[10] Blend films of PVC containing 4−25 wt % **1b** were prepared by solvent-casting from a dichloromethane solution. The films of PVC/**1b** (4 wt %), PVC/**1b** (10 wt %), PVC/**1b** (20 wt %), and PVC/**1b** (25 wt %) were homogeneous and reasonably transparent, which indicated that no phase separation at any higher level above micron size could be perceived. The miscibility of the films was investigated by differential scanning calorimetry (DSC). The thermal property and the transparency of PVC/**1** blend films are summarized in Table 3. Generally, the observation of a single glass transition temperature (T_g) for a blend pair is regarded as decisive evidence of polymer miscibility. The T_g of PVC was 78 °C, and that of **1b** was 66 °C. In the DSC measurement, the T_g of PVC was found to shift to lower temperatures with increasing **1b** contents up to 20 wt %. The thermal behavior evidently shows that PVC and **1b** are miscible

Table 3. Characterization of PVC/ Chitin-*graft*-poly(2-methyl-2-oxazoline) (1) Blend Films[a]

blend sample	content of **1**, wt %	transparency[b]	T_c,[c] °C	IR carbonyl band maxima,[d] cm^{-1}	contact angle against water,[e] deg
1a	0	T	78		94
	1	T	77	1632	94
	4	T	74	1632	94
	10	T/O	73	1632	92
	20	O	73	1638	87
	100	T		1638	29
1b	0	T	78		94
	4	T	75	1630	84
	10	T	73	1630	85
	20	T	69	1630	87
	25	T	66, 79	1642	74
	100	T	66	1642	14
1c	0	T	78		94
	25	T	75	1634	79
	40	T	69	1632, 1644	51
	50	O	65, 78	1638, 1645	57
	75	O	61, 77	1632, 1643	50
	100	T	61	1639	23

[a] Prepared by the solvent cast method from a dichloromethane solution. [b] Transparency of blend films: T, transparent; O, opaque. [c] Determined by DSC. [d] Determined by FT-IR. [e] The surface of the air side, measured at room temperature.

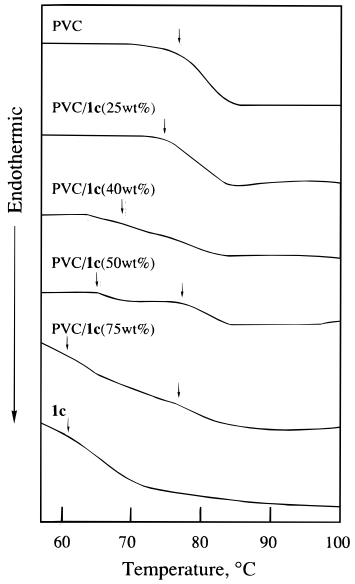

Figure 2. DSC curves of PVC/chitin-*graft*-poly(2-methyl-2-oxazoline) (**1c**) blend films. Heating rate, 5 °C/min. The arrow marks the position of T_g.

at this mixing ratio. The PVC/**1b** (25 wt %) blend gave two separate T_g values, suggesting microphase separation.

Similarly, the miscibility of PVC and graft copolymer **1c** was examined. The cast films containing **1c** lower than 40 wt % were homogeneous and reasonably transparent for miscible systems, while the films with 50 and 75 wt % **1c** were heterogeneous and distinctly opaque, indicating immiscibility. The results of DSC analysis agreed with the visual observations. Blends with **1c** content lower than 40 wt % show a single T_g in the intermediate region between those of the pure components (Figure 2). However, a remarkable broadening of the glass transition was observed in the PVC/**1c** (40 wt %) blend, which was commonly attributed to the presence of local concentration fluctuations[39] and indicated that this mixing ratio was almost the saturated composition for the miscibility of PVC and **1c**.[40]

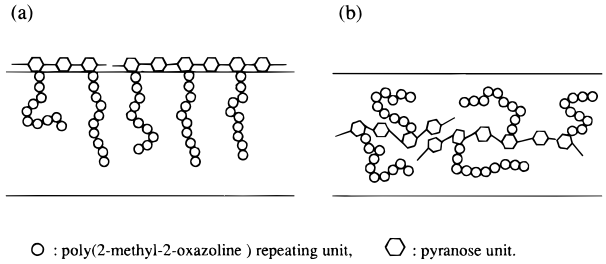

Figure 3. The possible existence state of the chitin segment in PVC/graft copolymer **1** blend films: (a) segregated on the surface; (b) intermingled with PVC.

These results seem to indicate that blends of PVC with the graft copolymers **1b** and **1c**, which have relatively longer poly(2-methyl-2-oxazoline) segments, exhibited miscibility up to higher graft copolymer content than PVC blends with graft copolymer **1a**, which has shorter side chains.

As confirmed by the DSC analysis, **1c** is considered to be an amorphous polymer, while PVC is semicrystalline under the present experimental conditions. The pure PVC showed a relatively sharp melting endothermic peak at 263 °C. On the other hand, the intensity of the melting peak is reduced, with a lower temperature shift of the peak appearing at 241 °C in the PVC/**1c** (25 wt %) blend. For polymer blends where one of the components crystallizes, a depression in the melting point implies that an interaction exists, to some extent, between the two components which governs the miscibility.[41,42]

Scanning electron microscopy (SEM) observation of the PVC/**1c** (40 wt %) blend film indicated that the surface was homogeneous and continuous at relatively high magnification (10000×). In contrast, a heterogeneous phase was observed at the same magnification on the PVC/**1c** (50 wt %) blend surface, which indicated two separated phases. This observation agrees very well with the results of the DSC analysis.

Segmental interaction between PVC and the poly(2-methyl-2-oxazoline) side chain of **1** was confirmed by FT-IR spectroscopy. Considering the chemical structure of the graft copolymer **1**, an interaction between a weakly acidic hydrogen of PVC and a slightly basic amide group of the poly(2-methyl-2-oxazoline) side chain is expected to occur in the blend. The absorption maxima arising from the amide group of graft copolymer **1** in the blends are summarized in Table 3. The carbonyl stretching band in dry graft copolymer **1b** appeared at 1642 cm^{-1}, while the vibration of PVC with 4−20 wt % **1b** was observed at 1630 cm^{-1}. The shift of 12 cm^{-1} to lower wavenumber and the line broadening are reasonably interpreted by the specific interaction between the carbonyl oxygen of **1b** and the methine proton of PVC.[28] The FT-IR data clearly indicated that PVC and **1b** were intimately intermingled. A similar shift of 5−7 cm^{-1} to lower wavenumber and the line broadening of the carbonyl band were observed in PVC/**1c** blends. However, the blends with more than 40 wt % **1c** content had two distinct carbonyl absorption maxima. The maximum at lower wavenumber is attributed to intermolecularly associated carbonyl groups, whereas the maximum at higher wavenumber corresponds to the contribution of free carbonyl groups. This result suggests that **1c** interacts with PVC to some extent even in immiscible blends (**1c** content > 40 wt %).

Figure 3 illustrates two possible models of the state of graft copolymer **1** in PVC/**1** blends. In one model,

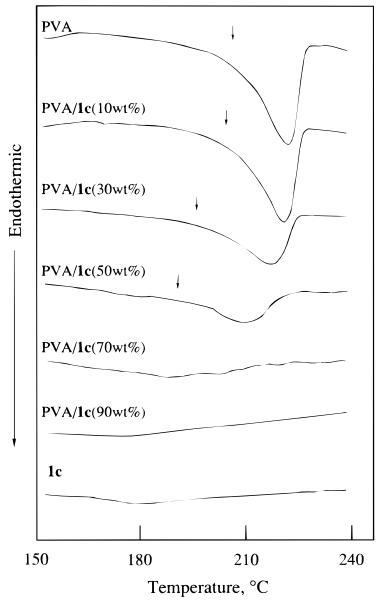

Figure 4. DSC melting thermograms of PVA/graft copolymer **1c** blend films. Heating rate, 5 °C/min. The arrow marks the position of T_m.

only poly(2-methyl-2-oxazoline) side chains are compatible with PVC, and the chitin component segregates at the surface (Figure 3a). In the other model, both the main chain segment and the side chain segment are miscible with PVC (Figure 3b). The surface characteristics of the films were investigated by the contact angle measurement against water. The results are summarized in Table 3. The water contact angle on the air side of the control PVC film was 94°. Although the contact angle on the air side of graft copolymer **1** was very low (14−29°), those of PVC/**1** miscible blends were relatively high. For example, the contact angle of the PVC/**1b** (20 wt %) miscible blend was 87°, which indicated that the surface was still hydrophobic in spite of blending with hydrophilic **1**. Therefore, it is considered that the miscibility of the chitin backbone in **1** is so good that the chitin segment would not migrate to the surfaces of the blends.[40]

Miscibility of PVA and Chitin-*graft*-poly(2-methyl-2-oxazoline) (1). PVA/chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**) solid films obtained by casting from an aqueous solution were optically clear irrespective of the blend composition. Characterization of the films was carried out by means of DSC. Figure 4 displays the melting thermograms obtained on the cast films of PVA/**1c** blends in the first scan. The pure PVA sample gave a relatively large and sharp melting endotherm (T_m) at 207 °C. As the **1c** content increases up to 50 wt %, the endothermic peak of PVA tends to lose its prominence with an accompanying depression in the T_m values.

It is now possible to estimate the composition dependence of not only the melting but also the glass transition behavior for a series of PVA/graft copolymer **1** blends. Table 4 gives the thermal properties of PVA/**1b** and PVA/**1c** blends. Each blend exhibited a single T_g. As the content of **1** was increased, the T_g of PVA shifted to lower temperature. Broadening of the width of the transition was not observed, which indicated that PVA and **1** were intimately intermingled over the whole composition range. There is a classical equation, the Gordon−Taylor equation[43] (eq 1), that correlates the T_g of a miscible blend system with its composition.

Table 4. Glass Transition Temperature (T_g) and Melting Point (T_m) of PVA/Chitin-*graft*-poly(2-methyl-2-oxazoline) (1) Blend Films[a]

blend sample	content of **1**, wt %	T_g,[b] °C	T_m,[b] °C
1b	0	72	212
	10	70	208
	30	68	206
	50	67	197
	70	67	*c*
	100	66	*c*
1c	0	69	207
	10	65	205
	30	64	197
	50	62	191
	70	62	*c*
	90	61	*c*
	100	61	*c*

[a] Prepared by the solvent cast method from an aqueous solution. [b] Determined by DSC. [c] Not detected.

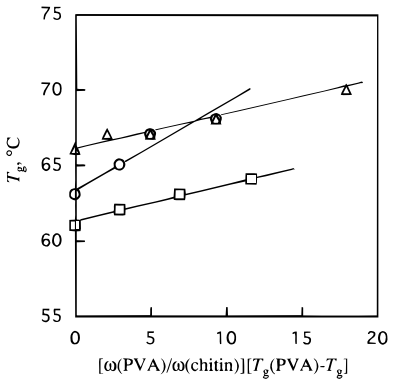

Figure 5. Gordon−Taylor plots of T_g data; PVA/graft copolymer **1b** blends (△), PVA/graft copolymer **1c** blends (□), PVA/poly(2-methyl-2-oxazoline) blends (○).

$$T_g = T_g(\text{chitin}) + k[\omega(\text{PVA})/\omega(\text{chitin})][T_g(\text{PVA}) - T_g] \quad (1)$$

where T_g(chitin) and T_g(PVA) are the T_g values of component **1** and PVA, ωs are the weight fractions, and k is an adjusting parameter related to the degree of curvature of the T_g-composition diagram. Figure 5 shows the Gordon−Taylor analysis of PVA/**1b**, PVA/**1c**, and PVA/poly(2-methyl-2-oxazoline) (M_n of polyoxazoline = 10 200)[11] blend systems, which give k = 0.21 (correlation coefficient, r = 0.99), 0.25 (r = 0.99), and 0.54 (r = 0.92), respectively. The k value from the PVA/poly(2-methyl-2-oxazoline) miscible blends was higher than those from the PVA/chitin derivative **1** miscible blend, which indicates that the interactions in the former blend are stronger than those in the latter. It was suggested that poly(2-methyl-2-oxazoline) side chains act as an effective "covalently linked compatibilizer" between the chitin main chain of **1** and PVA.

Interaction between the carbonyl groups of **1** and PVA was investigated by the FT-IR measurement. As stated above, the IR carbonyl band maxima of **1b** and **1c** appeared at 1642 and 1639 cm^{-1}, while those of the PVA/**1b** (10 wt %) and PVA/**1c** (10 wt %) blends were detected at 1630 and 1628 cm^{-1}, respectively. The shift of the blends is explained by hydrogen bonding between the carbonyl group of **1** and the hydroxy groups of PVA.

The miscibilities of the chitin derivatives with PVC and PVA are summarized in Table 5. The compatibility between PVA and randomly deacetylated chitin in the amorphous regions was suggested by DSC,[11,13] which

Table 5. Miscibility of Chitin-*graft*-poly(2-methyl-2-oxazoline) (1)[a]

polymer	miscibility PVC	miscibility PVA
chitin	−	−
partially deacetylated chitin	−	+[b]
chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**)	±[c]	+
poly(2-methyl-2-oxazoline)	±[d]	+[e]

[a] +, miscible; ±, partially miscible; −, immiscible. [b] References 11 and 13. [c] Miscible content of **1** is up to 40 wt %. [d] Miscible content of polyoxazoline is up to 50 wt %, according to ref 28. [e] Reference 11.

indicated that the chitin main chain has the potential to exhibit miscibility toward synthetic polymers. The crystal structure of native chitin with strong intra- and intermolecular hydrogen bonds blocks the formation of miscible blends with other polymers. The hydrogen bonds in chitin seem to be switched to favorable interactions between heteropolymers by chemical modification or introduction of the side chains. Actually, segmental interaction between PVC and the chitin main chain of **1** has been supported by means of temperature-programmed analytical pyrolysis techniques.[40] Therefore, it is speculated that both the main and side chains of **1** are intimately intermingled with PVA at the molecular level.

On the other hand, the partially deacetylated chitin showed immiscibility with PVC in similar experiments. However, **1** was miscible with PVC in the composition range lower than 40 wt %. Considering that the poly(2-methyl-2-oxazoline) homopolymer was miscible with PVC up to 50 wt %,[28] the effectiveness of the introduction of miscible poly(2-methyl-2-oxazoline) side chains is revealed in chitinous blends with PVC. This is attributed to the ability of poly(2-methyl-2-oxazoline) branches to disturb the crystal structure of chitin, which is reflected in their improved solubilities (see Table 2).

Conclusion

The chitin derivative having a monodisperse poly(2-alkyl-2-oxazoline) side chain, i.e., chitin-*graft*-poly(2-methyl-2-oxazoline) (**1**), showed much improved solubility in some common solvents and good miscibility toward some commodity polymers. Graft copolymer **1** was soluble in water, dimethyl sulfoxide, DMF, DMAc, and even in methanol. Graft copolymer **1** showed good miscibility with PVC in the blend composition range of **1** lower than 40 wt % and was miscible with PVA over the entire composition range. These fundamental data should provide a useful guideline when new polymeric materials, "biopolymer hybrids", are desired by blending between biopolymers and synthetic polymers.

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(1) Monodisperse: molecularly uniform according to the IUPAC recommendation.
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