Characterization of Chitin-Based Polymer Hybrids by Temperature-Programmed Analytical Pyrolysis Techniques. 1. Chitin-*graft*-poly(2-methyl-2-oxazoline)/Poly(vinyl chloride) Blends

Hiroaki Sato and Shin Tsuge*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Hajime Ohtani

Center for Integrated Research in Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Keigo Aoi, Akinori Takasu, and Masahiko Okada

Department of Applied Biological Sciences, School of Agricultural Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Received February 21, 1997; Revised Manuscript Received May 6, 1997[⊗]

ABSTRACT: Chitin-*graft*-poly(2-methyl-2-oxazoline)/poly(vinyl chloride) (PVC) blends were characterized 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) mainly focusing on their miscibility and sites of the intermolecular interactions. The blends degraded stepwisely in almost three stages corresponding to the degradation of respective blending polymers. However, each degradation peak temperature changed as a function of the blend composition, in particular that of the first degradation stage mostly corresponding to the dehydrochlorination stage for PVC showed a minimum temperature for the blend with the saturated composition of miscibility. During the dehydrochlorination stage for PVC, many characteristic products formed from the chitin derivative were also evolved, suggesting the intermolecular interactions between PVC and the chitin derivative. Among these, a specific hybrid product, benzoic acid reflecting the segmental interaction between PVC and the chitin derivative was observed only for the blend with the saturated composition of miscibility. The evolution peak temperatures and the amounts of the characteristic degradation products were also correlated to the miscibility of the blends. In addition, the mechanisms of the intermolecular interaction of the blends were discussed.

Introduction

Chitin, consisting mainly of 2-acetamide-2-deoxy-D-glucopyranose linked by β-(1→4) bonds, is a natural polysaccharide found particularly in the shells of crustacean 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 for its biomedical, biotechnological, and industrial applications.[1−4] However, it has been hitherto utilized only in limited fields mainly due to its poor solubility and reactivity caused by its rigid crystalline structure. In order to overcome this problem, various approaches have been examined to convert chitin into functional materials. Chitin or chitosan (*N*-deacetylated chitin) has been blended with other polymers to improve the property. However, only a few miscible blends with chitosan have been reported using cellulose,[5] poly(vinyl alcohol) (PVA),[6] and poly(ethylene oxide) (PEO).[7] On the other hand, chemical modifications of chitin or chitosan by grafting with synthetic polymers have been studied.[8−12] In addition to these approaches, various blends of commodity synthetic polymers with chitin derivatives which are miscible with various polymers have also been prepared. Recently, Aoi *et al.*[13] have synthesized chitin derivatives having poly(2-alkyl-2-oxazoline) side chains with a high miscibility toward various synthetic polymers. So far miscible blends of these chitin derivatives with commodity synthetic polymers such as poly(vinyl chloride) (PVC)[14] and poly(vinyl alcohol) (PVA)[15] have been successfully prepared. These blend systems containing chitin are expected to be new materials in the field of biomass utilization, which possess both the biospecific properties of chitin and the molding and mechanical properties of commodity polymers.

Characterization of these blend systems in miscibility and intermolecular interaction will provide good information to design new excellent 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. However, these thermal techniques give little chemical information about intermolecular interaction. Moreover, some biomaterials such as cellulose and chitin have no clear glass-transition temperature.

For the study of the intermolecular interaction in chitin/chitosan based polymer blends, X-ray diffraction has been applied.[5,16−19] However, since this technique is mainly focused on the crystallinity of the blend, it is difficult to obtain good information about the specific interaction sites. Although infrared spectrometry (IR)[18−20] and Raman spectroscopy[6,18] often provide good information about the interaction sites in the blends, it is difficult to discriminate the samples having many

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

S0024-9297(97)00239-8 CCC: $14.00

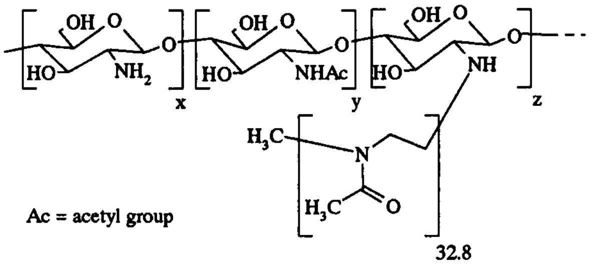

Figure 1. Structure of chitin-*graft*-poly(2-methyl-2-oxazoline). Repeating units of the main chain are randomly linked. *x*/*y*/*z* = 26/52/22.

similar functional groups. Moreover, these techniques generally require relatively large amounts of the sample because of their poor sensitivity. Since the scale of synthesized materials on an experimental basis is often small, a highly sensitive characterization method using a small sample size has been eagerly requested to be developed.

The thermal degradation behavior of a miscible polymer blend is often quite different from those of individual blending polymers alone. Nishioka *et al.*[21−24] have reported that the variation in the peak-top temperature for the decomposition of the blends containing cellulose measured by thermogravimetry (TG) can be correlated with their compatibility. They also suggested that the compatibility of the blends of grafted cellulose with poly(methyl methacrylate)[23] or with polyacrylonitrile[24] can be also estimated by TG, where the degradation temperature shift is attributed to the lowered crystallinity of cellulose.

On the other hand, the difference in the thermal degradation behavior for a given miscible polymer blend should be observed not only in the degradation temperature shift but also in the species of the degradation products reflecting intermolecular interaction in the blend system. Therefore, evolved gas analysis (EGA), in which the evolution behavior of the individual thermal degradation products measured as a function of temperature, might provide good information to evaluate the miscibility in the polymer blend system. Moreover, a very minute sample size about 0.1 mg or less is usually enough in the modern EGA equipped with highly specific and sensitive detectors such as a flame ionization detector (FID), a mass spectrometer (MS), and an atomic emission detector (AED).

In this study, thermal degradation behavior of various blend samples of the chitin derivative, chitin-*graft*-poly(2-methyl-2-oxazoline), with PVC was investigated by means of the modern analytical pyrolysis techniques such as temperature-programmed pyrolysis (TPPy)-MS, TPPy-AED, and TPPy-GC-MS. Variations of the thermal degradation products in species, their evolution temperature, and their amounts were correlated with the miscibility of the blend system. In addition, the mechanisms of the intermolecular interaction in the blends were also discussed.

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,[13] where living poly(2-methyl-2-oxazoline) side chains (degree of polymerization (DP) = 32.8, M_w/M_n = 1.18) were 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. In this derivative, the ratio of the introduced side chains for the free amino groups in the deacetylated chitin was about 45%, and its number-average molecular weight was about 9.8×10^5 determined by size exclusion chromatography (SEC) in H_2O using pullulan standards.

Table 1. Composition and Properties of Chitin-*graft*-poly(2-methyl-2-oxazoline)/PVC Blend Films

sample codes	composition (wt %) chitin derivative	PVC	T_g (°C)[a]	transparency[b]	miscibility[c]
	0	100	78	T	
B(25/75)	25	75	75	T	+
B(30/70)	30	70	74	T	+
B(40/60)	40	60	69	T	+
B(45/55)	45	55	66 and 79	O	−
B(50/50)	50	50	65 and 78	O	−
	100	0	66	*d*	

[a] Glass transition temperature. [b] T, transparent; O, opaque. [c] Miscibility of the blends was judged from T_g and transparency: +, miscible; −, immiscible. [d] Powder sample.

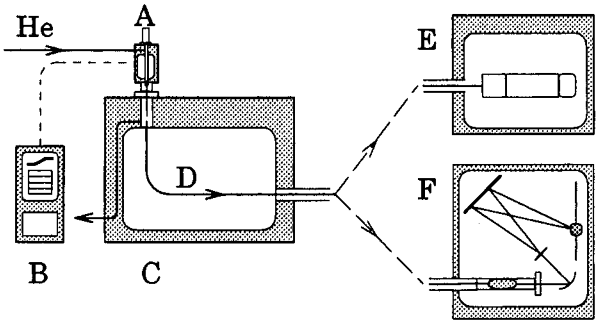

Figure 2. Schematic diagram of TPPy-MS and TPPy-AED systems: A, microfurnace; B, furnace controller; C, gas chromatograph; D, deactivated metal capillary; E, quadrupole mass spectrometer; F, atomic emission detector.

Blend films of chitin-*graft*-poly(2-methyl-2-oxazoline) with PVC (M_n = 68 000, Wako Pure Chemical Co.) were prepared by casting from a dichloromethane solution as described in a previous paper.[14] The composition of these blends is summarized in Table 1 together with their properties such as apparent transparency, glass-transition temperature determined by DSC, and estimated miscibility. The cast blend films containing up to 40% of the chitin derivative are estimated to be miscible from a single glass-transition temperature and their transparency, while the blend films containing larger than 40% of the chitin derivative are immiscible because they are opaque films having two glass-transition temperatures corresponding to the individual polymer phases for the blend samples.[25]

In addition, in order to confirm the origin of the thermal degradation products, a chitin-*graft*-poly(2-ethyl-2-oxazoline) in which the methyl groups of the *N*-acetyl groups of the polyoxazoline side chains are substituted to ethyl groups was also prepared[13] and blended with PVC by a blending ratio of 25/75 (w/w) to prepare a blend sample [B_{Et}(25/75)].

Measurements. Figure 2 shows a schematic diagram for the EGA measurements by TPPy-MS and TPPy-AED. In this system, temperature-programmable microfurnace pyrolyzer (Frontier Lab, PY-2010D) was directly coupled with a quadrupole MS (JEOL, AM-II 150) or an AED (Hewlett Packerd, HP-5921A) *via* a deactivated stainless steel capillary (Frontier Lab, UADTM-5N, 0.15 mm i.d. × 5 m long). The capillary was maintained at 280 °C in an oven of a gas chromatograph (GC) (Hewlett-Packerd, HP-5890 II) to prevent condensation of less volatile products in the capillary.

About 0.2 mg of a given sample in a platinum sample cup was heated in the pyrolyzer from 60 °C up to 700 °C at a heating rate of 10 °C/min under a He atmosphere with a flow rate of 50 mL/min. A part of the flow (1 mL/min) reduced by a splitter (50:1) was continuously introduced into either MS or AED through the capillary. Thus, the evolved products resulting from the thermal degradation of the sample during the programmed heating were introduced into the MS or AED

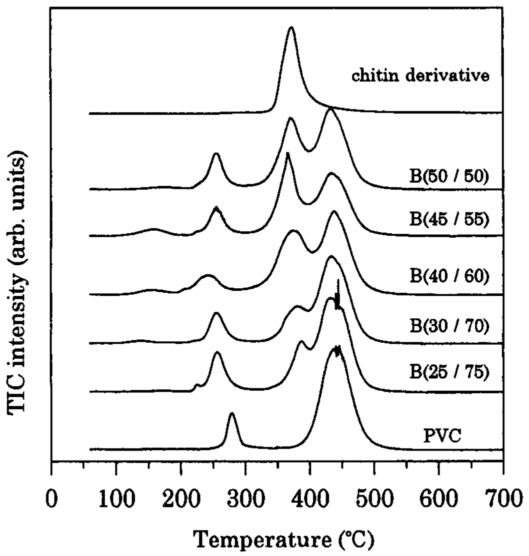

Figure 3. Evolution profiles of the thermal degradation products from the chitin derivative/PVC blend samples observed in total ion current by TPPy-MS.

without time delay. For the MS measurement, ionization was carried out by electron impact (EI) at 70 eV and the operating mass range was 10−300 amu with a scan rate of 2 s/scan. For the AED measurement, four emission lines were monitored: at 193 nm for C, at 174 nm for N, at 486 nm for H; at 479 nm for Cl. Since only neighboring emission lines are measured simultaneously by this instrument, duplicate measurements were carried out independently: the first run at 193 nm for C and at 174 nm for N, and the second at 486 nm for H and at 479 nm for Cl, respectively.

In order to identify the evolved products, TPPy-GC-MS was also carried out. This system is basically the same as that in Figure 2 except for a metal separation capillary column (Frontier Lab, Ultra ALLOY-CW; 0.25 mm i.d. × 30 m long) coated with immobilized poly(ethylene glycol) (0.25 μm film). During a programmed heating procedure, 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 into liquid N_2 in a Dewar vessel. After removing the Dewar vessel, the column temperature was initially set at 35 °C for 15 min and then heated up to 200 °C at a rate of 5 °C/min.

Results and Discussion

Thermal Degradation Behavior of the Blends Measured by TPPy-MS. Evolution profiles of the thermal degradation products from the chitin derivative/PVC blends measured by TPPy-MS are shown in Figure 3 together with those for the chitin derivative and PVC. These profiles are observed using total ion current (TIC) as a function of programmed temperature. The TIC curve of PVC homopolymer shows two-stage degradation: the first degradation stage at around 250−300 °C mainly corresponds to dehydrochlorination process to form polyene structure, while the second major degradation stage corresponds to the charring process at around 400−500 °C releasing aromatic hydrocarbons from the polyene structures resulting from dehydrochlorination at the first degradation stage.[26] On the other hand, the thermal degradation of the chitin derivative alone indicates apparently one stage degradation at around 350−400 °C.

Expectedly, the thermal degradation of the blend samples commonly takes place in three stages reflecting the degradation of both constituent polymers; the first degradation stage at around 200−260 °C may correspond to the dehydrochlorination process of PVC, the second at around 340−400 °C to the degradation process of the chitin derivative, and the third at around 400−500 °C to the charring process of PVC residue, respectively. However, the degradation peak temperatures for the first and the second degradation stages slightly shift with variation of the composition of the blend, while the corresponding temperatures for the third stage remain almost constant. As for the first degradation stage, the peak temperatures decrease with the increase in the content of the chitin derivative in the miscible blends [B(25/75), B(30/70), and B(40/60)] and show a minimum value for the B(40/60) which is almost the saturated composition for the miscibility estimated by DSC measurements,[25] whereas for the immiscible blends [B(45/55) and B(50/50)], the corresponding temperatures shift back to higher values. As for the second degradation stage, the peak temperatures remain almost constant for the immiscible blends, while those increase with decrease in the content of the chitin derivative in the miscible blends. These temperature shifts may correlate to the miscibility in the blends.

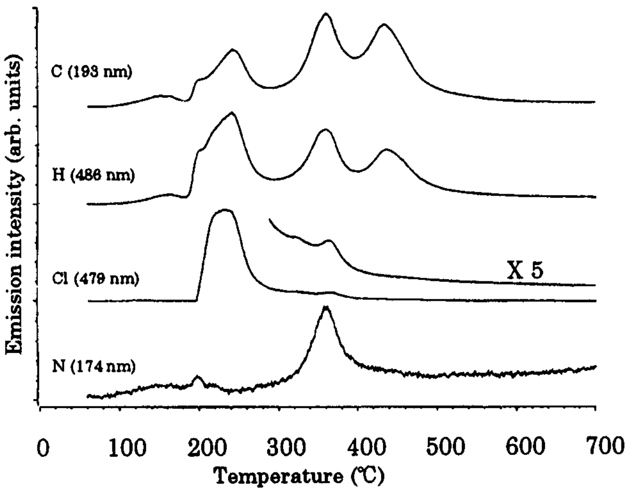

Figure 4. Atomic emission profiles of the thermal degradation products from the B(40/60) blend observed by TPPy-AED.

Thermal Degradation Behavior of the Miscible Blend Measured by TPPy-AED. Evolution profiles of the thermal degradation products from the B(40/60) blend measured by TPPy-AED are shown in Figure 4. These thermograms are depicted by tracing the variation of the emission intensities of C at 193 nm, H at 486 nm, Cl at 479 nm, and N at 174 nm, respectively. From the emission curves of C and H, three stages of the thermal degradation are roughly suggested. These results agree with those by the TPPy-MS measurements as shown in Figure 3. However, at the first stage starting around 200 °C, the emission peak of Cl is also clearly observed suggesting the quickened dehydrochlorination process of PVC, while the emission peak of N is mainly observed at the second degradation stage around 300−400 °C, corresponding to the degradation of the chitin derivative containing N atoms. At the third degradation stage around 420−480 °C, only emission peaks of C and H are observed due to the charring process of PVC releasing aromatic hydrocarbons. Here, it is interesting to note that a small peak of the N emission is also observed at around 200 °C, which coincides with those of the front shoulders of the first degradation stage for C and H. This fact also suggests that the intermolecular interactions are occurring to some extent in the miscible blend because the thermal

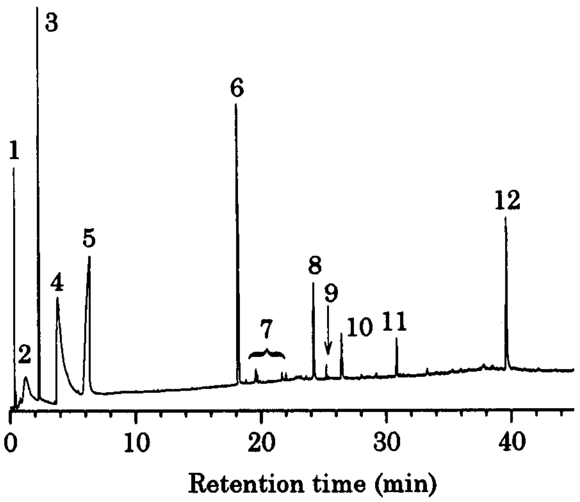

Figure 5. A gas chromatogram of the degradation products formed from the miscible blend [B(40/60)] during heating from 60 to 290 °C. The numbers correspond to those of the compounds in Table 2.

Table 2. Pyrolysis Products of the Blend Films at the First Degradation Stage

peak	products	MW	origin[a]
1	carbon dioxide	44	Ch
2	acetaldehyde	44	Ch
3	benzene	78	PVC
4	hydrogen chloride	36	PVC
5	water	18	Ch
6	acetic acid	60	Ch
7	methylindenes	130	PVC
8	1-methyl-2-pyrrolidinone	99	Ch
9	naphthalene	128	PVC
10	acetamide	59	Ch
11	levoglucosenone	126	Ch
12	benzoic acid	122	Ch + PVC

[a] Ch = the chitin derivative.

degradation of the pure chitin derivative begins at about 350 °C as shown in Figure 3. Furthermore, a small emission peak of Cl is also observed at around 360 °C as shown in the expanded curve of Cl mode in Figure 4, which coincides with that for the main degradation of the chitin derivative. This fact also suggests that some characteristic products reflecting the intermolecular interactions are evolved from the blend system.

Identification of Thermal Degradation Products and Their Origin. The results obtained from the first and the second degradation stages by TPPy-MS and TPPy-AED strongly suggested that some intermolecular interactions should take place between PVC and the chitin derivative in the miscible blends, which might be reflected in the degradation products. In order to identify these products evolved during the first degradation stage up to 290 °C, TPPy-GC-MS measurement was carried out. Because it was difficult to identify and determine the products evolved during the second degradation stage, the later discussion are mostly based on the results obtained from the first degradation stage.

Figure 5 shows the mass chromatogram of the products evolved in the first degradation stage from the B(40/60) blend in a heating range from 60 °C up to 290 °C within which the dehydrochlorination process of PVC is to be finished. The assigned peaks in this chromatogram are listed in Table 2. The degradation products such as HCl, benzene, and naphthalene are attributed to PVC origin in the blend system, while H_2O, acetaldehyde, acetic acid, and acetamide are to the chitin derivative origin. Here, it is interesting to note that benzoic acid is also formed as a hybrid product reflecting the segmental reactions between PVC and the chitin derivative.

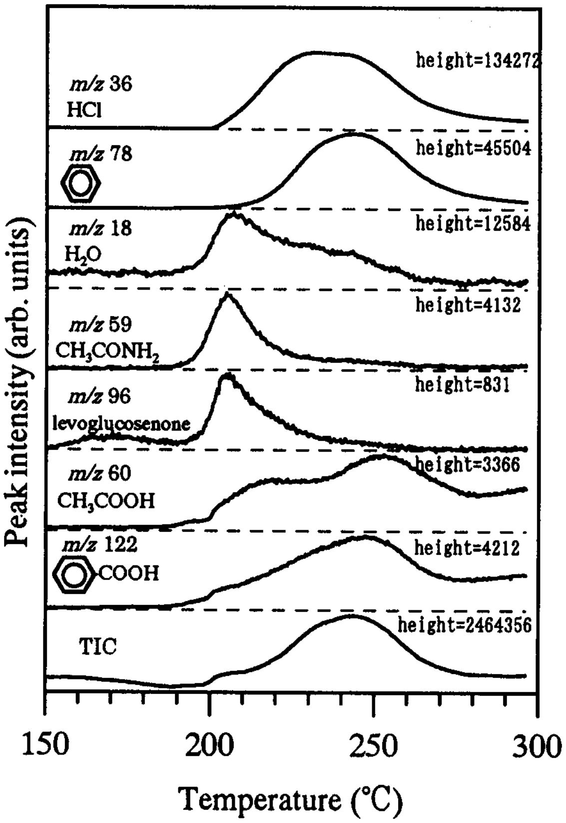

Figure 6. Selected ion monitoring curves and the TIC curve at the first degradation stage between 150 and 300 °C of the miscible blend [B(40/60)] measured by TPPy-MS.

Among the specific products, the segmental origins of some compounds can easily be identified on the basis of their structure; H_2O is mainly formed through dehydration of hydroxy groups in the chitin backbone and levoglucosenone is formed by rearrangement of the pyranose rings in the chitin main chain.[27] On the other hand, both acetic acid and acetamide could be formed from either *N*-acetyl groups in the chitin backbone or poly(2-methyl-2-oxazoline) side chains. In order to distinguish these origins, the thermal degradation products from the B_{Et}(25/75) were compared to those of the B(25/75). The main products were acetic acid and acetamide of the B(25/75), whereas in the case of the reference blend system [B_{Et}(25/75)] propionic acid and acetamide were mainly observed with minor acetic acid and propanamide formation. These facts suggest that acetic acid is almost exclusively produced from the poly(2-methyl-2-oxazoline) side chains, while acetamide is mainly from the *N*-acetyl groups in the chitin main chain.

Relationship between the Evolution Temperature of the Products and the Composition of the Blends. In order to discuss more detailed degradation process, the evolution behavior for each thermal degradation product was measured by TPPy-MS using a selected ion monitoring (SIM) mode. Figure 6 shows the SIM curves traced mostly at the molecular ion peaks of the main degradation products together with the corresponding TIC curve at the first degradation stage from 150 to 300 °C for the miscible blend sample [B(40/60)]. Here, the SIM curve at *m/z* 36 corresponds mainly to the evolution profile of HCl, at *m/z* 78 to that of benzene, at *m/z* 18 to that of H_2O, at *m/z* 59 to that of acetamide, at *m/z* 96 to that of levoglucosenone, at *m/z* 60 to that of acetic acid, and at *m/z* 122 to that of benzoic acid, respectively. The SIM evolution profiles of the products are mostly traced using their molecular ions, but that of levoglucosenone is traced using a noninterfering fragment ion at *m/z* 96 because its molecular ion (*m/z* 126) was hardly observed.[27]

Since the temperature range between 150 and 300 °C corresponds mainly to the dehydrochlorination process of PVC, the SIM curves at *m/z* 36 (HCl) and at *m/z* 78 (benzene) evolved from PVC show similar profiles to that of the TIC curve with a broad peak at around 220−250 °C. However, it is interesting to note that the characteristic products formed from the chitin derivative are also observed in this temperature range. Among these, the SIM curves at *m/z* 18 (H_2O), at *m/z* 59 (acetamide), and at *m/z* 96 (levoglucosenone) which may be formed from the chitin main chains show the peak at around 200 °C. This quickened evolution of acetamide (*m/z* 59) corresponds to the small emission peak of N at around 200 °C observed by TPPy-AED measurement as shown in Figure 4. On the other hand, the SIM curve at *m/z* 60 (acetic acid) apparently shows a peak at about 250 °C and a shoulder at around 200−230 °C. The fact that the SIM curve at *m/z* 122 for benzoic acid also shows a peak at about 250 °C suggests that the formation of acetic acid has a close correlation with that of benzoic acid, while the lowered peak temperature for acetamide suggests its different origin in the blend system. In addition, evolution peak temperatures of H_2O, acetamide, and levoglucosenone which may be formed from the chitin main chains are generally lower than that of HCl. This fact suggests that these products are mainly formed by the intermolecular interactions in the miscible blend systems rather than by the migration of the evolved HCl to the chitin derivative phase. For the other blends except the B(40/60), the evolution peak of acetic acid and the products formed from PVC such as HCl and benzene showed sharp peaks, while benzoic acid peak was hardly evolved. These facts suggest that the intermolecular interaction of the almost saturated blend [B(40/60)] might have a quite different miscible structures from those of the other blends.

Many of the evolution peak temperatures for the characteristic products listed in Table 2 shifted as a function of the blend composition. Among these the relationships for HCl and acetamide are shown in Figure 7. For each pure constituent polymer, HCl was evolved at 280 °C from PVC and acetamide was evolved at about 300 °C from the chitin derivative, respectively. However, both temperatures for all the blend samples are lowered and showed minimum temperatures for the B(40/60) (*ca.* 230 °C for HCl and *ca.* 200 °C for acetamide). Most of the other products also showed basically the same tendency. These temperature shifts could be reflecting the difference in the segmental intermolecular interactions and/or the miscibility in the blend systems. In particular, the peak temperature shift for acetamide can be correlated to the difference in miscibility. For the miscible blends, the peak temperature decreased with the increase in the content of the chitin derivative, whereas for the immiscible blends, the peak temperature increased with the increase in the content of the chitin derivative. The differences in peak temperature between B(25/75) and B(30/70) and between B(45/55) and B(50/50) are about 4 °C, respectively. Considering that the precision of the programmed temperature of the furnace used in this study is about ±1 °C, the temperature differences about 4 °C are significant. Therefore, the saturated composition of miscibility and/or the difference in miscibility for the blend systems can be evaluated using the shifts in the evolution temperatures of those degradation products by TPPy-MS. Basically the same experimental results were also possible to obtain by use of TPPy-AED where the emission intensities for N at 174 nm and Cl at 479 nm were monitored instead of the SIM monitoring for TPPy-MS.

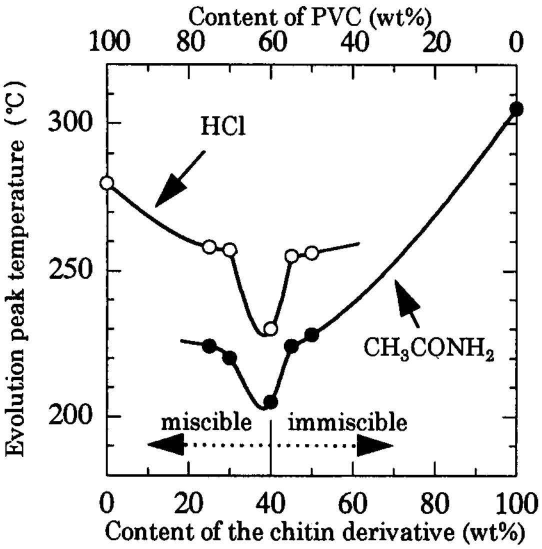

Figure 7. Relationship between composition of the blend and evolution peak temperature of hydrogen chloride and acetamide observed by TPPy-MS.

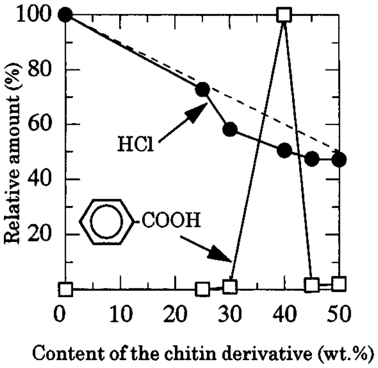

Figure 8. Relationships between composition of the blends and relative amounts of evolved HCl and benzoic acid measured by TPPy-MS: broken line (- - -), hypothetical HCl evolution change from blend samples supposing no intermolecular interaction.

Relationship between the Amounts of Evolved Products and the Composition of the Blends. Figure 8 shows the relationship between the composition of the blends and the relative amounts of evolved HCl and benzoic acid determined by use of peak area of the respective SIM traces per unit sample amounts at *m/z* 36 for HCl and *m/z* 122 for benzoic acid, where the observed peak area normalized by the maximum value was used as the relative amounts (%). If the intermolecular interactions are negligible in the blend systems, the relative amount of the evolved HCl would decrease linearly with the decrease in the content of PVC in the blends according to the broken line in the figure. However, the amounts of the evolved HCl from

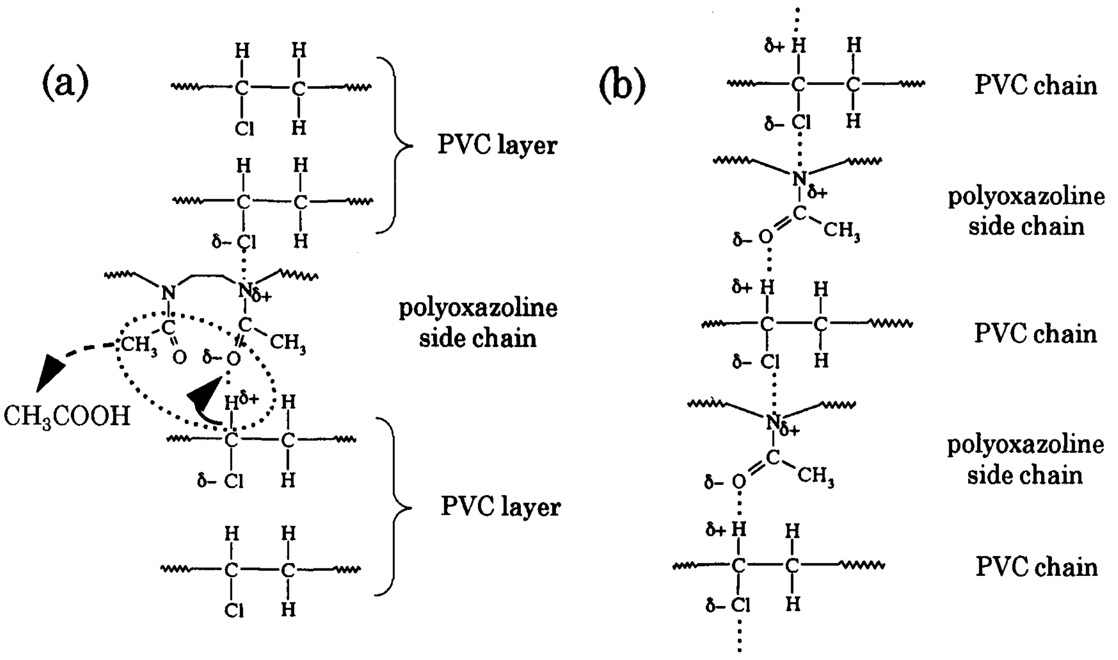

Figure 9. Possible segmental interaction between poly(2-methyl-2-oxazoline) side chains of the chitin derivative and PVC in the miscible blends: (a) the poly(2-methyl-2-oxazoline) side chains are incorporated in the PVC layer for the B(25/75) and the B(30/70) blends; (b) the poly(2-methyl-2-oxazoline) side chains and PVC chains are arranged alternately for the B(40/60) blend.

the blends were mostly lower than the broken line. This fact suggests that the dehydrochlorination from PVC is suppressed in the blend samples to some extent. Basically the same results were obtained for the various aromatic products such as benzene and naphthalene which were formed by rearrangement of polyene chains caused by dehydrochlorination of PVC. On the other hand, benzoic acid is observed exclusively from the B(40/60) but hardly from the other blends. This fact suggests that benzoic acid is formed only through the dense intermolecular interactions between PVC and the chitin derivative in the blend system. Therefore, the amounts of benzoic acid can be used to estimate the saturated composition of the miscibility for the blend system.

Possible Mechanisms of the Thermal Degradation of a Miscible Blend Correlated to the Intermolecular Interactions between PVC and the Chitin Derivative. Figure 9 shows the possible segmental interactions between poly(2-methyl-2-oxazoline) side chains of the chitin derivative and PVC. Figure 9a shows the case for the miscible blends in which the chitin derivative content is relatively low [B(25/75) and B(30/70)], where the polyoxazoline side chains are incorporated in the PVC phase. It is known that a good miscibility between PVC and poly(2-methyl-2-oxazoline) emerges from an interaction between a weakly acidic hydrogen of PVC and a slightly basic amide group of poly(2-methyl-2-oxazoline).[28] Similarly, an electrostatic interaction between PVC and poly(2-methyl-2-oxazoline) side chains of the chitin derivative will bind both polymers in these blend systems as shown in Figure 9a. In this case, since Cl and H atoms of PVC may be further polarized by this interaction to decrease the binding energies at C−Cl in the PVC chains, dehydrochlorination takes place at lower temperatures for the blend systems as shown in Figure 7. On the other hand, it is probable that the polarized tertiary hydrogen of PVC at this interaction site can be readily transferred to the carbonyl group in the chitin derivative to form acetic acid. As a result, dehydrochlorination is suppressed by the hydrogen extraction as shown in Figure 8, although it takes place at lower temperature.

Figure 9b shows the case for the blend with the saturated composition of miscibility [B(40/60)]. The thermal degradation behavior of this blend sample is considerably different from those of the other blends, where much denser intermolecular interactions participate in the miscible blend system with a comparable amount of the chitin derivative. In particular, the fact that the dehydrochlorination in this blend takes place at considerably lower temperature than the other blends suggests that the PVC chains lay in a more polarized environment. Here, it is probable that a negatively polarized Cl of PVC can interact with a positively polarized N of poly(2-methyl-2-oxazoline) rather than a positively polarized hydrogen of PVC. As a consequence, PVC chains and poly(2-methyl-2-oxazoline) side chains may easily be arranged nearly alternately as shown in Figure 9b. Because intermolecular interaction is much denser in the alternate arrangement structure, the carboxyl group caused by the interaction between PVC and polyoxazoline side chain as shown in Figure 9a may be transferred to polyene chains caused by dehydroxychlorination, resulting in the formation of benzoic acid.

Figure 10 illustrates the possible existence state of the chitin derivative molecules in the blend. Parts a and b of Figure 10 show possible models that a chitin layer and a PVC layer in a given miscible blend would be combined only through poly(2-methyl-2-oxazoline) side chains as compatibilizing anchors because of the expected poor compatibility between the both layers. Thus, it was postulated that the chitin main chains might emerge to the surface of the blend film as shown in Figure 10a, or in the bulk of the blend film to form a microphase separation structure as shown in Figure 10b. However, the fact that the surface of the miscible blend films was proved to have almost the same hydrophobicity as that of the PVC film by the contact angle measurement of the film samples against water suggested that the surface-emerging model was doubtful.[14] In addition, since any microphase separation structures of the blend samples were not observed by a scanning electron microscope, the micro-phase separa-

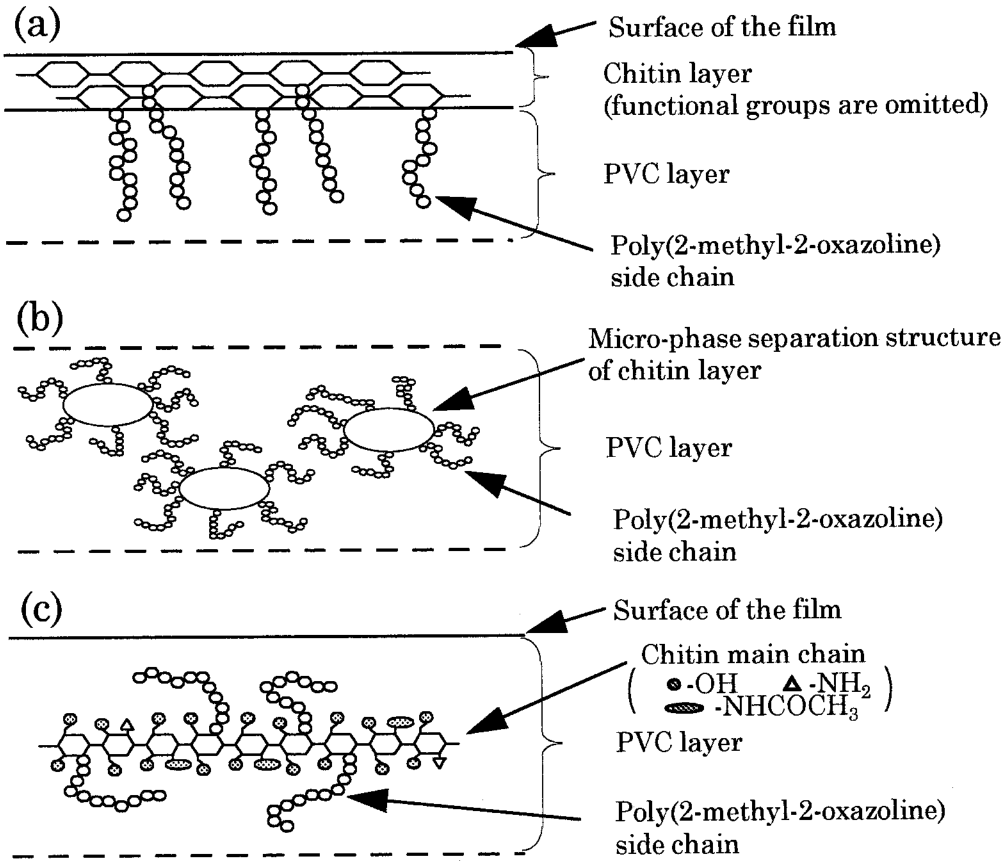

Figure 10. Possible existence state of the chitin derivative in the blend film: (a) the surface-emerging model and (b) the micro-phase-separation structure model. In these models, a chitin layer and a PVC layer are combined through poly(2-methyl-2-oxazoline) side chains as compatibilizing "anchors". (c) The whole miscible structure model. Since the chitin main chains also take part in the interaction with PVC, whole bodies of the chitin derivative molecules are contained in the PVC layer.

tion structures were also doubtful. On the other hand, in this study not only HCl formed from PVC chains and acetic acid from the poly(2-methyl-2-oxazoline) side chains but also the products from the chitin main chains such as acetamide from the *N*-acetyl groups, H_2O from the hydroxyl groups, and levoglucosenone from the pyranose rings were observed during the dehydrochlorination process of PVC at relatively lower temperatures around 200−300 °C as shown in Figure 6. This fact suggests that fairly denser intermolecular interactions might be taking place between the chitin main chains and PVC molecules. Thus, as shown in Figure 10c, it can be concluded that whole bodies of the chitin derivative molecules, including the chitin main chains, are contained in the PVC layer rather than in the surface-emerging layers or the micro-phase-separation structures.

Conclusion

The temperature-programmed analytical pyrolysis techniques such as TPPy-MS, TPPy-AED, and TPPy-GC-MS were demonstrated to be effective to evaluate the miscibility of the chitin derivative/PVC blends. The thermal degradation of the blend samples commonly took place in three stages reflecting the degradation of both constituent polymers, while the degradation peak temperatures shifted as a function of the blend composition. During the dehydrochlorination stage for PVC, the characteristic products formed from the chitin derivative through the intermolecular interaction were also observed for the miscible blends. Among these, benzoic acid was observed as a specific hybrid product reflecting the segmental reactions between PVC and the chitin derivative only for the blend with the saturated composition of miscibility. Many of the evolution peak temperatures for the characteristic products shifted as a function of the composition in the miscible blend samples. In addition, the amounts of these products also varied with the miscibility of the blend samples. Therefore, the shifts in the evolution temperatures and/or the variation of the amounts of the degradation products proved to be good measures to estimate the miscibility of the blend system. Thus observed thermal behaviors of the blend system also enabled discussion of the possible existence state and the interacting sites for the chitin derivative molecules in the blend system.

Acknowledgment. Financial supports by the Grant-in-Aid for Scientific Research (A) (07555262 and 09305056), (B) (09555262) and (C) (09650888) of the Ministry of Education, Science, Sports and Culture, Japan, and by the Grant, "Research for the Future" Program of the Japan Society for the Promotion of Science (JSPS-RFTF, 96R11601) are gratefully acknowledged.

References and Notes

(1) Muzzarelli, R. A. A. *Chitin*; Pergamon Press: Oxford, 1977.
(2) *Chitin, Chitosan, and Related Enzymes*; Zikakis, J. P., Ed.; Harcourt Brace Janovich: New York, 1984.
(3) *Chitin in Nature and Technology*; Muzzarelli, R. A. A., Jeuniaux, C., Gooday, G. W., Eds.; Plunum Press: New York, 1986.
(4) *Chitin and Chitosan*; Skjåk-Bræk, G., Anthonsen, T., Sandford, P., Eds.; Elsevier Applied Science: London, 1989.
(5) Isogai, A.; Atalla, R. H. *Carbohydr. Polym.* **1992**, *19*, 25.

(6) Miya, M.; Yoshikawa, S.; Iwamoto, R.; Mima, S. *Kobunshi Ronbunshu* **1983**, *40*, 645.
(7) Zhao, W.; Yu, L.; Zhong, X.; Zhang, Y.; Sun, J. *J. Macromol. Sci.-Phys.* **1995**, *B34*, 231.
(8) Kojima, K.; Yoshikuni, M.; Suzuki, T. *J. Appl. Polym. Sci.* **1979**, *24*, 1587.
(9) Shigeno, Y.; Kondo, K.; Takemoto, K. *J. Macromol. Sci.-Chem.* **1982**, *A17*, 571.
(10) Blair, H. S.; Guthrie, J.; Law, T.; Turkington, P. *J. Appl. Polym. Sci.* **1987**, *33*, 641.
(11) Kurita, K.; Kanari, M.; Koyama, Y. *Polym. Bull.* **1985**, *14*, 511.
(12) Yalpani, M.; Marchessault, R. H.; Morin, F. G.; Monasterios, C. J. *Macromolecules* **1991**, *24*, 6046.
(13) Aoi, K.; Takasu, A.; Okada, M. *Macromol. Chem. Phys.* **1994**, *195*, 3835.
(14) Aoi, K.; Takasu, A.; Okada, M. *Macromol. Rapid Commun.* **1995**, *16*, 53.
(15) Aoi, K.; Takasu, A.; Okada, M. *Macromol. Rapid Commun.* **1995**, *16*, 757.
(16) Hasegawa, M.; Isogai, A.; Onabe, F. ; Usuda, M.; Atalla, R. J. *J. Appl. Polym. Sci.* **1992**, *45*, 1873.
(17) Qurashi, M. T.; Blair, H. S.; Allen, S. J. *J. Appl. Polym. Sci.* **1992**, *46*, 255.
(18) Kim, J. H.; Kim, J. Y.; Lee, Y. M.; Kim, K. Y. *J. Appl. Polym. Sci.* **1992**, *45*, 1711.
(19) Wrzyszczynski, A.; Qu, X.; Szosland, L.; Adamczak, E.; Linden, L. A.; Rabek, J. F. *Polym. Bull.* **1995**, *34*, 493.
(20) Miya, M.; Iwamoto R.; Mima, S. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1149.
(21) Nishioka, N.; Ono H.; Karasuno, M. *Polym. J.* **1992**, *24*, 301.
(22) Nishioka, N.; Yoshida, N. *Polym. J.* **1992**, *24*, 1009.
(23) Nishioka, N.; Yamaoka, M.; Haneda, H.; Kawakami, K.; Uno, M. *Macromolecules* **1993**, *26*, 4694.
(24) Nishioka, N.; Nakano, Y.; Hirota, T.; Fujiwara, N.; Uno, M. *J. Appl. Polym. Sci.* **1996**, *59*, 1203.
(25) Aoi, K.; Takasu, A.; Okada, M. *Polym. Prepr. Jpn.* **1995**, *44*, E780.
(26) Montaudo, G.; Puglisi, C. *Polym. Degrad. Stab.* **1991**, *33*, 229.
(27) van der Kaaden, A.; Boon, J. J.; de Leeuw, J. W.; de Lange, F.; Schuyl, P. J. W.; Schulten, H.-R.; Bahr, U. *Anal. Chem.* **1984**, *56*, 2160.
(28) Kobayashi, S.; Kaku, M.; Saegusa, T. *Macromolecules* **1988**, *21*, 334.

MA9702399