Special Review

Review

Nylon 6-clay Hybrid: From Invention to Practical Use

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■ABSTRACT‖ We have dealt with the history of the basic research of nylon 6-clay hybrid developed by Toyota Central R&D Labs., Inc. until it was put to practical use as an automotive material. By dividing the stage of research into five stages (exploratory basic research, goal-oriented basic research, applied research, practical research and industry-oriented research), and looked back on research and management at each stage.

■KEYWORDS‖ Nylon 6, Clay, Hybrid, Nanocomposite, Automobile, Research Stage

1. Introduction

The corporate path from basic research to practical technology in product development is challenging and long, particularly for products that serve as industrial materials. Scaling up from laboratory synthesis to volume production lengthens its course, which generally comprises the five main stages of exploratory basic research, goal-oriented basic research, applied research, practical research, and industry-oriented research, as shown in **Fig. 1**. In most cases, the effort ends abruptly at "Devil River" when it falls from the narrow bridge from goal-oriented basic research to applied research, or in "Death Valley" when it falls into the ravine between applied research and practical research, or in the "Darwinian Sea" between practical research and industry-oriented research when it loses in the struggle for survival against competing technologies.

Nylon 6-clay hybrid (NCH) is an industrial material and technology that has successfully negotiated the entire course from basic research, when my own participation began, to practical application. This is a review of its progress through the related stages as seen from the perspective of technological development and research management. In outline, it begins with a key discovery in exploratory basic research, proceeds through goal-oriented basic research leading to the basic patents on to applied research with patenting of the applied technology, and then to practical research involving the work of many workers for materials optimization, establishment of volume production technology, and application to products. The industry-orientated stage included conference presentations and journal papers, to gain widespread recognition and establish the technology as the de facto standard.

2. Exploratory Basic Research

The discovery that ultimately led to the nanoscale hybrid of clay and nylon 6 was made by a specialist in ceramics, a field seldom associated with nylon and other synthetic polymers.

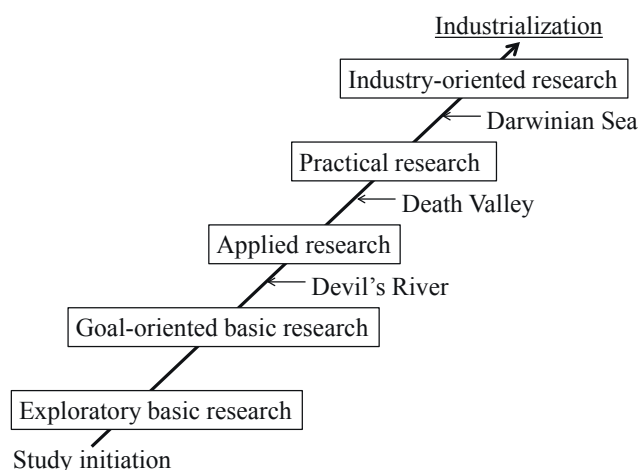Many laboratories have worked to improve the

Fig. 1 Research stages.

mechanical and thermal properties of polymers by adding fillers, and in some cases have found that the polymer properties can be substantially improved by decreasing the filler particle size and increasing the interface area between the filler and polymers. The methods available for this purpose, however, have generally been expensive, resulting in a low cost-performance and limited range of applications. The development of NCH required uniformly dispersing layers of nanometer-size filler particles in nylon 6 to obtain substantially heightened properties, at a reasonable cost.

The research on NCH originated in the work of an expert in ceramics rather than polymers, who noted a peculiar "rocky seashore smell" while extracting fossils from sedimentary material (mineral nodules). He inferred that the smell came from ancient polyamino acids (polypeptides) that had been locked into the sediment and preserved there for centuries. Polyamino acids are fragile organic compounds, and he became deeply interested in their evident stability in sediment. He thought this might provide a basis for technology that could mitigate future food crises, and together he led us to begin an investigation into the behavior of organic compounds between clay mineral layers, a structure that is closely related to that of sediments.

We decided to begin the investigation with sodium montmorillonite, a clay mineral that readily disperses in water. Its structure, as shown in **Fig. 2**, consists of 1-nm-thick silicate layers with sodium ions between them. When it is immersed in water, the sodium ions can readily be replaced by organic ammonium ions. If they are replaced by long-chain alkyl ammonium ions, for example, the result is a hydrophobic organified montmorillonite that separates from the water. In contrast, if the organified montmorillonite is placed in an organic solvent such a toluene, it absorbs the solvent in the interlayer spaces, swells, and disperses throughout the solvent.

The concept of swelling in this organified montmorillonite on exposure to organic solvents led us to investigate the possibility of similar swelling by organified montmorillonite in synthetic polymers. We mixed various polymers with organified montmorillonite above the polymer melting point, but could not find any polymer-organified montmorillonite system that exhibited swelling. The effort could have ended there, but we decided to investigate the possibility of inserting monomers into the interlayer spaces and polymerizing them there instead of simply inserting polymers, thus shifting the focus from polymer insertion to monomer insertion. This shift in focus was the initial key to ultimate success. It also led directly to an organizational integration of our research on inorganic and polymeric materials at a single laboratory, with favorable effects on the research operation.
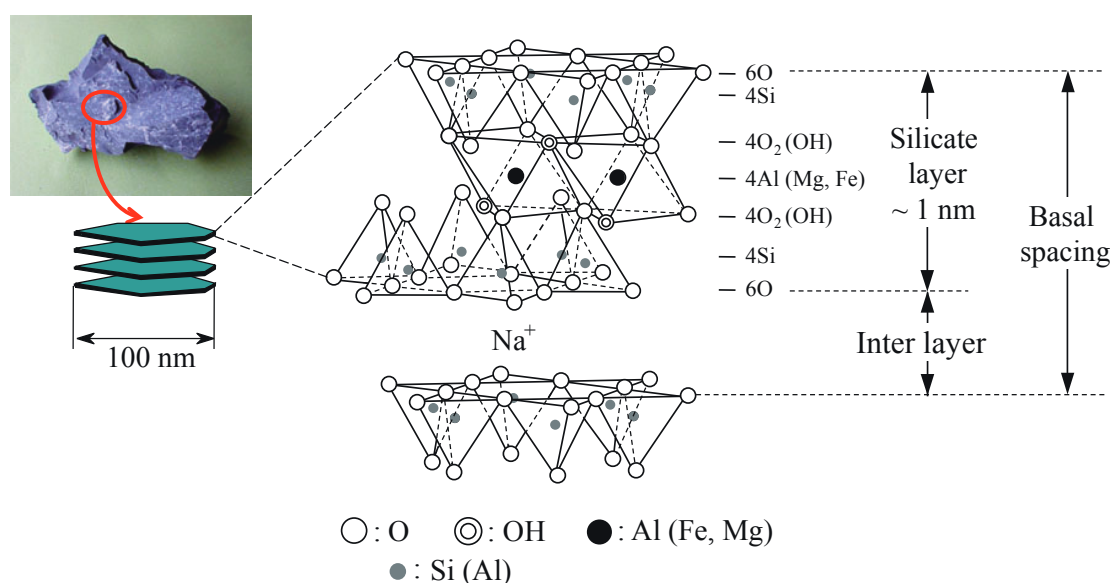

Fig. 2　Structure of montmorillonite.

3. Goal-oriented Basic Research

3. 1 Investigation on Clay Mineral (Montmorillonite) Organification

We chose nylon 6 monomer as the candidate for polymerization in the interlayer spaces of montmorillonite, and thus chose montmorillonite-nylon 6 composite as the target material. The nylon polymer (polyamide) was chosen primarily because of its similarity to polyamino acids (polypeptides) in chemical structure.

We presumed that the organifier (the organification agent) would have to satisfy three key conditions for efficient insertion and polymerization of the nylon 6 monomer:

(1) An ammonium ion ($-NH_3^+$) at one end, for ionic bonding to the silicate layer.
(2) A carboxyl group (-COOH) at the other end, as the starting point for monomer (ε-caprolactam) polymerization.
(3) A chain length of n carbons, for geometric compatibility with the monomer.

The first two conditions dictated the use of a compound with a basic structure of $NH_2(CH_2)_{n-1}COOH$. The value of n in the third condition was determined experimentally using glycine ($n = 2$), β alanine ($n = 3$), and other aminocarboxylic acids (up to $n = 18$) with their sodium ions replaced by ammonium ions, to obtain montmorillonite organification. We mixed the resulting organified montmorillonites with ε-caprolactam in the weight ratio 1:4, melted the mixture at 100°C, and investigated the X-ray diffraction (XRD) patterns for each resulting mixture at room temperature and at 100°C. **Fig. 3** shows the interlayer spacing for the organized montmorillonites as determined from the XRD peaks. The results showed that montmorillonites organified with amino acids having $n = 11$ or higher exhibited expansion of the interlayer spacing on melting of the ε-caprolactam, and thus swelled substantially, and on this basis we decided to use 12-aminododecanoic acid as the organifier for the interlayer synthesis of nylon 6.[1]

The procedure used for montmorillonite organification essentially consisted of first uniformly dispersing 300 g of sodium montmorillonite (cationic exchange capacity, 119 mmol/100 g) in 9 L of deionized water at 80°C in a homomixer, dissolving 154 g of 12-aminododecanoic acid and 72 g of

concentrated hydrochloric acid in 2 L of deionized water at 80°C, and then adding the aqueous solution of 12-aminodoceanoic acid and hydrochloric acid to the montmorillonite dispersion and stirring for 5 min. The resulting mixed dispersion was filtered to obtain solid aggregates, which were washed twice in water at 80°C. The aggregates were then freeze dried to obtain the organized montmorillonite (referred to as "12-montmorillonite") as a white power.

3. 2 Nylon 6 Synthesis in Silicate Interlayers

The procedure for synthesis of nylon 6 in the interlayer spaces of the 12-montmorillonite was essentially as follows.

We mixed ε-caprolactam and 12-montmorillonite in a mortar, vacuum dried and deoxygenated the resulting mixture in a 500-ml glass reaction vessel, and sealed the vessel. We then polymerized the ε-caprolactam by heating the reaction vessel at 120°C for 12 h followed by 250°C for 48 h. The 12-montmorillonite addition in the initial mixture was varied from 15 to 50 wt%. On polymerization completion, the resulting mixture was removed from the reaction vessel and pulverized in a mill grinder. The pulverized sample was then washed in water at 80°C to remove residual monomers and low-molecular-weight polymers, and then vacuum dried or 12 h at 80°C to obtain NCH. The quantity of 12-montmorillonite addition in weight percent is denoted by "α" in the term NCHα, and NCH samples containing 15, 30, and 50 wt% 12-montmorillonite are thus designated NCH15, NCH30, and NCH50,
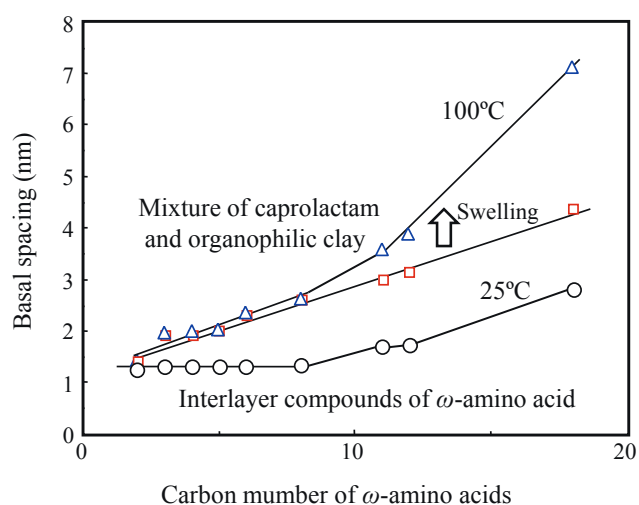

Fig. 3 Swelling behavior of organized clay by caprolactam.

respectively.[2]

As shown in **Fig. 4**, the XRD patterns for these NCHs indicated that the interlayer distance increased with decreasing montmorillonite content, thus indicating that ε-caprolactam synthesis occurred only in the interlayer spaces.

To investigate the state of montmorillonite dispersion, we press molded NCH sheets and observed their slices using transmission electron microscopy (TEM). As shown in **Fig. 5,** the images confirmed that montmorillonite silicate layers geometrically resembling nanoscale filaments were cleanly separated and dispersed in the nylon 6. When we exposed the slice surfaces to oxygen plasma, the nylon 6 was etched away and the silica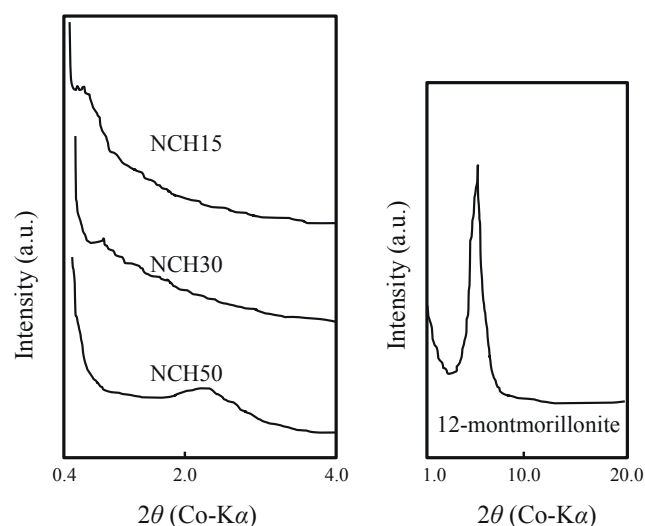te layers came into clear relief, as shown in **Fig. 6**, thus providing a three-dimensional view of their dispersion state and the first clear confirmation of swelling of montmorillonite induced by the polymer.[3] Viscoelastic measurements on NCHs showed, moreover, that they had a far higher elastic modulus than nylon 6 alone. In summary, the results showed that the montmorillonite was dispersed on a nanometer scale and exhibited increased interfacial contact, resulting in substantially higher strength.

From an operational perspective, the key to the success of this stage was the combination of researchers in both polymer synthesis and in polymer material properties, working together to advance the NCH research project.

It was during this stage that the basic patents[4] on the core technology for production were formulated. This opened the way for the next stage, which centered on research on volume production methods and product applications, which would require lowering the viscosity of the NCH melt and enabling injection molding.

4. Applied Research

4. 1　Moldability and Physical Properties

The flowability of 12-montmorillonite with 10 wt% or more added NCH was sufficient for press molding to fabricate test samples, but not for injection molding. We therefore reduced the 12-montmorillonite addition to 2, 5, and 8 wt%, to obtain NCHs which we designated NCH2, NCH5, and NCH8, respectively.

For comparison, we also kneaded melts composed

Fig. 4　X-ray diffraction patterns of NCH15, 30, 50 and 12-montmorillonite.

Fig. 5　Transmission electron micrograph of a section of NCH (clay content: 5 wt%).
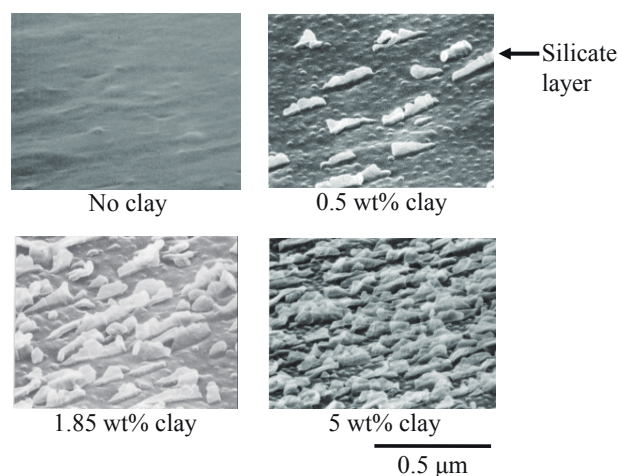

Fig. 6　Scanning electron micrograph of NCH film after oxygen plasma treatment.

of sodium montmorillonite (non-organified) and nylon 6 at 250°C on a twin-screw extruder. The resulting versions were designated NCC (nylon 6-clay composite), to distinguish them from NCH.

The NCH2, NCH5, and NCH8 melts exhibited low viscosity and excellent flow properties, and we found that injection molding was possible for NCHs made with 8 wt% or less montmorillonite addition. We injection-molded test pieces from these NCHs for tensile, bending, and impact testing and heat distortion temperature measurements under ASTM and JIS standards. As shown in **Table 1**, the test results verified the marked superiority of NCH over nylon 6 alone in both mechanical and thermal properties.[5]

4. 2 Other Properties – Gas and Water-vapor Permeability

In addition to the superiority of NCH over nylon 6 in strength, elastic modulus, heat distortion temperature, and other mechanical properties, we also found that the silicate monolayers in the nylon 6 effectively reduced gas penetration, resulting in a higher gas barrier than that for nylon 6 alone. **Table 2** shows the measured hydrogen and water vapor permeability of extrusion molded films 60 μm in thickness made from nylon 6 alone and from NCH (montmorillonite content 1.85 wt%). As indicated by this table, the NCH film gas barrier characteristics were found to be better regardless of the gas type. This is attributable to the circuitous path that must be followed by the gas in order to pass around the silicate layers.

The permeation coefficient for a given gas may be explained using a geometrical model of the dispersed silicate layers and the passage of the gas molecules within the NCH film, in which the silicate particles lie approximately parallel to the film surface. As indicated by Nielsen, the diffusion coefficient D for a liquid or gas in a composite material containing plate-like particles parallel to its surface can be calculated as

$$D = D_0 / \{1 + (L / 2d) \, V\}, \qquad (1)$$

where D_0 is the diffusion coefficient in the matrix itself,

Table 1   Properties of NCH compared to NCC and Nylon 6.

Specimen	Montmorillonite (wt%)	Tensile strength (MPa)	Tensile modulus (GPa)	Heat distortion temperature (ºC at 18.5 kg/cm²)
NCH2	1.9	76.4	1.43	118
NCH5	4.7	97.2	1.87	152
NCH8	7.1	93.6	2.11	153
NCC5	5.0	61.0	1.00	89
Nylon 6	0	68.6	1.11	65

Table 2   Permeability properties of NCH and Nylon 6.

Permeability	NCH (montmorillonite 0.74 vol%)	Nylon 6
Permeability of hydrogen $\times 10^{-11}$/cm³(STP)·cm·cm⁻²·sec⁻¹·cmHg⁻¹	1.79	2.57
Permeability of water vapor $\times 10^{-10}$/g·cm·cm⁻²·sec⁻¹·cmHg⁻¹	1.78	2.83

L is the length of the plate-like particles on one side, d is their thickness, and V is the their volume fraction in the composite material.

This equation yields $D/D_0 = 0.73$, where L is 100 nm, d is 1 nm, and V is 0.0074, which is close to the value of 0.63 obtained from our experiments on NCH permeation by hydrogen gas, and also matches the value found in the experiments on NCH permeation by water vapor. This clearly indicates that the effectiveness of the NCH gas barrier is indeed attributable to the geometrical "detour effect" imposed on gases by the montmorillonite silica layers.[6]

4. 3 Improvement of NCH Production Method

With the method of NCH synthesis described in Sec. 3, it took two days to obtain the NCH. We therefore investigated the possibility of alternative methods that would enable faster, simpler NCH synthesis.

4. 3. 1 One-pot NCH Production

We designed and investigated a process of ε-caprolactam addition to non-organified montmorillonite and its polymerization in the same vessel, which we call the "one-pot" method of NCH production, and found that NCH can be readily produced by mixing sodium montmorillonite, ε-caprolactam, and phosphoric acid in a single reaction vessel to polymerize the ε-caprolactam, and that the resulting NCH is very nearly the same as that obtained with the method of polymerization described in Sec. 3, in terms of both silicate layer dispersion and mechanical properties. The one-pot method was thus successful, and effectively shortened the time required for NCH production.[7]

4. 3. 2 Dry Production Process

We also developed a process which eliminated the polymerization step by directly kneading nylon 6 and organified montmorillonite in a twin-screw extruder. The use of a single-screw extruder resulted in insufficient dispersion of the silicate layers in the nylon 6, but we found that effective dispersion was obtained by mixing the two in the twin-screw extruder. We call this the "dry production process". Experiments on this type of process and the resulting

mechanical properties have also been reported by the Chinese Academy of Sciences[8] and by the University of Texas.[9]

4. 3. 3 Wet Production Process

A substantial part of the overall cost of NCH production by the method described in Sec. 3 is the cost of synthesizing and using organified montmorillonite obtained with ammonium ions. To eliminate the need for organified montmorillonite and the attendant cost, we designed and investigated a process in which a slurry consisting of sodium montmorillonite silicate layers uniformly dispersed in water is pumped into a twin-screw extruder, where it is mixed and kneaded with the nylon 6 melt, followed by removal of the slurry water by evaporation under reduced pressure, as shown schematically in **Fig. 7**(a). This method was also found to yield NCH with the silicate layers uniformly dispersed in the nylon 6 matrix while eliminating both the need for organified montmorillonite and the need for organification, and is therefore deemed a low-cost method of NCH production. As shown together with the mechanical properties in **Table 3**, the heat distortion temperature for this material is somewhat lower than that for NCH obtained by the method described in Sec. 3, which is attributable to the absence of ionic bonds between the silicate layers and nylon 6.[10]

4. 4 NCH Synthesis Using Other Clays

We also synthesized nylon 6 clay hybrids with synthetic mica, saponite, and hectorite instead of the montmorillonite clay mineral, and refer to the resulting nanocomposites as NCHM, NCHP, and NCHH, respectively.

All three of these, like NCH, were found to contain uniformly dispersed molecular-level silicate layers of 1 nm thickness, but the widths varied with the clay mineral. As shown by TEM imaging, the layer width for the synthetic mica was 100 nm, which was the same as that for montmorillonite, but those for saponite and hectorite were both 50 nm.

Table 4 shows the mechanical properties of these nanocomposites and NCH. At both 23 and 120°C, their tensile strengths were NCH (montmorillonite) > NCHM (synthetic mica) > NCHP (saponite) ≥ NCHH (hectorite), and their heat distortion temperatures

were NCH > NCHM > NCHP > NCHH. In summary, the results showed that clay size and ion-exchange capacity significantly affect the nanocomposite properties.[11]

The pace of research in this stage was accelerated by the addition of materials science researchers, and the range of measurements was widened from mechanical properties to thermal, optical, and gas permeation properties, all of which would be related to expanding the range of applications. We also began closely considering the requirements for proceeding from laboratory-scale synthesis toward practical production, which facilitated a transition to the next stage of research.

5. Practical Research

5. 1 Research on NCH Volume Production

Research on low-cost volume production of NCH was performed jointly with Ube Industries, Ltd., a leading nylon 6 manufacturer, and with the participation of Toyota Motor Corporation, a major materials user, for early identification of applications for the NCH product as a material for automotive and other components. The research was thus a joint project, called the "TTU (Toyota Motor-Toyota CRDL-UBE Industries) Project" in our company. Key subjects of investigation included montmorillonite quantity, nylon 6 molecular weight, optimum ε-caprolactam

(a) Na-montmorillonite + Water
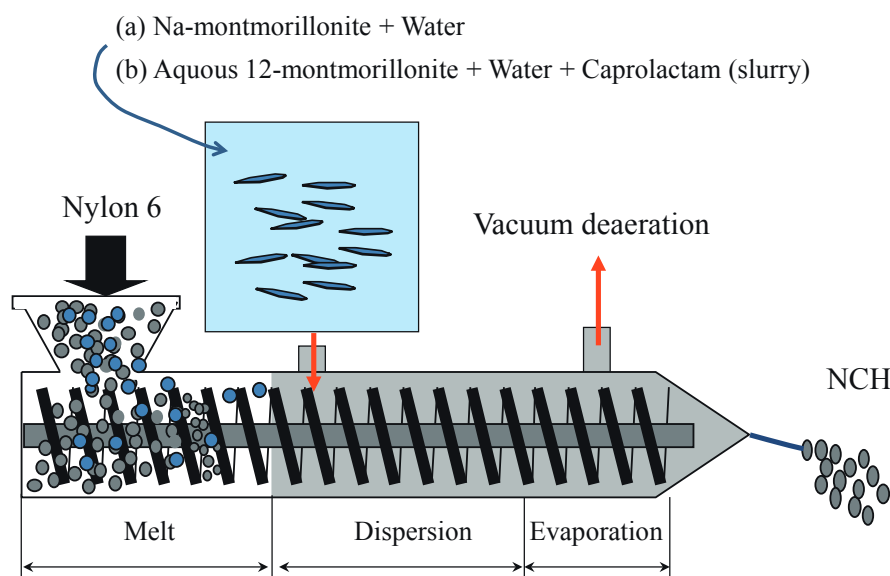(b) Aqueous 12-montmorillonite + Water + Caprolactam (slurry)

Fig. 7 Schematic figures depicting the compounding process.
(a) Wet production process, (b) clay slurry compounding process.

Table 3 Properties of NCH produced by clay slurry compounding process.

Specimen	Clay content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Heat distortion temperature (℃ at 18.5 kg/cm^2)
Nylon 6	0	69	1.10	75
Synthesized NCH	1.9	76	1.43	118
Clay slurry compounding NCH	1.6	82	1.38	102

polymerization conditions (e.g., temperature and time), additives, and cost reduction. All of these investigations were completed and the material in product form was obtained after two years.

Practical low-cost production of NCH was developed by Ube Industries. It includes a new process for montmorillonite dispersal in nylon 6, in which an aqueous dispersion of sodium montmorillonite is organized by 12-aminododecanoic acid and a montmorillonite swelling agent is added to form a slurry, which is then injected into a twin-screw extruder and kneaded there with nylon 6 to obtain the NCH. The NCH production process with this slurry is shown schematically in Fig. 7 (b), and is essentially as follows.[12]

In 2.1 L of water, 100 g of montmorillonite is dispersed and 28.1 g of 12-aminododecanoic acid and 12 ml of concentrated hydrochloric acid are added, followed by stirring for 1 h at 80ºC. The resulting mixture is filtered on a Buchner funnel and washed well to obtain a water-containing composite ("aqueous 12-montmorillonite") with a solid content of 88 wt%. Water and ε-caprolactam are then added and mixed in a vessel to obtain a slurry, which is injected into a twin-screw extruder with a screw diameter of 30 mm, where it is kneaded into the nylon 6 melt. The strands of kneaded material discharged from the extruder nozzle are water cooled and cut into pellets, which are immersed in hot water to remove the ε-caprolactam (which acts as an aqueous 12-montmorillonite

dispersant) and then vacuum dried. It has been verified that the resulting NCH has exactly the same state of silicate layer dispersion and mechanical properties as NCH obtained by polymerization of ε-caprolactam in silicate layer interspaces as described in Sec. 3.

5. 2 Automotive-part Applications

As the technology for volume production of NCH emerged, we began investigating prospective applications in the field of actual automotive parts. Toyota Motor Corporation looked for parts that would benefit from the use of NCH, and produced prototypes. One example was a timing belt cover conventionally produced from nylon 6 containing 30 wt% glass fiber (GF). It was found that a cover made from NCH met all mechanical and thermal requirements (**Fig. 8**) and also reduced the cover weight to 160 g from the 210-g weight of the GF-reinforced cover by eliminating the high molecular weight of the GF. It also improved the appearance. The GF reinforcement in the conventional cover resulted in an irregular cover surface and a poor coated appearance. The uniformly flat surface of the NCH cover, in contrast, contributed to an excellent coated appearance. The good external appearance of the belt cover proved to be a new, previously unavailable product feature.

The excellent gas barrier properties of NCH also led to its adoption in food wrapping films. It meets the gas-barrier requirements for such films in a broad

Table 4   Properties of NCH synthesized using different type of clay.

Properties		NCH	NCHM	NCHP	NCHH	Nylon 6
Clay		Montmorillonite	Mica	Saponite	Hectorite	None
Tensile strength/MPa	23ºC	97.2	93.1	84.7	89.5	68.6
	120ºC	32.3	30.2	29.0	26.4	26.6
Elongation/%	23ºC	7.3	7.2	>100	>100	>100
Tensile modulus/GPa	23ºC	1.87	2.02	1.59	1.65	1.11
	120ºC	0.61	0.52	0.29	0.29	0.19
Heat distortion temperature/ºC		152	145	107	93	65
Heat of fusion/ J/g		61.1	57.2	51.5	48.4	70.9
Heat of fusion/ J/nylon 6 1g		63.6	59.6	53.4	50.4	70.9

range of temperatures, as shown in **Fig. 9**, as a result of the tortuous path imposed on gases as a physical effect of the silicate layers. This led to its adoption in other products, including fuel tanks, fuel hoses, and plastic bottles for carbonated beverages.

In the course of this practical research stage, many patent applications were filed for parts and application products made with NCH and NCH polymer alloys.[13]

One key to the success of this stage was the participation from the outset of Toyota Motor Corporation as a potential user, and its implementation of cost-conscious materials synthesis and performance-focused parts evaluation methods, and by Ube as a world leader in nylon 6 production and expertise. This led to completion of the practical research stage in a very short period of two years. The three companies met once a month to discuss their results, refine operational management, and chart the course for early problem resolution and task accomplishment. Another key factor in this stage was the addition of specialists in corporate intellectual property who formulated the patent map and worked to obtain strong, valuable patents, thereby facilitating the progress of next stage of research.

6. Industrialization Research

As a material enters general use in an expanding range of composite and product applications, it is accompanied by rising production volumes and falling production costs, thereby reducing product price. To expand the range of NCH use and promote its adoption as a regular polymeric material, we performed activities directed well beyond the Toyota Group, including publication of technical papers, presentations to academic and industrial conferences, and extensive patent licensing. We submitted our first papers on NCH two years after commencement of its first practical application, and the first three were published in 1993.[1,2,5] With the cooperation of our intellectual property department, we began licensing related patents to companies in Japan and abroad, and developed an organization for marketing and sales of NCH as a regular polymer material.

Research was focused on extension of the clay hybrid technology developed for nylon 6 to other resins, and led to new technologies for effective utilization of the properties of polyimide,[14] polystyrene,[15] phenol resin,[16] polyolefin (polypropylene[17,18] and polyethylene[19]), rubber (EPR,[20] EPDM,[21] IIR[22]), SEBS,[23] and polycarbonate[24], the synthesis of their clay hybrids, and systematic production of these polymer-clay hybrids. For this work, we were honored to receive the 2008 SPSJ (Society for Polymer Science, Japan) Award for Outstanding Achievement. All of these research activities at Toyota Central R&D Labs., Inc. had a major worldwide impact, spurring research on polymer-clay hybrids in many countries, and citations of our published papers now number over a thousand.

For corporate researchers, patent writing and advancement of practical use constitute major achievements, and it has not been possible in many cases to compose papers summarizing this work for publication in scientific and industrial journals. Corporations are generally sensitive to the risk of

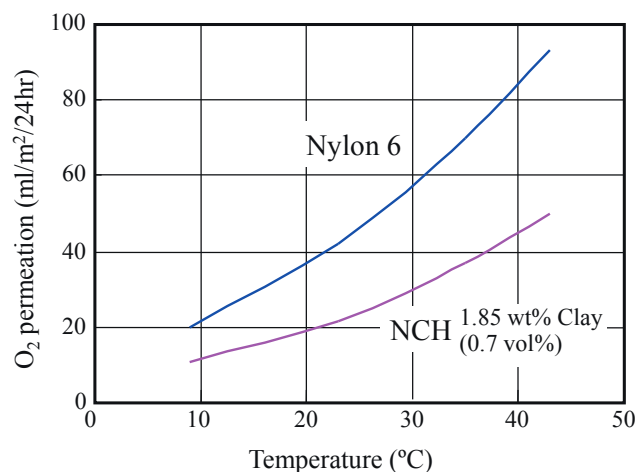**Fig. 8**　Timing belt cover produced by NCH.

Fig. 9　Gas barrier properties of NCH.

divulging hard-won, valuable know-how, and do not necessarily favor public disclosure of research in journals. For NCH, papers could not be written for publication until two years after its first practical use, and even then this mode of disclosure was possible only because of the strong relationship of trust among those who were responsible for research management at the companies involved.

The key to the success of the research in this stage for extension and diversification of the clay hybrid technology in an expanding range of industries may well have been the intense pursuit of its application to materials other than nylon 6.

Acknowledgement

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