

Polymer/silicate Interaction in Nylon 6-Clay Hybrid Studied by Temperature Programmed Pyrolysis Techniques

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ABSTRACT: Nylon 6-clay hybrid (NCH) was characterized by temperature-programmed pyrolysis (TPPy) techniques such as TPPy-mass spectrometry and TPPy-gas chromatography mainly focusing on the interaction between nylon 6 molecule and the surface of silicate monolayers in the NCH samples, which leads to the superior properties of the hybrid nanomaterials. Pyrolysis profile of nylon 6 matrix in the NCH samples was gradually shifted to lower temperature region with increase in the clay content. The yields of main pyrolysis products such as ϵ -caprolactam from the NCH samples decreased with increase in the clay content, whereas those of the nitrile compounds significantly increased. These results suggested that the clay surface accelerate *cis*-elimination reaction of nylon 6 matrix in the NCH samples to form the nitrile compounds rather than intramolecular amide exchange to ϵ -caprolactam. Based on the changes in pyrolysis behaviors of nylon 6 matrix in the NCH samples, the interaction between positively charged NH proton of nylon 6 molecules and negatively charged clay surface was proposed which would stabilize the six-membered transition state during pyrolysis. [DOI 10.1295/polymj.38.171]

KEY WORDS Nylon 6-clay Hybrid / Polymer-silicate Interaction / Nanocomposite / Pyrolysis / Gas Chromatography / Mass Spectrometry /

In the past decade, much interest has been paid to polymer-layered silicate nanocomposite materials, because they frequently exhibit various unique properties which could not be manifested in the case of a constituent polymer alone.^{1–6} Nylon 6-clay hybrid (NCH) is the herald of the polymer-layered silicate nanocomposite materials, in which each silicate monolayer with *ca.* 1 nm thick is homogeneously dispersed in nylon 6 matrix.⁷ Because NCH has various excellent properties over pure nylon 6 such as high strength, high modulus, high distortion temperature, and low gas permeability, it has been utilized as industrial materials such as automotive parts and package films.^{8–10}

The interaction mechanisms between nylon 6 molecules and clay surface in NCH are of great interest to understand their unique properties. So far, the interaction between amino acid and clay mineral in intercalated compounds of montmorillonite with glycine as the model NCH was estimated using ¹⁵N cross polarization magic angle spinning (CP/MAS) nuclear magnetic resonance spectroscopy (NMR).⁹ In this study, it was suggested that the cationic terminal amino groups of nylon 6 molecules might interact strongly with negatively charged clay surface. The crystalline structures

of nylon 6 molecules in NCH, which have been often characterized by X-ray diffraction and electron microscopy,^{11,12} would also relate to the polymer-clay interaction. Although α -type crystalline is favored in pure nylon 6, the considerable formation of γ -type crystalline of nylon 6 has been observed in NCH by wide angle X-ray diffraction (WAXD) and transmission electron microscopy.¹³ The crystalline phase of polyamide in NCH has been also confirmed by Fourier transform infrared spectrometry (FTIR) measurements.¹⁴ The molecular level interaction between polymer chain and clay mineral in NCH, however, has not been fully clarified.

On the other hand, the thermal properties such as glass-transition temperature (T_g) and melting point (T_m) of polymer blend and/or hybrid systems, in which much dense interactions between the constituent polymers exist in molecular level, are often quite different from those estimated from the behaviors of the corresponding pure polymers. Thus thermal analysis techniques such as differential scanning calorimetry (DSC) have been frequently used for evaluating the miscibility of polymer blend systems. In addition, thermal decomposition of a polymer blend also often

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exhibits unique profiles, which has been frequently monitored by thermogravimetry (TG). Recently, thermal degradation behavior of nylon 6/clay nanocomposites was also discussed using TG coupled with FT IR.^{15,16}

Meanwhile we have demonstrated that the temperature programmed pyrolysis (TPPy) technique, that is a modern evolved gas analysis (EGA) equipped with highly specific and sensitive detectors such as a mass spectrometer (MS) and an atomic emission detector (AED), was successfully applied to the characterization of chitin-based polymer hybrids.^{17,18} In these studies, the observed evolution profiles of the characteristic products were interpreted in terms of the intermolecular interaction in the blend systems.

In this paper, the TPPy techniques were applied to the characterization of the NCH samples to investigate the interactions between nylon 6 molecules and clay surface in NCH. The pyrolysis product of the nylon 6 matrix in the NCH samples was on-line monitored as a function of temperature by a mass spectrometer (MS) directly connected with the pyrolysis device. In addition, the individual products formed during the TPPy process were characterized in detail by using TPPy-gas chromatography (GC) technique. By comparing the observed pyrolysis behavior of NCH with that of conventional nylon 6-clay composites (NCC), in which multi-layer structure of clay minerals was maintained in the nylon 6 matrix, the interaction between nylon 6 and clay surface in the NCH samples were discussed.

EXPERIMENTAL

Samples

Table I summarizes the NCH and NCC samples used in this study. ϵ -Caprolactam purchased from Wako Co. and montmorillonite "Kunipia F" supplied by Kunimine Ind. Co. were used as the raw materials for the NCH samples. The NCH samples were prepared according to the previous paper.⁶ At first, so-

dium ions in the montmorillonite were exchanged for ammonium ions of 12-aminododecanoic acid. Then, various contents of the organophilic montmorillonite (up to *ca.* 15 wt %) were mixed with ϵ -caprolactam monomer. The polymerizations were carried out at 250 °C for 6 h. It was confirmed by the transmission electron micrograph observation that clay silicate monolayers were dispersed in the nylon matrix in the prepared NCH samples.¹⁹ The resulting products were mechanically crashed and washed with water at 80 °C for 1 h to remove residual monomer and oligomers. To compare with NCH, the NCC samples were prepared by blending nylon 6 (UBE Ind. Co., $M_n = 15,000$) and the montmorillonite in a twin screw extruder (Japan Steel Works LTD. TEX30 α -45.5BW, L/D = 45.5). The final contents of montmorillonite in the NCH and NCC samples were listed in Table I along with the number average molecular weight (M_n) of the nylon 6 moiety. The clay contents were calculated from the residual weight after burning the samples. M_n of the nylon 6 moiety in NCH was determined by end group analysis of carboxylic acid through titration with a hot benzyl alcohol solution of NaOH. All the samples were cryo-milled into fine powder by a freezer mill (Spex 6750) at liquid nitrogen temperature (−196 °C) prior to TPPy measurements.

TPPy Measurements

The TPPy-MS system used in this study is basically the same as that described in our previous papers.^{17,18,20} In this system, a temperature-programmable microfurnace pyrolyzer (Frontier Lab, PY-2010D) attached to a GC (Hewlett Packard, HP-5890) injector at 300 °C was directly coupled with a quadrupole MS (JEOL, AM-II 150) *via* a deactivated stainless steel capillary (Frontier Lab, UADTM-5M, 0.25 mm i.d. \times 5 m long). About 0.2 mg of a sample was used for TPPy measurements, which should be small enough to achieve instantly thermodynamic equilibrium during programmed heating. A given sample placed in a platinum sample cup was heated in the pyrolyzer from 150 up to 600 °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 MS through the transfer capillary. The transfer capillary was maintained at 300 °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 10–500 amu with a scan rate of 0.3 s/scan.

In order to identify and quantify the individual evolved products, TPPy-GC measurement was also

Table I. NCH and NCC samples

Sample codes	Clay contents (wt %)	Number average molecular weight (M_n) of Nylon 6
NCH-A	1.7	15000
NCH-B	4.5	9000
NCH-C	8.4	5500
NCH-D	12.4	4000
NCC-A	1.3	15000
NCC-B	3.8	15000
NCC-C	7.4	15000
NCC-D	10.8	15000
Control Nylon 6		15000

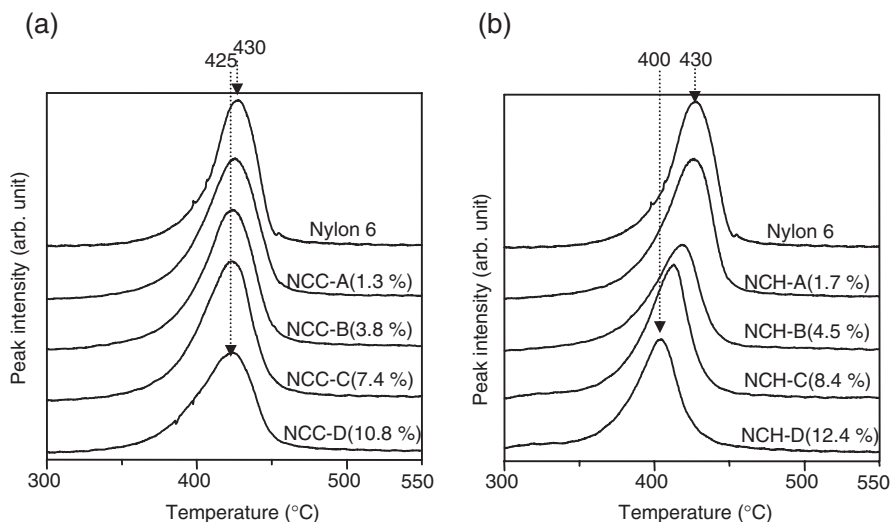


Figure 1. Evolution profiles of pyrolysis products from (a) NCC and (b) NCH samples observed by TPPy-MS in total ion current mode. Peak intensities are normalized by weight of nylon 6 matrix in the samples.

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⁺-5; 0.25 mm i.d. × 30 m long) coated with immobilized 5% diphenyl-95% dimethylpolysiloxane (0.25 μm film). During the programmed heating periods from 150 up to 600 °C for 45 min, the thermal decomposition products were trapped at the entrance part of the GC column held at −196 °C using a microjet cryotrap (Frontier Lab, MJT-1030E). In addition to mass spectrometer, a flame ionization detector (FID) and FTIR (Bourne Scientific Infrared Chromatography) were also used for the detection of the separated products for quantification and complementary identification, respectively. In the TPPy-GC/FTIR measurement, HP 6890 GC was used instead of HP 5890. After finishing the TPPy procedure, the column temperature was quickly raised to 50 °C and then heated up to 300 °C at a rate of 5 °C/min and held for 10 min. The other conditions were basically the same as those for the TPPy-MS measurement described above.

RESULTS AND DISCUSSION

TPPy-MS Measurement

Figure 1 shows the evolution profiles of the pyrolysis products from (a) NCC and (b) NCH samples with different clay contents together with control pure nylon 6 observed by TPPy-MS in a total ion current (TIC) mode. Here the peak intensities are normalized by the weight of nylon 6 matrix in the samples. The TIC curve of control nylon 6 shows apparently single-stage decomposition in the temperature range between *ca.* 350 and 460 °C with a peak top at around 430 °C. The evolution profiles of the NCC samples (Figure 1a) are almost equivalent to that of control

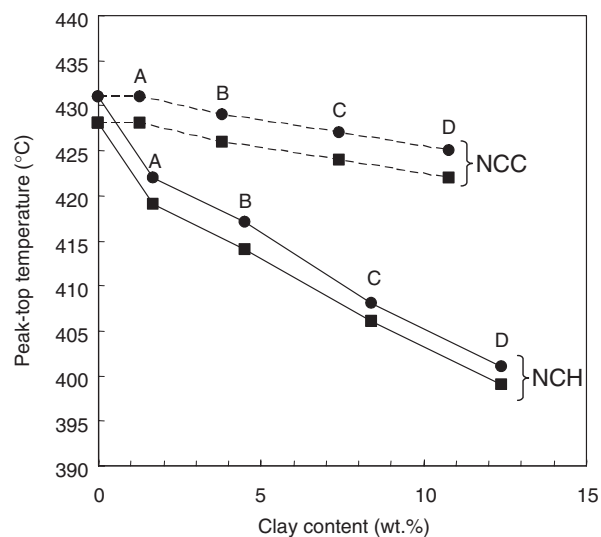


Figure 2. Relationship between clay content and peak-top temperatures observed by TPPy-MS in selected ion monitoring mode at m/z 96 (●) corresponding to fragment ions of nitrile compounds and m/z 113 (■) to parent ion of ϵ -caprolactam for NCH (straight line) and NCC (dotted line) samples.

nylon 6; the change in the peak-top decomposition temperature is quite small (*ca.* 5 °C) even for the highest clay content (NCC-D). On the other hand, those of the NCH samples (Figure 1b) clearly shift to lower temperature region with the increase in the clay content. This result might be caused by the introduction of the clay monolayers dispersed in nylon 6 matrix for NCH.

In order to study the thermal decomposition behavior of nylon 6 influenced by the clay in detail, the changes in the evolution temperature of some representative products of nylon 6 during TPPy were precisely examined using selected ion monitoring (SIM)

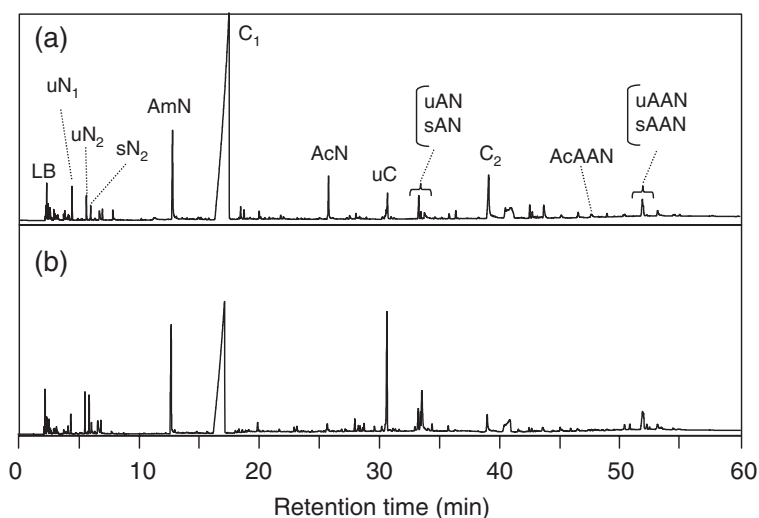


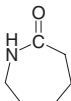
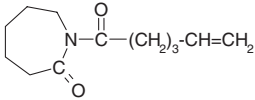
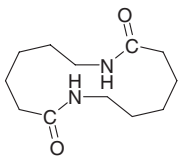
Figure 3. Pyrograms observed by TPPy-GC: (a) control pure nylon 6, (b) NCH-D (12.4 wt % clay). Peak assignments are listed in Table II and peak intensities are normalized by weight of nylon 6 matrix in the samples.

mode. Figure 2 shows the relationship between the peak-top temperatures of the SIM thermograms at m/z 113 and 96 observed for the NCH and NCC samples together with those for control nylon 6. Here, the ion observed at m/z 113 corresponds to molecular ion of ϵ -caprolactam, whereas that at m/z 96 to the characteristic fragment of nitrile compounds, respectively, both of which are known to be the major pyrolysis products of nylon 6.^{21–23} Although the average molecular weight of the nylon matrix in NCH-A is comparable to those of NCC-A and control nylon 6 ($M_n = 15000$), the peak-top decomposition temperatures for NCH-A are significantly lower than those for NCC-A and control nylon 6. Furthermore, as the clay content in the NCH samples increases up to 12.4 wt %, the peak-top temperatures of both compounds gradually lowered from *ca.* 430 °C to *ca.* 400 °C. In the case of NCC samples, however, the shift in the decomposition temperature are limited to only 5 °C even for the NCC sample with the higher clay content (up to 10.8 wt %). This fact indicates that pyrolysis reactions of nylon 6 are considerably influenced by the molecular-level interaction between nylon 6 matrix and clay surface rather than molecular weight of nylon 6 matrix.

TPPy-GC Measurement

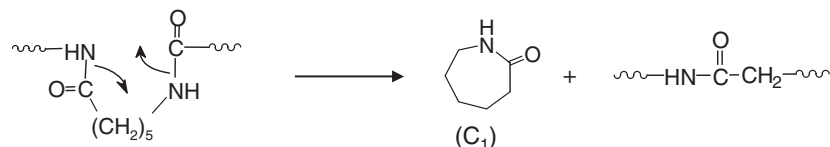
Figure 3 shows TPPy gas chromatograms of (a) control nylon 6 and (b) NCH-D (12.4 wt % clay). The thermal decomposition products of nylon 6 matrix during TPPy were identified by TPPy-GC/MS and TPPy-GC/FTIR measurements. The assigned products are listed in Table II. On the both pyrograms, a strong peak of ϵ -caprolactam (C_1) is commonly observed together with ϵ -caprolactam dimer (C_2), various nitrile compounds (peak symbols containing **N**),

Table II. Pyrolysis products of nylon 6 identified by TPPy-GC/MS

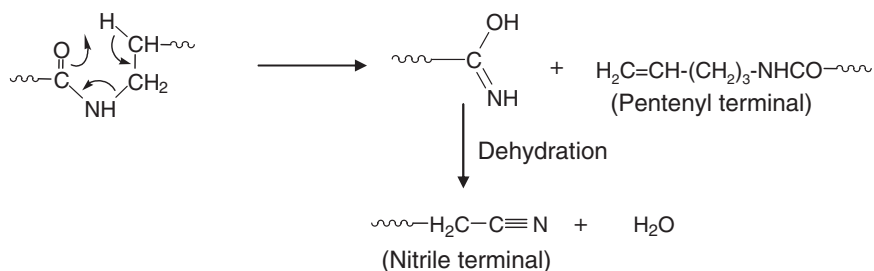
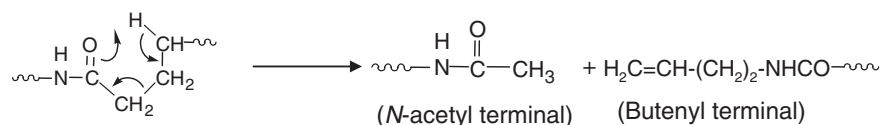
Peak ^a	Products
LB	low boiling point products such as propylene
uN ₁	CH ₂ =CH(CH ₂) ₂ -CN
uN ₂	CH ₂ =CH(CH ₂) ₃ -CN
sN ₂	CH ₃ (CH ₂) ₄ -CN
AmN	NC-(CH ₂) ₅ -NH ₂
C ₁	
AcN	CH ₃ -CONH-(CH ₂) ₅ -CN
uC	
uAN	CH ₂ =CH(CH ₂) ₃ -CONH-(CH ₂) ₅ -CN
sAN	CH ₃ -(CH ₂) ₄ -CONH-(CH ₂) ₅ -CN
C ₂	
AcAAN	CH ₃ -CONH-(CH ₂) ₅ -CONH-(CH ₂) ₅ -CN
uAAN	CH ₂ =CH(CH ₂) ₃ -CONH-(CH ₂) ₅ -CONH-(CH ₂) ₅ -CN
sAAN	CH ₃ (CH ₂) ₄ -CONH-(CH ₂) ₅ -CONH-(CH ₂) ₅ -CN

^aAbbreviations are the same as those in Figure 3. N: nitrile terminal, Am: amine terminal, A: amide linkage, Ac: *N*-acetyl terminal, C: caprolactam monomer, u: unsaturated hydrocarbon terminal, s: saturated hydrocarbon terminal.

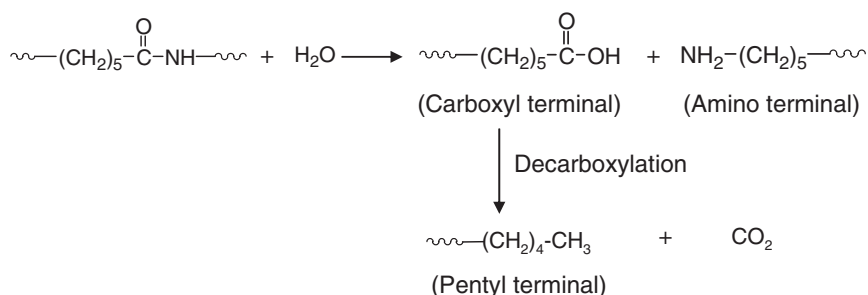
and a hybrid compound of ϵ -caprolactam (**C**) and an unsaturated (**u**) hydrocarbon terminal (**uC**). The fundamental pyrolysis mechanisms of nylon 6 have been already reported by using flash Py-GC at 500 °C²² and direct Py-MS in vacuum ion source.²⁴ However, the



Scheme 1.

(a) β -CH hydrogen transfer(b) γ -CH hydrogen transfer

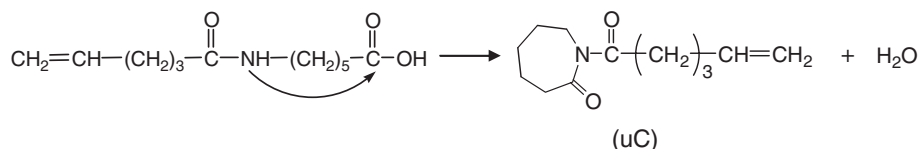
Scheme 2.



Scheme 3.

pyrolysis products of nylon 6 observed by TPPy-GC were somewhat different from those by flash pyrolysis in the previous reports. For example, the relative yields of 5-aminocapronitrile (**AmN**), 5-acetaminocapronitrile (**AcN**) and the hybrid compound (**uC**) were much more enhanced in the case of TPPy. This difference in the pyrolysis behavior should be mostly attributed to the slower heating rate for TPPy.²⁵ Scheme 1 shows the possible formation mechanism of ϵ -caprolactam (**C**₁), through intramolecular amide-exchange reaction.^{22,25} The cyclic dimer (**C**₂) should be produced in a similar manner. Another major pyrolysis pathway of polyamide is generally known to be *cis*-elimination reaction to cleavage polyamide chain.^{21,22} As shown in Scheme 2, two types of the transition states are possible for nylon 6; one is caused by β -CH proton transfer to form a pair of intermedi-

ates having amide and hexenyl termini (Scheme 2a) and the other is by γ -CH proton transfer to a pair of *N*-acetyl and butenyl termini (Scheme 2b). The amide terminus would be further dehydrated into a nitrile group under the given TPPy conditions. In addition, hydrolysis of the amide linkage to generate a pair of carboxyl and amino termini would be also possible as shown in Scheme 3. The intermediate having a carboxyl terminal could be further decomposed by decarboxylation to form a saturated hydrocarbon (pentyl) terminal. The formations of most of the observed products can be explained by either combination of the chain cleavages in Schemes 2 and 3. Moreover, as shown in Scheme 4, the hybrid compound of ϵ -caprolactam and a pentenyl terminal (**uC**) might be produced by the intramolecular cyclization of a carboxyl terminal moiety formed by hydrolysis (Scheme 3).



Scheme 4.

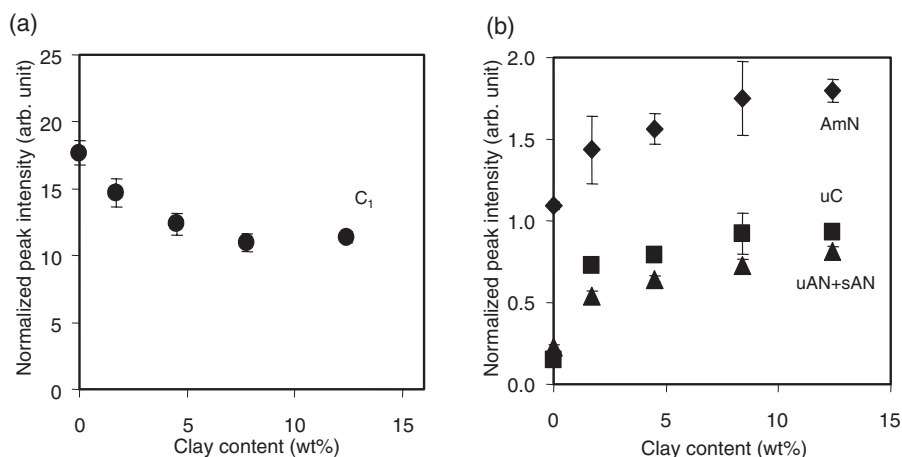


Figure 4. Changes in the yield of pyrolysis products of nylon 6 from NCH samples with clay content: (a) ϵ -caprolactam (C_1), (b) nitrile (AmN, uAN + sAN) and hybrid (uC) compounds.

Here, it is interesting to note that relative yields of several products are considerably different between the chromatograms of NCH and control pure nylon 6 as shown in Figure 3. The peak intensities of ϵ -caprolactam monomer (C_1) and dimer (C_2) and the products having *N*-acetyl group (AcN and AcAAN) from the NCH sample are obviously weaker than those from control nylon 6. On the other hand, the peak intensities of the nitrile compounds except for AcN and AcAAN and hybrid compound (uC) are significantly stronger for NCH.

Figure 4 shows the relationship between the clay content and the peak intensities of ϵ -caprolactam (C_1), some nitrile compounds without *N*-acetyl terminal (AmN, uAN + sAN), and the hybrid compound (uC) observed in TPPy gas chromatograms of control nylon 6 and the NCH samples. The yield of ϵ -caprolactam gradually decreases with increase in the clay content and the decrement for NCH-D is *ca.* 35% in comparison with the case of control nylon 6 (Figure 4a), while that of the nitrile and hybrid compounds considerably increase (Figure 4b). The decreased yields of ϵ -caprolactam during TPPy with increase in the clay content were also reported in a recent work about thermal decomposition of nylon 6-clay nanocomposites using TG/FTIR followed by GC-MS measurements of the evolved products.¹⁶ These observations are consistent with those observed by TPPy-MS measurements shown in Figure 2. The obtained results indicate that changes of the observed peak intensities

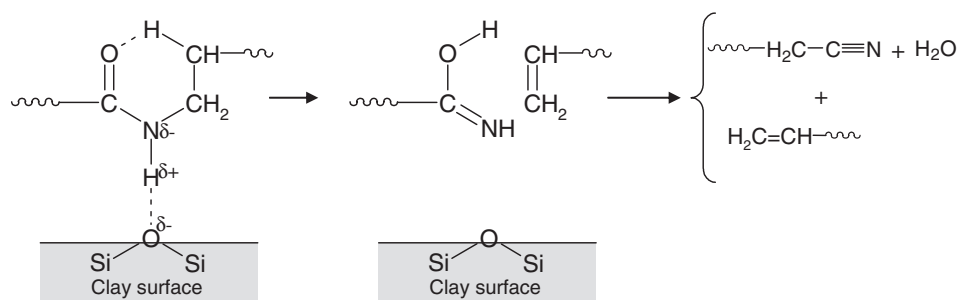
with the clay content in the NCH samples would reflect the difference in the segmental interactions between nylon 6 molecule and clay surface.

Possible Interaction between Nylon 6 and Clay Surface in NCH

The prominent influences of clay on the pyrolysis of nylon 6 matrix observed for the NCH samples can be summarized as follows: (1) lowering of pyrolysis temperature, (2) enhancement of the formation of the nitrile compounds, and (3) suppression of the formation of ϵ -caprolactam and *N*-acetyl products.

The lowering of pyrolysis temperature of nylon 6 matrix in the NCH samples suggests that clay surface act as catalyst for the pyrolysis of nylon 6 matrix. In the NCH samples, the surface area of clay interacting with nylon 6 molecules would be proportional to the clay content, because the clay monolayers are highly dispersed in the nylon 6 matrix.¹⁹ Therefore, the pyrolysis temperature is substantially decreased with the increase in the clay content. On the other hand, in the NCC samples, the effective surface area of the clay is limited even for the higher clay content since the silicate layers are condensed in the nylon 6 matrix. Hence, the pyrolysis temperature of nylon 6 matrix in the NCC samples is hardly changed.

The suppression of the formation of ϵ -caprolactam from the NCH samples and enhancement of that of various nitrile and hybrid compounds as shown in Figure 4 would also suggest that catalytic effect of



Scheme 5.

clay surface accelerating *cis*-elimination reaction rather than intramolecular amide exchange. As shown in Scheme 2, two types of *cis*-elimination reactions are possible, *i.e.*, β - and γ -CH proton transfer. The suppression of the formation of *N*-acetyl compounds such as AcN and AcAAN suggests that the catalytic effect on the clay surface promotes predominantly the β -CH proton transfer type *cis*-elimination reaction to form nitrile terminal. Therefore, the possible interaction catalyzing the *cis*-elimination reaction can be proposed as shown in Scheme 5. In this mechanism, the interaction between positively charged NH proton of nylon 6 molecules and negatively charged clay surface would stabilize the six-membered transition state and promote the *cis*-elimination reaction with β -CH transfer. As a result, the amounts of various nitrile compounds formed from nylon 6 matrix would increase in the presence of clay. At the same time, the water produced by dehydration of amide terminus into nitrile would enhance hydrolysis of amide linkages to form a pair of carboxyl and amino terminals (Scheme 3). Since the carboxyl terminals could be converted to pentyl ones and cyclic moieties in the hybrid compound, the increasing formation of amino compound (**AmN**), pentyl compounds (**sN2**, **sAN**, and **sAAN**) and hybrid compound (**uC**) with increase in the clay content (Figure 4b) also supports the proposed interaction between nylon 6 and the clay surface.

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