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Characterization of Chitin-Based Polymer Hybrids by Temperature-Programmed Analytical Pyrolysis Techniques. 2. Chitin-*graft*-poly(2-methyl-2-oxazoline)/Poly(vinyl alcohol) Blends

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ABSTRACT: Chitin-*graft*-poly(2-methyl-2-oxazoline)/poly(vinyl alcohol) (PVA) blends were characterized by means of analytical pyrolysis techniques such as temperature-programmed pyrolysis−mass spectrometry (TPPy−MS), TPPy−gas chromatography (TPPy−GC) and Py−GC mainly in terms of their miscibility and the site of the intermolecular interaction. The thermal degradation of the chitin derivative/PVA blends took place apparently in two stages reflecting the degradation of both constituent polymers. However, peak-top temperatures for both degradation stages changed as a function of blend composition; the first degradation stage, mostly corresponding to the dehydration of PVA, shifted to higher temperatures when the chitin derivative content is increased in the blend. Although the yields of 2-butenal from the PVA moiety increased by blending the chitin derivative, those of acetamide and *N*-ethylacetamide from the chitin derivative moiety exhibit an opposite trend. These temperature shifts and the variations in the yields of the pyrolysis products suggested that intermolecular interactions might be contributing to a differing extent as a function of the blend composition. Moreover, the observed degradation behaviors for the chitin derivative/PVA blends showed the opposite trend for the case of the chitin derivative/PVC blend system previously investigated. Thus, the observed degradation mechanisms of this blend system were discussed by comparison with those for the chitin derivative/PVC blend system.

Introduction

Chitin is a natural polysaccharide found particularly in the shell of crustaceans such as crab and shrimp, the cuticles of insects, and the cell walls of fungi. Because chitin is one of the most abundant biopolymers next to cellulose, much interest has been paid to its biomedical, biotechnological, and industrial applications.[1] However, it has been hitherto utilized only in limited fields mainly due to its poor solubility and reactivity caused by its rigid crystalline structure. To overcome this problem, various approaches such as blending with other polymers[2−5] and chemical modifications of chitin by grafting with synthetic polymers[6−12] have mainly been attempted to convert chitin into functional materials. Among these, chitin derivatives having poly(2-alkyl-2-oxazoline) side chains with a high miscibility toward various synthetic polymers were blended with commodity synthetic polymers such as poly(vinyl chloride) (PVC)[13,14] and poly(vinyl alcohol) (PVA).[14,15] Such miscible blends of chitin derivatives and commodity polymers on a molecular level are expected to yield new functional materials, which combine biospecific properties of chitin with molding and mechanical properties of commodity polymers.

Characterization of these blend systems in miscibility and intermolecular interaction will provide good information to design excellent functional materials. In conventional characterization of polymer blends, measurements of glass-transition temperature (T_g) by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been mainly used for estimating their miscibility.[16] However, some polysaccharides such as chitin and cellulose do not exhibit any clear T_g. Moreover, these thermal methods give little chemical information about intermolecular interaction.

Recently, in the previous paper, we have reported that the miscibility and the sites of the intermolecular interaction of a chitin-*graft*-poly(2-methyl-2-oxazoline)/PVC blend system can be evaluated by means of temperature-programmed analytical pyrolysis techniques such as temperature-programmed pyrolysis−mass spectrometry (TPPy−MS), TPPy−atomic emission detection (TPPy−AED), and TPPy−gas chromatography (TPPy−GC), which are various evolved gas analysis (EGA) techniques.[17] In this study, the observed evolution profiles of the characteristic products were interpreted in terms of the mechanisms of the intermolecular interaction of the blend system.

In this paper, basically the same analytical pyrolysis techniques including TPPy−MS, TPPy−GC−MS, and

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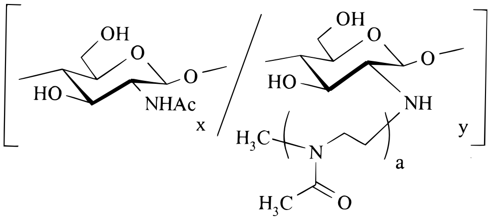


Figure 1. Structure of chitin-*graft*-poly(2-methyl-2-oxazoline). Repeating units of the main chain are randomly linked. x/y = 52/48. Average degree of polymerization of the side chain: a = 19.6. Ac = acetyl group.

Table 1. Composition and Thermal Properties of Chitin-*graft*-poly(2-methyl-2-oxazoline)/PVA Blend Films[a]

sample codes	composition (wt %)		thermal properties[b]	
	chitin derivative	PVA	T_g (°C)[c]	T_m (°C)[d]
	0	100	72	212
B(10/90)	10	90	70	208
B(30/70)	30	70	68	206
B(50/50)	50	50	67	197
B(60/40)	60	40	67	*e*
B(70/30)	70	30	67	*e*
	100	0	66	*e*

[a] Reference 14. [b] Determined by DSC. [c] Glass transition temperature. [d] Melting point. [e] Not detected.

Py−GC were applied to the characterization of a chitin-*graft*-poly(2-methyl-2-oxazoline)/PVA blend system. Thus, observed degradation mechanisms of this blend system were discussed by comparison with those for the chitin derivative/PVC blend system.

Experimental Section

Samples. A modified chitin, chitin-*graft*-poly(2-methyl-2-oxazoline) was prepared as a material for blends according to a previous paper,[11] where living poly(2-methyl-2-oxazoline) side chains (average degree of polymerization; DP = 19.6, $M_w/M_n = 1.1_2$) was selectively grafted onto free amino groups of the partially N-deacetylated chitin (degree of acetylation; DA = 52%). The possible structure of the chitin derivative is shown in Figure 1. The ^{1}H NMR spectra of this derivative indicated that the polyoxazoline side chains were almost quantitatively introduced into the free amino groups in the deacetylated chitin main chain. The number-average molecular weight (M_n) of the chitin derivative was about 3.9×10^5 as determined by size exclusion chromatography (SEC) in H_2O using pullulan standards.

PVA (Nacalai Tesque; M_n = 88 000; saponification value = 99−100%) was used without further purification. The triad tacticity in PVA determined by ^{1}H NMR spectroscopy was 30% syndiotactic, 19% isotactic, and 51% heterotactic.[14]

Blend films of chitin-*graft*-poly(2-methyl-2-oxazoline) with PVA were prepared by casting from an aqueous solution as described in previous papers.[14,15] The composition of these blends is summarized in Table 1 together with their thermal properties such as T_g and melting point (T_m) determined by DSC. As the chitin derivative content increases up to 50 wt %, the melting point gradually decreased from 212 to 197 °C. This behavior suggests that the crystallinity of the PVA moiety is lowered by blending. Moreover, all blend films are apparently transparent and have single T_g. In addition, the correlation between the T_g values and the content of the chitin derivative obeyed the Gordon−Taylor relationship,[18] suggesting miscible blends.[14,15]

Measurements. The TPPy−MS system used in this study is basically the same as described in the previous papers.[17,19] In this system, a temperature-programmable microfurnace pyrolyzer (Frontier Lab, PY-2010D) attached to a GC (Hewlett-Packard, HP-5890) injector was directly coupled with a quadrupole MS (JEOL, AM-II 150) via a deactivated stainless steel capillary (Frontier Lab, UADTM-5N, 0.15 mm i.d. × 5 m long). Because the sample size often affects its thermal degradation behavior more or less, restricted sample size as little as 0.2 mg was used throughout the TPPy measurements to achieve rapid thermodynamic equilibrium during heating the organic sample with lower thermal conductivity. A given sample placed in a platinum sample cup was heated in the pyrolyzer from 60 up to 700 °C at a heating rate of 10 °C/min under helium atmosphere with a flow rate of 50 mL/min. A part of the flow (1 mL/min) reduced by a GC splitter (50:1) was continuously introduced into the MS through the transfer capillary. The transfer capillary was maintained at 280 °C in the GC oven to prevent condensation of less volatile products in the capillary. For the MS measurement, ionization was carried out by electron impact (EI) at 70 eV, and an operating mass range was 10−300 amu with a scan rate of 2 s/scan.

To identify the evolved products, TPPy−GC−MS measurement was also carried out. In this case, the capillary transfer line for the TPPy−MS system was replaced by a metal capillary separation column (Frontier Lab, Ultra Alloy-17; 0.25 mm i.d. × 60 m long) coated with immobilized poly(methylphenylsiloxane) (0.15 μm film). A selective sampling device (Frontier Lab, SS-1010D) was additionally inserted between the GC splitter and the separation column in order to achieve the indirect flow switching.[20] By using this device, only the thermal degradation products evolved during a desired temperature (or time) range can be introduced into the column, whereas the other products can be exhausted through the splitter vent. During the programmed heating periods from 240 up to 340 °C for 10 min and from 340 up to 480 °C for 14 min, the thermal degradation products were trapped in a part (ca. 15 cm) of the separation column coiled into about 2 cm in diameter for two turns at about 20 cm apart from the injection port by immersing in liquid N_2 in a Dewar vessel. After removing the Dewar vessel, the column temperature was initially set at 30 °C for 5 min and then heated to 280 °C at a rate of 5 °C/min. The other conditions were basically the same as the TPPy−MS measurement described above.

To make quantitative evaluation of the degradation products from the blend samples in a flash pyrolysis at around 600 °C, an ordinary Py−GC measurement was also carried out. The Py−GC system used in this study was basically the same described in our previous work,[21] where the microfurnace pyrolyzer (Frontier Lab, PY-2010D) was attached to a GC (Shimadzu GC-17A) equipped with a flame ionization detector (FID). The platinum sample cup containing about 0.2 mg of a given sample was dropped into the center of the pyrolyzer heated at 600 °C. The other conditions were basically the same as the TPPy−GC measurement.

Results and Discussion

Evolution profiles of the thermal degradation products from the chitin derivative/PVA blends measured by TPPy−MS in a total ion current (TIC) mode as a function of programmed temperature are shown in Figure 2 together with those for the chitin derivative and PVA. The TIC curve of PVA alone apparently shows two-stage degradation; a large peak at around 240−350 °C with a peak top at ca. 260 °C accompanied by a shoulder at ca. 300 °C, and another small one at 380−460 °C with a peak top at ca. 430 °C, respectively. The first degradation stage at around 240−350 °C mainly corresponds to the dehydration process of PVA to form a polyene structure.[22] The peak shoulder at ca. 300 °C might be attributed to the difference in stereoregularity among PVA chains because the observed mass spectra for the shoulder fraction were basically the same as those at around 260 °C. The second degradation stage at around 380−460 °C corresponds to the charring process with releasing aromatic hydrocarbons from the polyene structures formed during the preceding dehydration at the first stage.[22] On the other hand, as for the chitin derivative, apparently one-stage degradation is taking place at around 350−400 °C.[17]

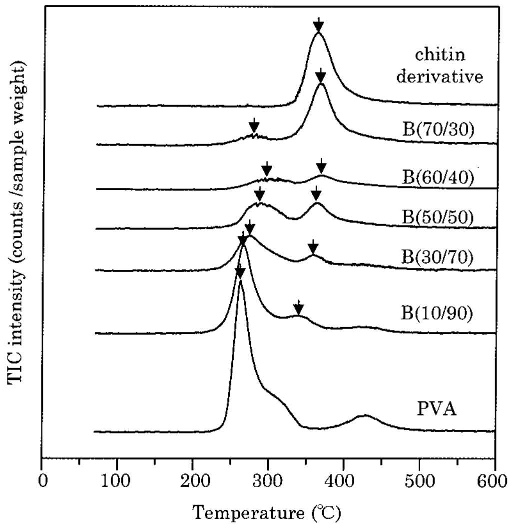


Figure 2. Evolution profiles of the thermal degradation products from the chitin derivative/PVA blend samples observed in total ion current by TPPy−MS.

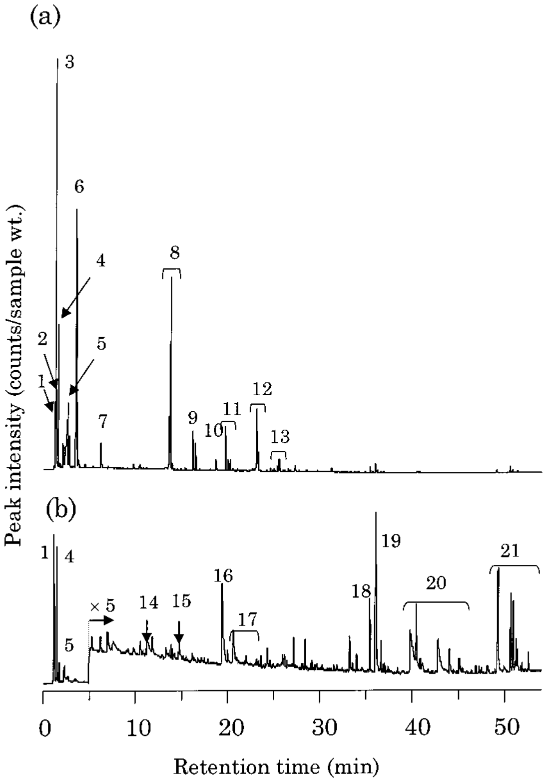


Figure 3. TIC chromatograms of the degradation products formed from the B(60/40) blend during heating ranges (a) 240−340 °C and (b) 340−480 °C. The numbers correspond to those of the compounds in Table 2.

The thermal degradation of the blend samples occurs apparently in two stages, reflecting the degradation of both constituent polymers; the first degradation stage at around 240−350 °C can be correlated to the dehydration process of PVA and the second one at around 340−400 °C to the degradation process of the chitin derivative, respectively. However, the charring process of the PVA moiety that should take place at around 380−460 °C is hardly observed on the thermograms for the blend samples except for the B(10/90) blend sample with the highest PVA content. Here, it is interesting to note that the peak-top temperatures of the both degradation stages slightly shift as a function of the composition of the blend. As for the first degradation stage, the peak-top temperatures increase with the increase in the content of the chitin derivative and show a maximum value for the B(60/40) blend sample, whereas the corresponding temperature for the B(70/30) blend sample shifts back to a lower value. As for the second degradation stage, the peak-top temperatures slightly change depending on the blend composition: for the blends with the content of the chitin derivative down to 60 wt %, the peak-top temperatures remain almost constant, while those decrease with decrease in the content of the chitin derivative smaller than 60 wt % in the blends. Such thermal degradation behavior may correlate to the miscible state in the blends.

Here, it is interesting to note that the temperature shifts of the first and second stages for the chitin derivative/PVA blends show an opposite trend to the observations for the chitin derivative/poly(vinyl chloride) (PVC) blends investigated previously,[17] where the first degradation stage mainly corresponding to degradation of vinyl-type polymer constituent (dehydrochlorination process of PVC) shifted to lower temperatures by blending the chitin derivative and the second one (degradation of the chitin derivative constituent) to higher temperatures with decrease in the content of the chitin derivative for the miscible blends. These opposite trends will be discussed later in detail.

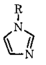
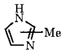
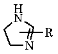
The thermal degradation products were then identified by TPPy−GC−MS. Figure 3 shows the TIC chromatograms of (a) the evolved products cold-trapped during the first degradation stage from 240 to 340 °C and (b) those during the second stage from 340 to 480 °C for the B(60/40) blend sample. The assigned products are listed in Table 2. In addition, the relationship between the degradation products and their corresponding original structures of the constituent polymers is shown in Figure 4.

The major products such as water and various unsaturated and aromatic aldehydes observed in Figure 3a may be formed during the first degradation stage through the dehydration of PVA followed by scission of the resulting polyene chains as shown in Figure 4a.[22] In this case, the products originating from the chitin derivative and hybrid products originating from both constituent polymers, which were considerably observed during the first degradation stage of the chitin derivative/PVC blends,[17] are almost absent in the chromatogram (Figure 3a).

On the other hand, various degradation products originating from the chitin derivative, of which peak intensities are much smaller than those for PVA (the first stage) mainly because of the lower degradation efficiency of the chitin derivative molecules,[21] are formed during the second degradation stage as shown in Figure 3b, while the products from PVA are hardly observed. Among the products from the chitin derivative as shown in Figure 4b, acetamide (**14**) is mainly formed from the chitin main chains,[17,21] while acetone (**4**), acetamide derivatives (**15 18** and **19**) such as *N*-ethylacetamide (**15**), and various nitrogen containing heterocyclic compounds such as 1*H*-imidazole derivatives (**16 17**) could be formed through scission and/or rearrangement in polyoxazoline side chains.

Then, the dependence of the blending ratio on the degradation behavior of the PVA moiety in the blend system was studied by TPPy−MS in a selected ion monitoring (SIM) mode. Figure 5 shows the thermal

Table 2. Pyrolysis Products of the Blend Films

peak	products	structure [a]	MW
1	carbon dioxide	CO_2	44
2	water	H_2O	18
3	acetaldehyde	CH_3-CHO	44
4	acetone	CH_3-CO-CH_3	58
5	acetic acid	CH_3-COOH	60
6	2-butenal	CH_3-CH=CH-CHO	70
7	3-penten-2-one	CH_3-CO-CH=CH-CH_3	84
8	2,4-hexadienal	CH_3-$(CH=CH)_2$-CHO	96
9	benzaldehyde	Ph-CHO	106
10	unknown ($C_7H_{10}O$)[b]		110
11	monomethylbenzaldehydes	CH_3-Ph-CHO	120
12	2,4,6-octatrienal	CH_3-$(CH=CH)_3$-CHO	122
13	2,4,6,8-decatetraenal	CH_3-$(CH=CH)_4$-CHO	148
14	acetamide	CH_3-CO-NH_2	59
15	*N*-ethylacetamide	CH_3-CO-NH-CH_2-CH_3	87
16	1H-imidazole derivatives		
17	monomethyl-1H-imidazoles		82
18	acetamide derivatives	CH_3-CO-NH-R	
19	acetamide derivatives	CH_3-CO-NH-R	
20	2-imidazoline derivatives		
21	unknown		

[a] Ph: phenyl group. R: functional groups which were not identified. [b] Estimated from the mass spectrum by EI.

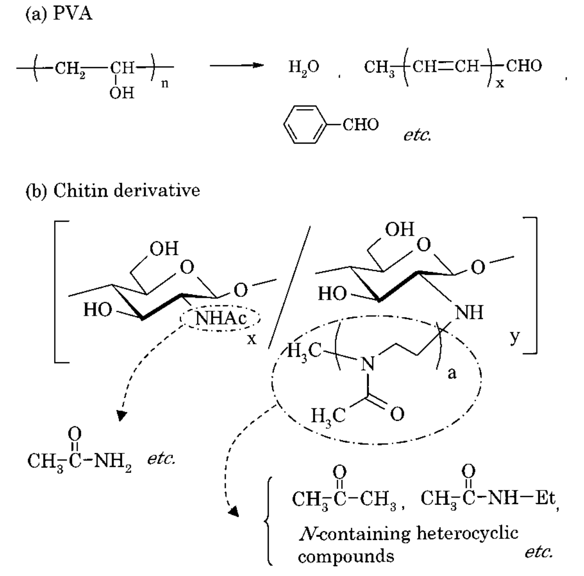


Figure 4. Thermal degradation pathways of (a) PVA and (b) the chitin derivative.

degradation profiles using SIM curves traced at the molecular ion peaks of water (*m*/*z* 18) and 2-butenal (*m*/*z* 70) during the first degradation stage from 200 to 350 °C for (a) PVA alone and those for (b) the B(60/40) blend sample. In this figure, each peak height is normalized by its observed maximum value to compare their evolution trend.

As for the thermogram for PVA alone shown in Figure 5a, water (*m*/*z* 18) caused by the dehydration with a peak maximum at around 260 °C is preceded by the evolution of 2-butenal (*m*/*z* 70) with a peak maximum at around 270 °C. The other homologous aldehydes such as acetaldehyde, 2,4-hexadienal, and 2,4,6-octatrienal also showed basically the same evolution profiles as that for 2-butenal. On the other hand, as shown in Figure 5b, both of the evolution profiles for water and 2-butenal for the B(60/40) blend sample shift to higher temperatures by ca. 50 °C than those for PVA alone. Moreover, almost comparable evolution profiles for water and 2-butenal in the front portion below 290 °C for the B(60/40) blend sample suggest that dehydration and scission of the main chain of PVA in the blend are in turn taking place nearly at the same time. These facts suggest that the dehydration process of the PVA moiety in the blend system is suppressed to some extent due to the intermolecular interaction with the counter constituent.

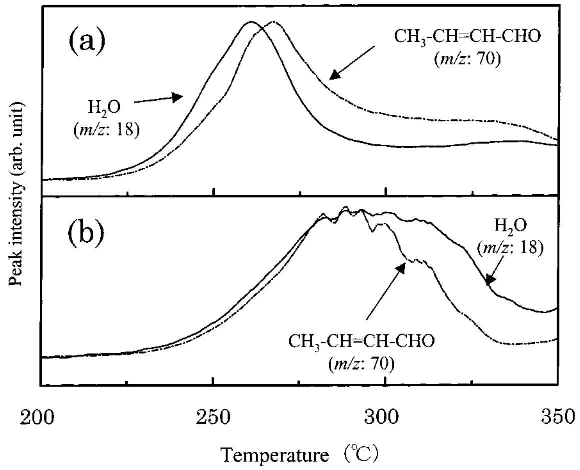


Figure 5. Selected ion monitoring curves for water (*m*/*z* 18) and 2-butenal (*m*/*z* 70) at the first degradation stage between 200 and 300 °C of (a) PVA and (b) the B(60/40) blend sample measured by TPPy–MS. Peak heights of each curve are normalized by the maximum in the temperature range.

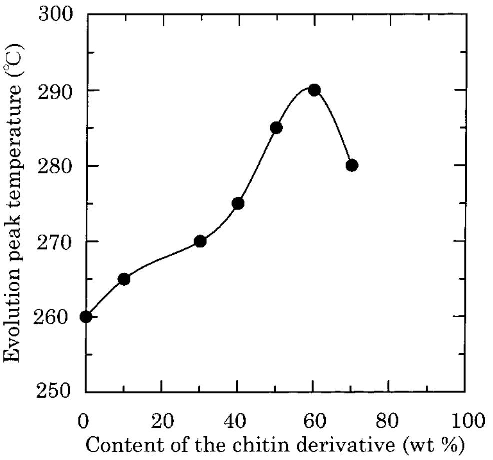


Figure 6. Relationship between composition of the blend and evolution temperature of 2-butenal observed by TPPy–MS.

Figure 6 shows the relationship between the peak-top temperature of 2-butenal evolved from PVA moiety and the content of the chitin derivative in the blend samples. Although 2-butenal was evolved at ca. 260 °C from PVA alone, it was evolved at higher temperatures from the blend samples, showing a maximum at ca. 290 °C for the B(60/40) blend sample. Most of the evolution profiles of the degradation products from PVA also showed basically the same tendency.

It has been reported in the previous paper[17] that for the case of the chitin derivative/PVC blend system, the

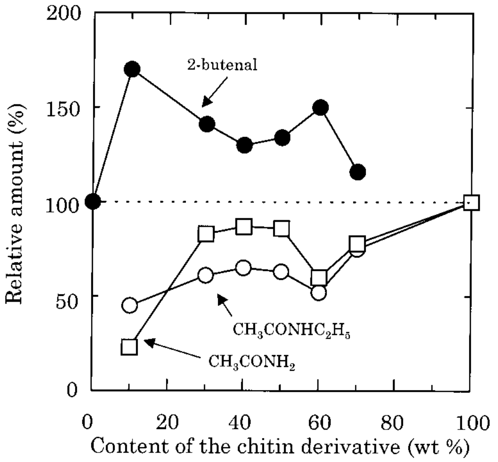


Figure 7. Relationship between composition of the blend and relative amounts of evolved 2-butenal from PVA, acetamide from the chitin main chains of the chitin derivative, and *N*-ethylacetamide from the polyoxazoline side chains of the chitin derivative, respectively, measured by Py−GC: broken line (- - -), hypothetical evolution amount for each product from blend samples supposing no intermolecular interaction.

evolution temperatures for the degradation products such as HCl during the first degradation stage were lowered by blending, reflecting the difference in the segmental intermolecular interactions and/or miscibility in the blend systems. Although the temperature shifts for the chitin derivative/PVA blends showed an opposite trend against the case of the chitin derivative/PVC blends, the observed temperature shifts could be also attributed to the differences in the segmental intermolecular interactions and/or miscibility in the blend systems. Judging from the maximum temperature shift, a much denser intermolecular interaction would be permitted in the B(60/40) blend sample. While these chitin derivative/PVA blend systems were already estimated to be miscible over the whole composition range by their DSC measurements,[14,15] the observations by TPPy−MS measurement strongly suggest that the B(70/30) blend sample, which showed a lower evolution temperature at ca. 280 °C, might be in a far less miscible state than the B(60/40) blend sample is.

Figure 7 shows the relationship between the contents of the chitin derivative in the blend samples and the relative amounts of the representative pyrolysis products such as 2-butenal mainly formed from PVA, acetamide from the chitin main chains in the chitin derivative, and *N*-ethylacetamide from the poly(2-methyl-2-oxazoline) side chain in the chitin derivative, observed at 600 °C by means of Py−GC. Here, the observed peak intensity per unit amount of the corresponding polymer components in the blend was normalized by those for the pure polymers. Reproducibility of the normarized peak intensities in relative standard deviation by three measurements for the B(60/40) blend was 1.5% for 2-butenal, 9.5% for acetamide, and 10.8% for *N*-ethylacetamide, respectively.

If the intermolecular interactions were negligible in the blend systems, each constituent polymer would be pyrolyzed independently to form each product according to the broken line in the figure. Actually, however, the relative amounts of each product from the blend samples change depending on the blend composition reflecting the intermolecular interaction. Moreover, it is interesting to note that the evolved amounts of 2-butenal from PVA and the evolved amounts of acetamide and *N*-ethylacetamide from the chitin derivative show a contrasting tendency.

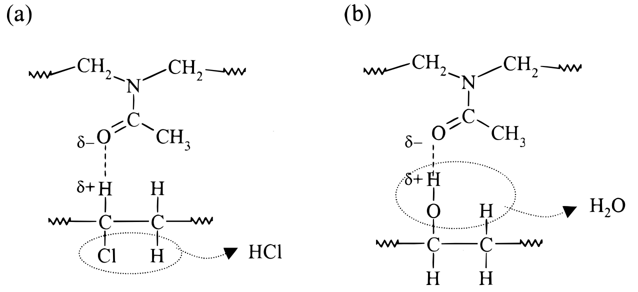


Figure 8. Possible segmental interaction between polyoxazoline side chains of the chitin derivative and vinyl-type polymers: (a) the chitin derivative/PVC blend system, and (b) the chitin derivative/PVA blend system.

As for the 2-butenal produced from PVA, the relative yields are increased by blending with the chitin derivative. This fact may be caused by lowered crystallinity of PVA in the blend system, where PVA molecules may be highly dispersed in the chitin derivative phase due to dense intermolecular interaction. As a result, the main chain cleavages of PVA in the blend system may be much more favored than the charring process caused by the intramolecular interaction is. In fact, as shown in Figure 2, the products reflecting the charring process of the PVA moiety was hardly observed on the thermograms at around 400−450 °C for the blend samples. These observations contrasted with the case for the chitin derivative/PVC blends,[17] where the yields of the degradation products from a vinyl-type polymer constituent (PVC) such as HCl and the various aromatic components decreased by blending with the chitin derivative.

On the other hand, as shown in Figure 7, the relative amounts of acetamide produced from the chitin main chains and *N*-ethylacetamide from the polyoxazoline side chains of the chitin derivative considerably decrease by blending with PVA. Moreover, the dependence of the relative amounts of the both products on the blend composition shows almost comparable tendency over the whole composition range. This fact suggests that the PVA molecules in the blend system can interact not only with the polyoxazoline side chains but also with the chitin main chains in the chitin derivative molecules to affect the degradation behavior of the whole molecules of the chitin derivative.

Here, it is interesting to note that the B(60/40) blend shows a peculiar behavior: the relative amounts of the products from the chitin derivative show minimum values, while 2-butenal from PVA exhibits a maximum value. In addition, the facts that the degradation temperatures of the PVA moiety in the blends became the highest for the B(60/40) blend sample (Figure 2) and that the evolution peak temperature of 2-butenal exhibited a maximum for the same blend sample (Figure 6) suggest that denser intermolecular interactions are specifically taking place between the chitin derivative and PVA in the B(60/40) blend sample.

Figure 8 shows the possible segmental interactions between the chitin derivative and vinyl-type polymers (PVC or PVA), which might be correlated to the shifts of the degradation temperature. Figure 8a shows the case for the chitin derivative/PVC blend system investigated previously, where an interaction between a weakly acidic tertiary hydrogen of PVC (as an electron acceptor) and a weakly basic carbonyl group of the chitin derivative (as an electron donor) may bind both polymers.[17] In this case, since Cl and tertiary H atoms of PVC may be more polarized by this interaction to decrease the binding energies at the C−Cl bonds in PVC chains, dehydrochlorination took place at lower temperatures for the blend systems. On the other hand, the decrease in the yields of the degradation products from PVC such as HCl and benzene and the formation of some specific hybrid products originating from both constituent polymers could be attributed to the assumption that the polarized tertiary hydrogen of PVC at this interaction site might be readily transferred to the counter polymer chain.

On the other hand, it was already confirmed by FT-IR measurements for the chitin derivative/PVA blend system that the hydrogen-bonding interaction would also participate between a hydrogen of the hydroxyl group of PVA chains as the electron acceptor and the carbonyl group of the polyoxazoline side chains in the chitin derivative as the electron donor.[14,15] In this case, as shown in Figure 8b, the hydroxyl groups of PVA chains, which can be eliminated by a dehydration reaction, would take part in this interaction causing the shift of the dehydration temperature of the PVA moiety in the blend system to higher values for the blend systems as shown in Figures 2 and 6. Moreover, the fact that no hybrid products originating from both constituent polymers were observed suggests that the hydroxyl group favors dehydration rather than transition to the counter polymer chains.

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