



## Special Review

Review

# Nanocomposites Based on Organic and Inorganic Materials and Their Unique Properties and Functions

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■**ABSTRACT**|| Nylon 6-clay hybrids created by Toyota Central R&D Labs., Inc. (Toyota CRDL) ahead of the world exhibit superior properties and unique functions such as higher elastic modulus, higher heat distortion temperature, better barrier properties and flame retardancy by the dispersion of small amounts of nanosized clay platelets. In this review, the history of polymer nanocomposites will be briefly summarized. Next, we review not only the research results of Toyota CRDL on polymer-clay nanocomposites, but also those achieved by researchers all over the world to provide an overview of their properties, functions, specificities, and mechanisms to understand the essence of nanocomposites. In the second half, several topics of highly functional nanocomposites researched at Toyota CRDL to cope with important issues will be examined. Through these reviews, the future outlook for nanocomposites will be discussed in terms of maximization of the nano-effect, multifunctionality, and systematization of the knowledge base.

■**KEYWORDS**|| Polymer, Clay, Carbon Nanotube, Boron Nitride, Nanocomposite, Nano-effect, Functional Material

## 1. Introduction

A polymer-based composite is a material in which fillers such as fibers and particles are dispersed in a polymer matrix. Composites can exhibit new properties and functions that cannot be realized by the polymer alone. For example, carbon fiber reinforced plastics (CFRPs), in which a high strength and high rigidity carbon fiber and resin are compounded, exhibit excellent specific strength and specific rigidity. CFRPs have been put into practical application in aircrafts, automobiles, blades for wind power generation, and more by exploiting their lightweight properties. In addition to a large variety of polymer types in the matrix, polymer-based composites are also diverse according to the composition, shape (fibrous, particulate, plate-like), size, and mechanical properties of the filler, whereby various properties and functions are achieved, such as reinforcement, conductivity, water-impermeability, and antimicrobial properties.

Most polymer-based composites until the 1990s were macrocomposites with filler sizes of several tens of micrometers or larger. What kind of specific properties and functions can be expected for nanocomposites in which the filler sizes are reduced to the nanometer range? Are there any so-called nano-effects of such

nanocomposites? In the first half of this review, the history of nanocomposites will be briefly summarized. Next, we review not only the research results of Toyota Central R&D Labs., Inc. (Toyota CRDL) on nylon 6-clay hybrids (NCHs) and polymer-clay nanocomposites (PCNs), but also the important research results achieved by researchers all over the world, to provide an overview of their properties, functions, specificities, and mechanisms to understand the essence of nanocomposites. In the second half, several highly functional nanocomposites researched at Toyota CRDL to cope with important issues will be briefly introduced. Through these reviews, the future outlook of nanocomposites will also be discussed.

## 2. History of Nanocomposites

To begin with, many organisms currently utilize nanocomposites.<sup>(1,2)</sup> For example, shells are natural high-strength organic-inorganic nanocomposites comprised of a laminate structure of hard calcium carbonates and polymers such as soft proteins, which exhibit both strength and toughness that cannot be attained by the individual components. Bones are also considered a type of nanocomposite. Organisms have formed nanocomposites in individuals for the survival

of species since ancient times.

In industry, carbon black, which is a type of nanomaterial, was found to serve as a reinforcing filler for rubbers in 1904, and has since been used for tires and various rubber products.<sup>(3)</sup> In the late 1970s, Takayanagi et al. proposed the concept of molecular composites,<sup>(4)</sup> where the aim was to establish a strengthening principle by replacement of a macrofiller with one wholly aromatic polyamide molecular chain, which is a rigid polymer. In a molecular composite, (1) the aspect ratio ( $L/D$ :  $L$  and  $D$  represent the length and diameter of the reinforcing filler) of the filler is easily increased to thereby enhance both the strength and the elastic modulus of the molecular composite, and (2) the strength of the molecular filler corresponds to the theoretical strength due to the covalent bonds of the main chain, unlike a macrofiller, which typically contains defects that cause a considerable lowering of strength with respect to the theoretical strength. Therefore, it was predicted that molecular composites would be ideal composites. Molecular composites composed of wholly aromatic polyamide as a filler and a soft aliphatic polyamide as a matrix exhibited an excellent reinforcement effect, although the rigid polymer chains were dispersed as aggregated nanofibers.<sup>(5)</sup>

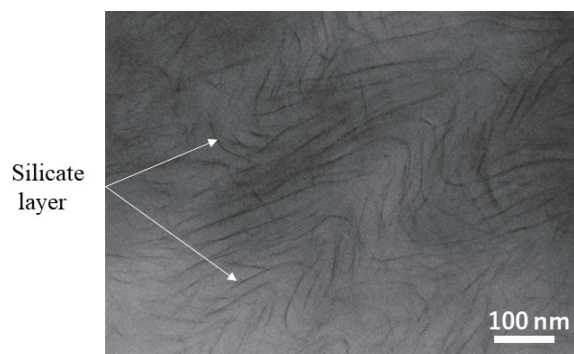
The usefulness of polymer-based nanocomposites was clearly recognized and attracted attention around the world with nylon 6-clay hybrid (NCH), invented by Toyota CRDL in the 1980s, and put into practical use with Toyota Motor Corporation and Ube Industries, Ltd. in 1990 as an engine timing belt cover for automobiles (**Fig. 1**).<sup>(6-27)</sup> NCH is a nanocomposite in which aluminosilicate layers (sizes: 1 nm thick, ca. 100 nm wide) of the clay are uniformly dispersed as a rigid filler in a nylon 6 matrix, as shown in **Fig. 2**. The nylon 6 molecular chains are ionically bonded through their terminal ammonium groups to the negatively charged aluminosilicate layers. NCHs containing only a few weight percent of the clay exhibit excellent properties, such as high rigidity and high heat distortion temperature, when compared with nylon 6, while maintaining moldability and surface quality equivalent to nylon 6. They also provide excellent functions such as improved impermeability to small molecules such as oxygen and water, and flame retardancy. The range of their application has been expanded to fields such as food packaging films and more.

Subsequently, Toyota CRDL continued to research PCNs consisting of not only nylon 6 but also a variety of matrix resins.<sup>(28-47)</sup> In many PCNs, the problem to be solved was how to disperse the clay in the matrix resins. In addition, along with the diversification of the required functions, research and development was conducted on nanocomposites combined with functional nanofillers, such as carbon nanotubes (CNTs) with both electrical and thermal conduction properties, or with the thermally conductive but insulating hexagonal boron nitride (h-BN).<sup>(48-55)</sup>

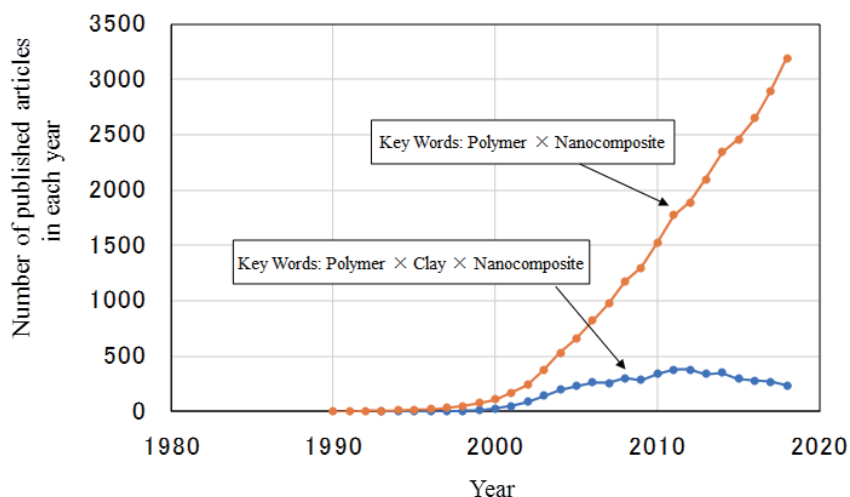
Since the first introduction of NCHs at an ACS Meeting in 1987,<sup>(10)</sup> research and development on nanocomposites has continued to proliferate, not only at Toyota CRDL, but all over the world, as indicated in **Fig. 3**. More than 4800 PCN-related reports have



**Fig. 1** Timing belt cover for an automobile engine made from NCH.



**Fig. 2** Transmission electron micrograph of NCH (Clay Content: 5 wt%).



**Fig. 3** The numbers of published articles in each year related to polymer clay nanocomposites and polymer nanocomposites obtained by Web of Science.

been published (based on survey results by the “Web of Science” in February 2019). The number of articles including nanocomposites with fillers other than clay (CNTs, graphene, cellulose nanofibers, etc.) has surpassed 27000 to date. At the same time, the citation numbers of NCH and PCN papers by Toyota CRDL have been increasing significantly since the early 1990s. Toyota CRDL is now also regarded as “The Birthplace of Nanocomposites”.

### 3. Properties and Functions of NCHs

The properties, functions, and specific phenomena of NCHs will first be reviewed with a focus on the nano-effects. We have already published details of the fabrication methods and structures of NCHs, as well as their development chronology in other papers;<sup>(6-27)</sup> therefore, these details would not be given here.

#### 3.1 Elastic Modulus and Heat Resistance

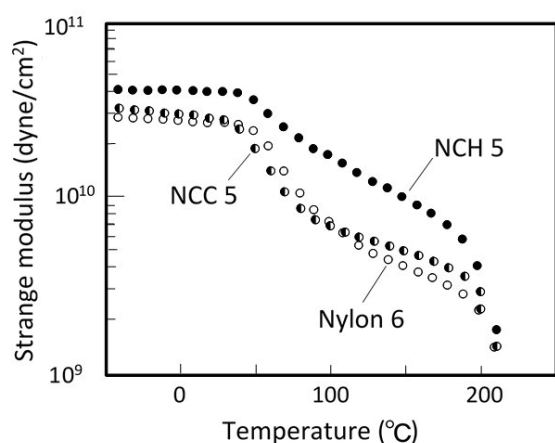
NCHs exhibit several superior mechanical properties compared with nylon 6, representative examples of which are shown in **Table 1**. A particularly remarkable feature is that through the addition of a small amount of clay, in the order of a few weight percent, the elastic modulus of NCHs was significantly improved without a substantial sacrifice in moldability.<sup>(15)</sup> The reinforcement effect for the NCH was superior, especially above the glass transition temperature

of nylon 6 ( $T_g$ : ca. 50°C), compared to nylon 6, as indicated in **Fig. 4**, which shows the dependence of the storage modulus on the temperature. On the other hand, a nylon 6-clay macrocomposite (NCC) produced by a simple melt-mixing of nylon 6 and clay, in which the clay agglomerates were dispersed with sizes in the order of several 100  $\mu\text{m}$ , exhibited less or almost no reinforcement effect (Fig. 4). The thermal distortion temperature, as an index of heat resistance, was improved from 65°C for nylon 6 to 152°C for the NCH by the addition of only 4.7 wt% clay (Table 1). What is the cause of such specificity appearing in nanocomposites? Furthermore, if the type of clay (aspect ratio: hectorite < saponite < montmorillonite < synthetic mica) was changed, then the reinforcement efficiency of the NCHs increased with the aspect ratio of the clay.<sup>(7,15)</sup> What is the mechanism that determines the reinforcement effects?

There are roughly two trains of thought regarding the reinforcement mechanism of a nanocomposite. The first is represented by micromechanics, a standpoint that can be explained by composite theory (assuming that the physical properties of fillers and matrices in nanocomposites are the same as those of each individual component).<sup>(56-61)</sup> The second is to assume a nano-effect where the nanocomposite has an interface with an enormous area due to the small nanofiller size with respect to the microsized fillers.<sup>(62)</sup> The matrix polymer of the nanocomposite at the matrix-nanofiller interface behaves differently to the bulk polymer due to the

**Table 1** Mechanical properties of NCHs with different clay contents and nylon 6.

Property	Comment	Unit	NCH2	NCH5	NCH8	Nylon 6
Tensile strength	23 °C	MPa	76.4	97.2	93.6	68.6
	120 °C		29.7	32.3	31.4	26.6
Elongation	23 °C	%	>100	7.30	2.5	>100
	120 °C		>100	>100	51.6	>100
Tensile modulus	23 °C	GPa	1.43	1.87	2.11	1.11
	120 °C		0.32	0.61	0.72	0.19
Flexural Strength	23 °C	MPa	107	143	122	89.3
	120 °C		23.8	32.7	37.4	12.5
Flexural modulus	23 °C	GPa	2.99	4.34	5.32	1.94
	120 °C		0.75	1.16	1.87	0.29
Charpy impact strength (without notch)		$\text{kJ} \cdot \text{m}^{-2}$	102	52.5	16.8	>150
Heat distortion temperature		°C	118	152	153	65
Coefficient of thermal expansion	Flow direction	$\text{cm} \cdot \text{°C}^{-1}$		$6.3 \times 10^{-5}$		$11.7 \times 10^{-5}$
	Perpendicular direction			$13.1 \times 10^{-5}$		$11.8 \times 10^{-5}$



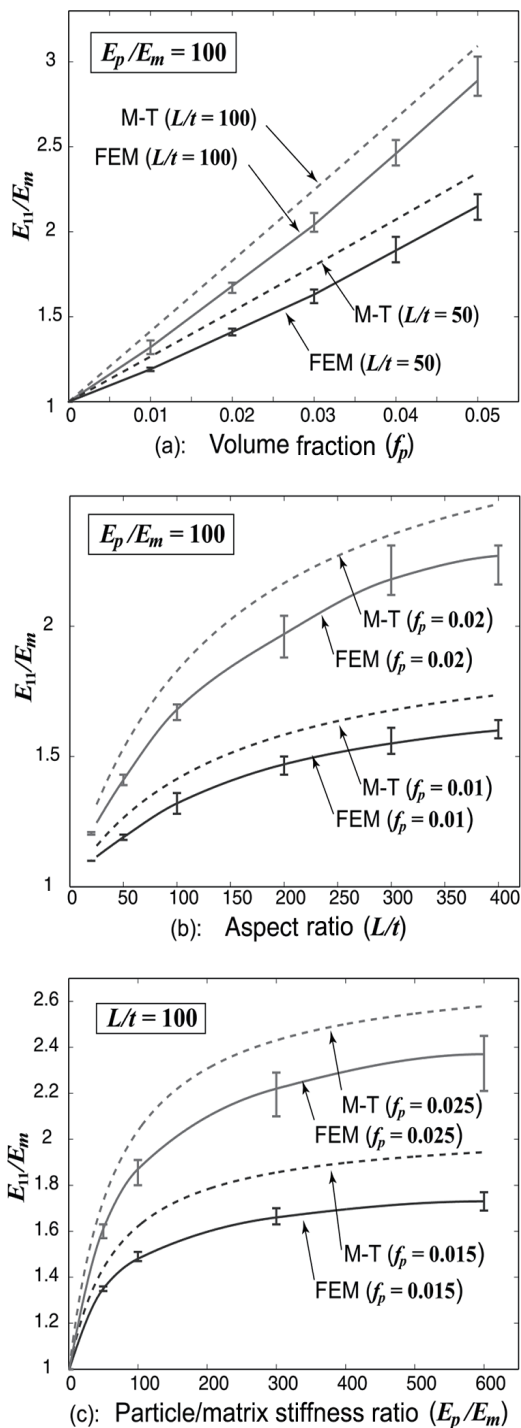
**Fig. 4** Temperature dependences of storage the modulus of NCH 5 (clay content: 4.2 wt%) obtained by organically modified clay catalyzed polymerization of  $\epsilon$ -caprolactam, NCC 5 (clay content: 5 wt%) obtained by melt-excluding with clay and nylon 6.

constraint effect by the nanofillers. The question is which approach is correct?

The reinforcement effect of the elastic modulus for NCHs was discussed using the micromechanics model by comparison with a macroscopic glass fiber-reinforced nylon 6.<sup>(56)</sup> By extracting the structural parameters (matrix: elastic modulus; filler: elastic modulus, volume fraction, shape and aspect ratio, dispersibility, orientation, etc.) in each composite, analysis was conducted using composite theories, i.e., the Halpin-Tsai equation<sup>(57,58)</sup> and the Mori-Tanaka theory.<sup>(59,60)</sup> The clay had a reinforcement efficiency

that was approximately three times higher than that of the glass fiber, and the same elastic modulus could be obtained by clay addition at only 1/3 the weight of the glass fiber. The composite theories could satisfactorily capture the elastic modulus behavior of both types of composites. Therefore, the reasons for the more efficient reinforcement effect of the NCH were determined as follows: (1) the elastic modulus of the clay (178 GPa) is higher than that of the glass fiber (72.4 GPa), (2) the aspect ratio of the clay (ca. 57) is larger than that of the glass fiber (ca. 20), and (3) the clay particles are plate-like (two-dimensional), while the glass fibers are fibrous (one-dimensional).<sup>(56)</sup>

Attempts have been made to elucidate the reinforcement mechanism of NCHs by stress analysis using a two-dimensional finite element method (FEM).<sup>(61)</sup> Various clay dispersion models were constructed, assuming perfectly bonded interfaces, followed by stress analysis using the FEM to give the elastic modulus enhancement efficiency, i.e., the ratio of the elastic modulus of NCH to that of nylon 6 ( $E_{11}/E_m$ ). The experimental results of NCH could be satisfactorily explained by the FEM analysis.<sup>(61)</sup> The  $E_{11}/E_m$  values obtained by the FEM were also consistent with the Mori-Tanaka model (M-T) shown in **Fig. 5**. The reinforcement mechanism was also clarified how the outer stress applied to the model was transmitted from the matrix to the clay platelets based on the strain distribution. The elastic modulus enhancement mechanism of the nanocomposite basically follows almost the same principle as that of macrocomposites and can be explained in a coherent manner by each parameter, including the filler volume fraction ( $f_p$ ),



**Fig. 5** Plane strain FEM results for NCHs in comparison with the uniaxial results of Mori-Tanaka (M-T) model: dependence of composite/matrix stiffness ratio ( $E_{11}/E_m$ ) on (a) volume fraction of particle ( $f_p$ ); for aspect ratio of particle ( $L/t$ ) = 50 and 100, particle/matrix stiffness ratio ( $E_p/E_m$ ) = 100; (b)  $L/t$ ; for  $f_p = 0.01$  and  $0.02$ ,  $E_p/E_m = 100$ ; (c)  $E_p/E_m$ ; for  $f_p = 0.015$  and  $0.025$ ,  $L/t = 100$ .

shape, aspect ratio ( $L/t$ ), degree of orientation, and elastic modulus ratio of filler to matrix ( $E_p/E_m$ ). This model provides suggestions on how to enhance the elastic modulus of the nanocomposites. These are to increase (1)  $f_p$  (Fig. 5(a)), (2)  $L/t$  (Fig. 5(b)) and (3)  $E_p/E_m$  (Fig. 5(c)), (4) disperse the filler uniformly; and (5) induce orientation in the direction to be reinforced. NCHs based on clays with larger aspect ratios (e.g., synthetic mica and montmorillonite) exhibit higher reinforcement efficiency compared to NCHs based on clays with smaller aspect ratio (e.g., saponite and hectorite).<sup>(7,15)</sup>

These results may indicate the absence of nano-effects (absolute size effect of filler) in NCHs, at least with respect to the elastic modulus.

### 3.2 Tensile Strength, Elongation and Toughness

Although the addition of a small amount of clay could improve the tensile strength of NCHs, as the amount of added clay increases, a transition to brittleness occurs below the  $T_g$  of nylon 6, and the tensile elongation and impact strength of NCHs are decreased, as shown in Table 1.

How can we improve the toughness of NCHs? A method that could be used to improve the toughness of NCHs to some extent was discovered serendipitously.<sup>(24)</sup> Through the addition of a small amount of hexamethylenediamine at the time of polymerization to produce NCH, the dispersion structure of the clay layer was controlled from a single layer level to a plurality of levels; however, the brittleness of the NCH was improved even more significantly. What is the reason for the improved brittleness? Transmission electron microscopy (TEM) observations of NCH samples under stretching were performed.<sup>(63)</sup> Micro voids were formed by delamination between clay and clay at the part where several layers of clay were laminated in the samples. The delamination process was considered as the reason for the slight increase in toughness. This mechanism may also be assumed to work for the high toughness of the NCH modified with diamine. It was also reported that the toughness was improved by preparing NCH with a melt-extruding method using nylon 6 with larger molecular weight as a matrix polymer.<sup>(64)</sup> However, in either case, the improvement of toughness may be insufficient, depending on the application. For nanocomposites, one of the important issues would be to establish the

three essential features of the mechanical properties, i.e., toughness, elastic modulus, and strength.

In recent years, attempts have been made to analyze the maximum yield strength of nanocomposites by estimating the properties and shapes of the interfaces from experimental values,<sup>(65,66)</sup> or to predict the yield strength using multiscale simulation techniques including molecular dynamics simulation.<sup>(67)</sup> Such analytical techniques and simulation technologies are also important to elucidate the mechanisms for the strength and toughness of nanocomposites and achieve further increases in strength and toughness.

### 3.3 Recyclability

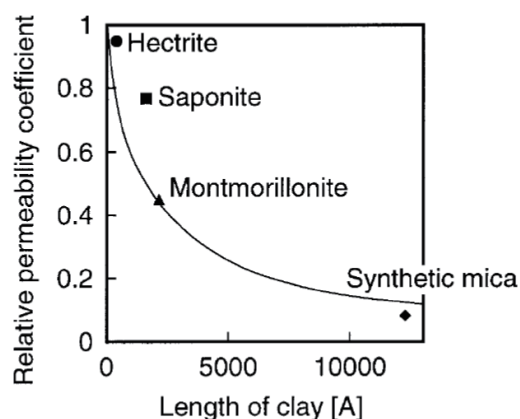
The mechanical properties of a thermoplastic glass fiber or a carbon reinforced composite are gradually decreased when they are subjected to repeated material recycling. The main reason is that macroscopic fibers undergo rupture as a result of a melt shearing process. The fiber lengths are subsequently shortened, and the reinforcement effect is weakened. For a NCH (clay content: 1.35 wt%), it was reported there was no significant deterioration of the mechanical properties due to material recycling, even after five times material recycling.<sup>(68)</sup> Why is NCH less prone to degradation of the mechanical properties by recycling? It was estimated that the fracturing of clay by the melt shearing process during recycling was not as extreme as that in a macroscopic fiber, a relatively large aspect ratio was maintained, and the reinforcement effect was sustained.<sup>(68)</sup> Considering a recycling-oriented society, nanocomposites with ease of recyclability will be important.

### 3.4 Barrier Properties and Flame Retardancy

NCH samples exhibit excellent barrier properties against permeation of low molecular weight molecules, such as water and oxygen, compared to nylon 6.<sup>(18,19)</sup> For example, with the addition of 0.74 vol% clay, the permeability coefficient of a NCH film for water vapor and hydrogen was 70% or less that of a nylon 6 film, and as the amount of clay addition was increased, the impermeability was improved. This barrier effect could be quantitatively explained using an FEM model in terms of non-permeable two-dimensional clay platelets dispersed in a matrix, which were oriented parallel to the film surface and perpendicular to the direction

of permeation, whereby the path of permeation movement became longer due to a bypass effect.<sup>(20)</sup> The barrier properties were significantly dependent on the volume fraction, aspect ratio, and orientation of the clay, as well as other factors.<sup>(20)</sup> This barrier effect is reported not only for NCHs, but also for PCNs, such as polyimide clay nanocomposites<sup>(30,31)</sup> (shown in Fig. 6) and olefin type nanocomposites,<sup>(47)</sup> and is one of the useful functions of PCNs. By taking advantage of these characteristics, these nanocomposites have been put into practical applications such as food packaging films, beverage containers, and rubber fuel hoses.<sup>(69)</sup>

Imparting flame retardancy to generally flammable polymer materials is an important issue from a practical point of view. Gilman et al. indicated that NCHs exhibited better flame retardancy than nylon 6 by the difference in exothermic behavior when a constant incident heat was applied using a cone calorimeter, as shown in Fig. 7.<sup>(70)</sup> The mechanism for the flame retardancy in NCHs was presumed to be the inhibition of the supply of thermal decomposition products (gas, etc.) of nylon 6 and thus suppression of combustion due to the formation of inorganic barrier layers by the accumulation of clay generated as a combustion residue. The same type of flame retardancy function was reported for polypropylene and polystyrene clay nanocomposites.<sup>(71)</sup> Flame retardant agents, which are low molecular weight compounds, are typically added to impart flame retardancy to polymers. However, the addition of these compounds to polymers lowers

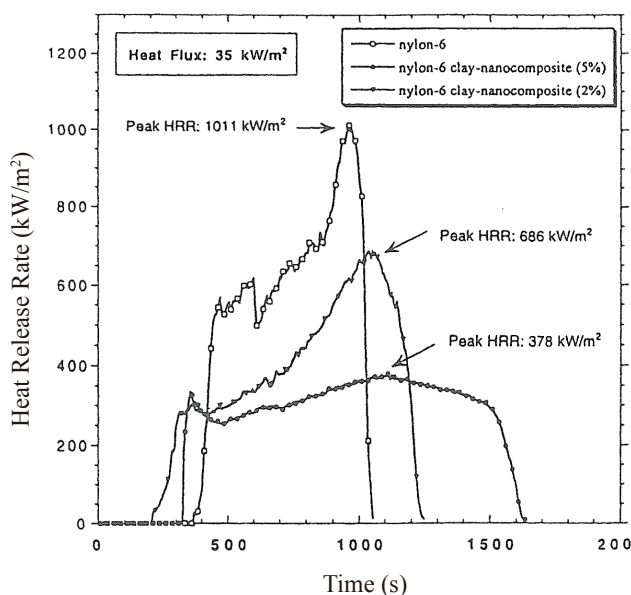


**Fig. 6** Dependence of clay length (the thicknesses of all the clay are about 10 Å) on relative permeability coefficients (water vapor) of polyimide clay nanocomposites (clay content: 2 wt%).

their thermal and mechanical properties. Clay nanocomposites are an attractive technology capable of achieving both flame retardancy and desirable mechanical properties as a multifunctional material. In a reported example, NCH has been applied to an olefin-based floor material surface layer to achieve dehalogenation and improve flame retardancy in flooring materials for railway vehicles.<sup>(72)</sup>

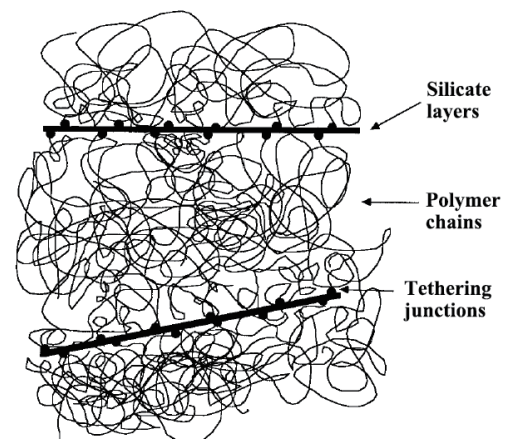
### 3.5 Rheological Specificities

The rheological behavior of a nanocomposite in the molten state is one of the important characteristics that affects not only the moldability, but also the structure of the final molded body. The specific rheological behavior of NCHs has been reported.<sup>(73,74)</sup> NCHs have a characteristic structure in that the terminal ammonium groups of the polyamide are ionically bonded to the clay, which is referred to as an “end-tethered polymer layered silicate nanocomposite”, as indicated in Fig. 8.<sup>(73)</sup> While typical polymers melt and flow in thread-like random coils, it is estimated that a plurality of polymers flow in a state of ionic bonding with a clay platelet. The rheological behavior of NCHs is shown in Fig. 9.

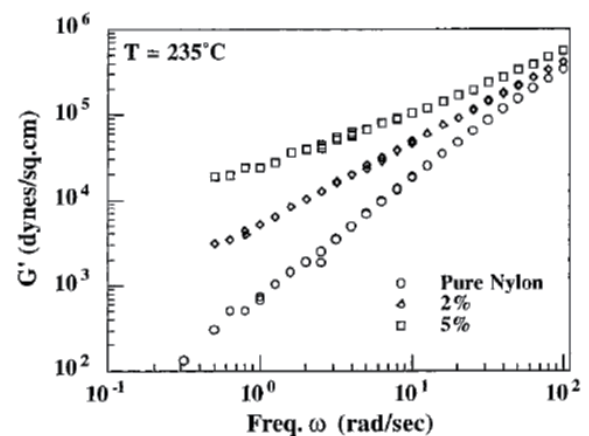


**Fig. 7** Comparison of the heat release rate (HRR) plot for nylon 6, nylon 6 clay-nanocomposite (clay content: 2 wt%) and nylon 6 clay-nanocomposite (clay content: 5 wt%) at 35 kW/m heat flux.

In the high frequency region, NCH exhibited a viscosity approximating that of nylon 6, which was a normal liquid behavior. In the low frequency region, the viscosity was higher than nylon 6 and, with an increase in the clay content, there was less dependence on the frequency. This behavior suggested that the NCHs exhibited rheological properties close to a solid state. Substantially similar conclusions and discussions resulted in other rheology studies on



**Fig. 8** Schematic diagram describing the end-tethered nanocomposites. The layered silicates are highly anisotropic with a thickness of 1 nm and lateral dimensions (length and width) ranging from several 100 nm to a few microns. The polymer chains are tethered to the surface via ionic interactions between the silicate layer and the polymer end.



**Fig. 9** Rheological behaviors (Storage modulus:  $G'$  versus frequency:  $\omega$ ) of NCHs (clay loadings: 2 wt% and 5 wt%) and nylon 6 at 235°C.

PCNs.<sup>(75,76)</sup> It is presumed that this solid-like behavior was induced by a three-dimensional network structure based on the “end-tethered polymer layered silicate nanocomposite” in Fig. 8. The rheological behavior of NCH and PCN is suitable for an injection molding process from a practical perspective. In the region of high shear rate, the viscosities of NCHs and PCNs remain close to that of the matrix resins and the flowability is good; in a low shear rate region such as when filling a mold, the viscosity increases to prevent the occurrence of burrs.

### 3.6 Specificity of Crystallization Behavior

The crystallization behavior of crystalline polymers has an impact on their molding cycle time and mechanical properties, and is thus one of the important factors in the molding process. Many investigations have been conducted on the crystallization behavior of NCHs.<sup>(77-81)</sup> The crystallization behavior of NCHs is affected by various factors such as the melt temperature, shear history, crystallization temperature, cooling rate, and is thus rather complicated.<sup>(80)</sup> The characteristic features of NCHs in much research are as follows. (1) The crystallization rates of NCHs typically increase compared to nylon 6. (2)  $\gamma$ -Type crystals are more likely to be generated than the thermodynamically stable  $\alpha$ -type crystals that are usually grown in nylon 6. (3) NCHs do not typically develop the spherulites that are observed in nylon 6. These results suggest that the clay surfaces promote the crystal nucleation of nylon 6, as generally observed with fillers. What type of structure can there be in the interface layers of NCHs? The existence of transcrystals with thicknesses of several nanometers, specific to the clay surface, as well as epitaxially grown lamellar crystals referred to as a shish-kebab type of structure were observed using TEM,<sup>(78)</sup> as shown in **Fig. 10**. Furthermore, by subjecting NCH to annealing treatments, further improvement of the elastic modulus has been reported.<sup>(78)</sup> These results indicate that there would be a potential for changing the matrix structure and properties according to the nanofiller employed in the nanocomposites.

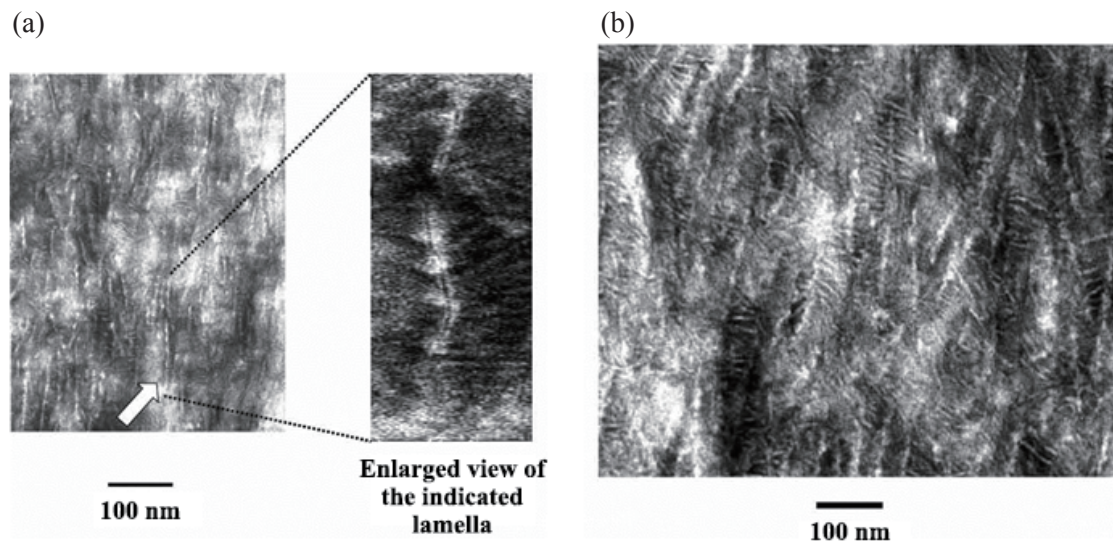
Several abnormal crystallization behaviors of NCH have been reported.<sup>(77,80)</sup> The degree of crystallinity in nylon 6 decreased as the cooling rate was increased, whereas the NCH showed an opposite trend.<sup>(77)</sup> Furthermore, when nylon 6 was quenched from the molten state in an isopropanol solution at 5°C, it

became amorphous.<sup>(80)</sup> On the other hand, NCH was instantaneously crystallized to the  $\gamma$ -form by the same quenching condition.<sup>(80)</sup> How can we interpret this abnormal crystallization behavior of NCH? It is probably necessary to understand the melting states of NCHs. The relationships of pressure-volume-temperature for nylon 6 and NCH in the molten state were precisely measured to determine that the specific volume of NCH decreased by 1–1.5% with respect to that of nylon 6 in the molten state.<sup>(82,83)</sup> Based on these results, it was presumed that the surfaces of clay in the molten NCH were uniformly covered with solidified nylon 6 molecules up to a thickness of 6 nm.<sup>(82,83)</sup> It may be possible to explain the ultrafast crystallization behavior of NCH by assuming that the solid phase structure may be close to a crystal nucleus. If this is the case, then the induction time of crystal nucleation would be extremely shortened. The crystal growth distance from the clay surface nuclei would also be very short because the distance to an adjacent clay particle would be from several tens of nanometers to several hundreds of nanometers. This is an effect that exceeds the nucleation effect of typical macrofillers and may be regarded as a nano-effect unique to NCH. The transcrystal structure shown in Fig. 10 may be related to these findings.

### 3.7 Specificity of Orientation and Crystallinity Distribution in Molded Bodies

Interesting results have also been shown regarding the orientation of clay and nylon 6 molecular chains and crystals in films and molded bodies after extrusion or injection molding of NCHs.<sup>(26,80,84)</sup> Briefly, in an extruded film, the clay was oriented in the extrusion direction throughout the film, while in the injection molded body, the clay was oriented in the injection direction in the vicinity of the surface of the molded body and randomly oriented as it moved toward the center part. Another characteristic was the presence or absence of an oriented structure in the polymer. In a nylon 6 film or injection molded body, the orientation of nylon 6 molecular chains and crystals relaxed to random orientations during the molding process, which left almost no oriented structure. In contrast, the orientation structures of the nylon 6 molecules and crystals were maintained in a considerable portion of the NCH. This is possibly due to that relatively narrow space between the oriented clay platelets that





**Fig. 10** Typical transmission electron micrographs of NCH crystallized at 170°C and 210°C. The enlarge part shown (a) is from the indicated lamella in the original picture. The black strip inside the white part is clay. The white part is transcystal region on the clay surface. (b) shows the typical shish-kebab type of structure.

can maintain the orientation of the matrix polymer, which is a type of nano-effect. From this orientation specificity of matrix molecules in nanocomposites, the clay particles have been described as an “orientation enhancer” and the similarity with the orientation structure of liquid crystalline polymers has been noted.<sup>(84)</sup> Such orientations of clay and polymer molecules or crystals have led to improved barrier properties in films and molded bodies, as well as improvements in the reinforcement effect in the direction of orientation.

As a result of the anisotropic orientation of clay particles and polymer molecules in NCHs, the coefficients of linear thermal expansions of NCH molded bodies have also been determined as anisotropic, as shown in Table 1 and reported elsewhere.<sup>(85)</sup> When formed into a flat plate, the thermal expansion coefficient of the NCH decreased in the flow direction (FD) and in the perpendicular direction (TD), whereas it increased in the thickness direction (ND) compared with the nylon 6 molded body. The efficiency to suppress the thermal expansion coefficient in NCHs was higher than that in ordinary macrofiller composites. This is advantageous in the case of a flat plate because the thermal expansion can be suppressed efficiently in the in-plane direction.

In the injection molding process, in addition to the distribution of shear rate, the temperature gradient also

varies between the skin portion and the core portion of a molded body. On the surface, although also dependent on the mold temperature, the body is generally rapidly cooled (crystallized at a lower temperature), while gradually cooled (crystallized at a higher temperature) in the core part. There is thus a distribution in the degree of crystallinity of an ordinary molded body due to this difference in temperature history. These crystallinity distributions were determined as being reversed between nylon 6 and NCH.<sup>(79)</sup> In nylon 6, the degree of crystallinity was higher in the core layer than in the surface layer, but conversely in NCH, the degree of crystallinity in the surface layer was higher. If an NCH molded body could be prepared with a larger surface layer ratio, then the mechanical properties could be improved due to both a higher degree of crystallinity and an orientation effect. Nylon 6 and NCH molded bodies with larger surface layer ratios were prepared by reducing the thickness of the molded body from 2 mm to 0.5 mm, and their mechanical properties were measured.<sup>(86)</sup> The mechanical properties of nylon 6 were not significantly changed, while those of NCH were significantly improved by reducing the thickness of the molded body.

NCHs thus exhibit specific behavior as nano-effects in various aspects during processing, such as (1) the molten state, (2) flow characteristics, (3) crystallization

behavior, (4) and orientation within a molded body. To take advantage of such nanocomposites requires control of the forming process to maximize the potential of the nanocomposite to exceed the prediction of composite theories, while understanding the relationship between this set of processes and the behavior of the nanocomposite.

#### 4. PCN Based on Various Matrix Resins at Toyota CRDL

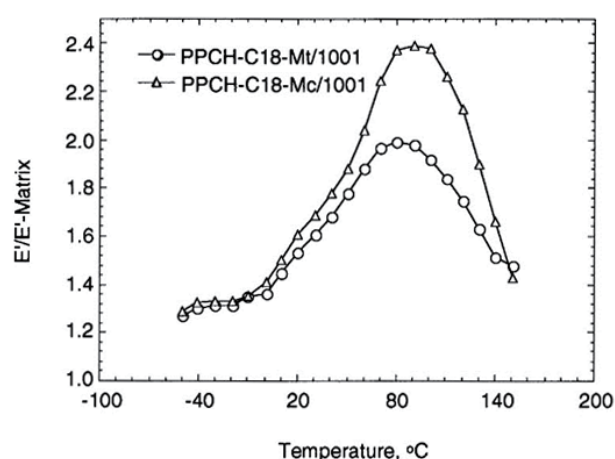
Besides the research and development on NCHs, research on PCNs has been conducted with various matrix resins at Toyota CRDL.<sup>(29-47)</sup> Representative examples include PCNs using polypropylene,<sup>(32-35,37)</sup> polyethylene,<sup>(40)</sup> rubber,<sup>(39,41,45,47)</sup> polystyrene,<sup>(36)</sup> acrylic resin,<sup>(29)</sup> and polyimide<sup>(30,31)</sup> as matrix polymers.

Films of the polyimide clay nanocomposite, in which exfoliated silicate layers maintained a high aspect ratio, have been successfully produced by a solution method and exhibit very high barrier properties and low thermal expansion.<sup>(30,31)</sup> When synthetic mica with a high aspect ratio ( $L/D = 1230$ ; 12300 Å long, 10 Å thick) as a filler was added at 2 wt%, the nanocomposite film exhibited a permeability coefficient of 1/10, as shown in Fig. 6, and a low linear thermal expansion coefficient that was 60% of that for the polyimide film without the filler.

Resin materials most widely used are olefin-based resins such as polypropylene (PP) and polyethylene (PE), and polyolefin rubbers (EPM, EPDM, etc.). Polypropylene is used as a body plate material and interior material for automobiles. At Toyota CRDL, successful synthesis of nanocomposites based on olefin-based resins was a very important target. However, polar clay and non-polar polyolefin were not readily compatible, dispersion of the clay was an important issue. The dispersibility of organically modified clay in polyolefins was significantly improved by the attachment of polar functional groups (such as maleic anhydride groups) to the olefin polymers, due to the strong interaction with polar clay surfaces. After this discovery, research on PCNs could be advanced. For example, in the PP type nanocomposites,<sup>(32-35,37)</sup> it became possible to disperse organically modified clay and maleic anhydride modified PP by melt-mixing with a twin-extruder. Through the addition of a small amount of clay, the strength and elastic modulus were improved compared with PP and talc PP composites

with similar amounts of fillers. Examples of the relative dynamic storage moduli ( $E'/E'$ -matrix) of the PP/1001 (maleic anhydride-modified PP oligomer as a compatibilizer)-clay nanocomposites based on montmorillonite (Mt) and synthetic mica (Mc) compared with those of PP/1001 blends as a function of temperature are shown in Fig. 11.<sup>(34)</sup> By a similar technique, nanocomposites in various resin systems such as polyethylene clay nanocomposite,<sup>(40)</sup> rubber nanocomposites,<sup>(39,41,45,47)</sup> and polystyrene clay nanocomposite<sup>(36)</sup> have been successfully produced, and the elastic modulus and barrier properties were improved in much the same manner as with the NCHs.

Acrylic resins are commonly used in paints and coatings. To produce a smooth coating film surface, it is necessary for the paint or coating to exhibit pseudo-plasticity, so that the viscosity of the paint is low at high shear rate (i.e., the paint can be easily applied) and high at low shear rate (i.e., the paint does not easily drip). Acrylic resin-clay hybrid dispersions were synthesized by mixing acrylic resins obtained by copolymerization with ethyl acrylate, acrylic acid, and N,N-dimethylaminopropylacrylamide-methyl chloride salt, with an aqueous clay suspension.<sup>(29)</sup> The viscosity of a dispersion with more than 3 wt% of clay was significantly dependent on the shear rate and exhibited pseudoplasticity. Furthermore, hybrid coating films, which were obtained by crosslinking,



**Fig. 11** Relative dynamic storage moduli ( $E'/E'$ -matrix) of the PP/1001 (1001: maleic anhydride modified PP oligomer)-clay nanocomposites based on montmorillonite (Mt) and synthetic mica (Mc) to that of PP/1001 blends as a function of temperature.

exhibited lower permeability coefficients for O<sub>2</sub> and N<sub>2</sub> gases and higher storage modulus E', with increasing clay content

In the future era, materials based on renewable resources such as biomaterials will be important. PCNs such as plant oil-based resins have been synthesized and exhibit superior properties such as heat resistance.<sup>(43)</sup> Bio-based polycarbonates based on dianhydro-D-sorbitol/clay nanocomposites have also been successfully prepared and exhibit higher elastic modulus than the pristine polycarbonate.<sup>(46)</sup> Clay is abundant in nature; therefore, hybrids that consist of inexpensive, abundant and renewable resources are expected to contribute to global sustainability.

## 5. Research Topics on Functional Nanocomposites at Toyota CRDL

### 5.1 Nanocomposites with High Thermal Conductivity

Along with the miniaturization and higher output of electronic devices such as electric vehicles, high intensity LED lighting, and smartphones, it is important to find a solution for heat dissipation. Resin materials are used as insulating materials because of their excellent moldability and lightweight properties in electronic devices. However, resins generally have low thermal conductivity (ca. 0.2 W m<sup>-1</sup> K<sup>-1</sup>); therefore, compounding with a filler that has high thermal conductivity (e.g., alumina, h-BN, etc.) is indispensable. CNTs have high thermal conductivity (ca. 2000-6000 W m<sup>-1</sup> K<sup>-1</sup>) and a fibrous structure with an extremely high aspect ratio; therefore, the thermal conductivity of resins could be improved by compounding a small amount of CNTs, due to the continuous network of CNTs that is formed. However, CNTs are also electrically conductive; therefore, they cannot be used in applications that require insulating properties.

By careful control of the composition and the structure of the resins, nanocomposites with improved thermal conductivity were successfully produced by dispersing multi-walled CNTs (MWCNTs) while maintaining highly insulating characteristics, as shown in **Fig. 12**.<sup>(48,49)</sup> For example, MWCNT/nylon 6/polyphenylene sulfide (PPS)/(3-glycidyloxypropyl)tri-methoxysilane (1/77.5/21/0.5 vol%) composites with novel morphology were designed and fabricated, as shown in **Fig. 12(b)**.<sup>(49)</sup> In this composite, the MWCNT ends were capped

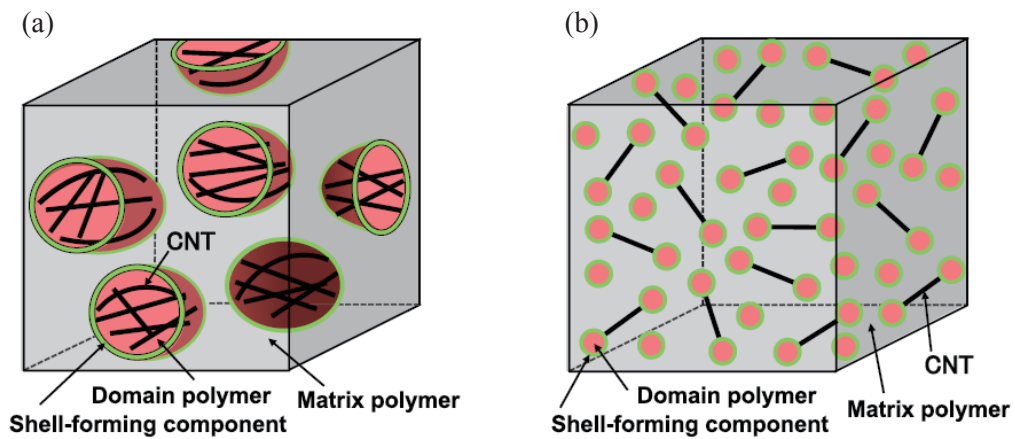
with nanosized PPS domains as a domain polymer to prevent the formation of electrically conductive paths, and MWCNT-PPS nanodomain-linked structures were uniformly dispersed in nylon 6 as a matrix polymer, which led to an enhanced elastic modulus, heat resistance and improved thermal conductivity (0.406 W m<sup>-1</sup> K<sup>-1</sup>) and insulating properties (2.3 × 10<sup>14</sup> Ω cm).

Another important approach is nanocomposites with thermally conductive and insulating nanofillers.<sup>(50,51)</sup> Boron nitride nanosheets (BNNSs) are insulating materials with high thermal conductivity (300-2000 W m<sup>-1</sup> K<sup>-1</sup>), high strength and rigidity, heat resistance, and chemical stability. Highly soluble, noncovalently functionalized BNNSs (NF-BNNSs) with chlorosulfonic acid (CSA) were prepared by the facile and direct exfoliation of h-BN by the solution process. These NF-BNNSs acted as excellent nanofillers to improve both the in- and through-plane thermal conductivities of insulating polymers.<sup>(50)</sup> The through-plane thermal conductivity of NF-BNNS/poly(methyl methacrylate) (PMMA) nanocomposite films containing 2-80 wt% of BNNSs was much greater than those of h-BN/PMMA macrocomposites films in which h-BN particles were not dispersed uniformly in the matrix, as shown in **Fig. 13**. Instead of CSA, ionic liquid (IL) was also used for the high-yield, mild, facile exfoliation of h-BNs into few-layered BNNSs. NF-BNNS/IL/polymer composites with high thermal conductivity and high electrical insulation were also reported.<sup>(51)</sup>

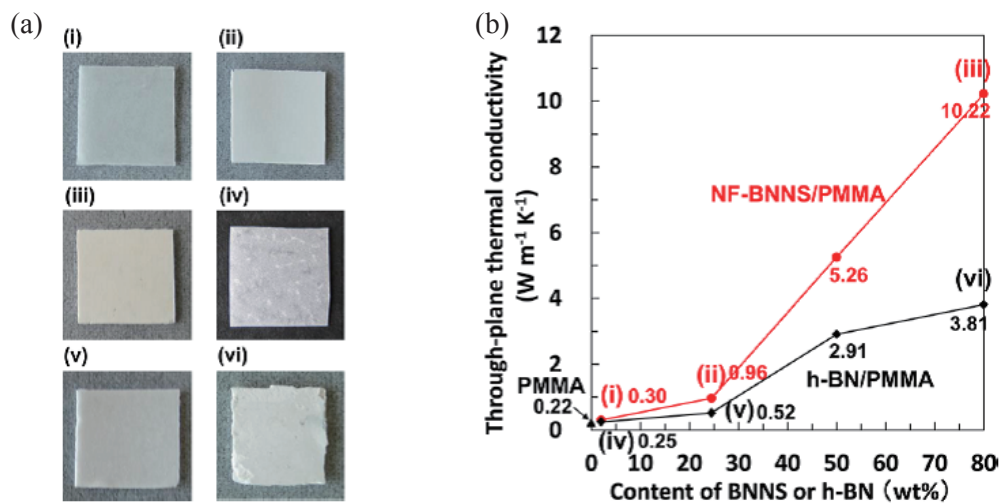
### 5.2 Dielectric Nanocomposites

Dielectric materials are mainly used in condensers for electrical energy storage. There are various types of dielectric materials such as ceramics or polymers. Polymer dielectric materials are characterized by features such as their flexibility, lightweight nature, and good processability. However, their use is restricted due to a low dielectric constant ( $\epsilon' = 2-3$ ). To impart a higher dielectric constant while taking advantage of the characteristics of polymers, compounding of a polymer with an inorganic material (e.g., ferroelectric barium titanate, etc.) with high dielectric constant have been studied. However, in simple compounding, there can be an issue of deteriorated reliability, such as a decrease in dielectric breakdown strength ( $E_{DB}$ ) and non-uniformity of the dielectric characteristics.

To solve such issues, PMMAs were grafted onto



**Fig. 12** Schematic diagrams of (a) morphology of CNT/polymer composite with high thermal conductivity and good electrical insulation and (b) novel morphology for CNT/polymer composite having high elastic modulus in addition to high thermal conductivity and good electrical insulation.



**Fig. 13** (a) Photographs of films ( $10\text{ mm} \times 10\text{ mm} \times 0.3\text{ mm}$ ) of NF-BNNS/PMMA composites having different BNNS loadings ((i) 2, (ii) 24.5, and (iii) 80 wt%), and h-BN/PMMA composites with different h-BN loadings ((iv) 2, (v) 24.5, and (vi) 80 wt%). (b) Through-plane thermal conductivities of films of NF-BNNS/PMMA composites, h-BN/PMMA composites, and PMMA.

barium titanate (BT) particles using surface-initiated polymerization, as shown in **Fig. 14**.<sup>(52)</sup> The obtained core-shell particles were blended with additional PMMA to yield nanocomposites where the core-shell BT particles were dispersed uniformly and could not approach each other due to the PMMA shells (PMMA-BT, Fig. 14(b)).<sup>(52)</sup> On the other hand, a composite of PMMA and BT particles without

grafting yielded a nanocomposite where the BT nanoparticles were inhomogeneously dispersed (PMMA/BT, Fig. 14(a)). The reliability of the dielectric properties of PMMA-BT was evaluated and compared to that of PMMA/BT. The homogeneous distribution of the BT particles for PMMA-BT had no significant influence on the reliability of the complex relative permittivity while it improved the reliability of the

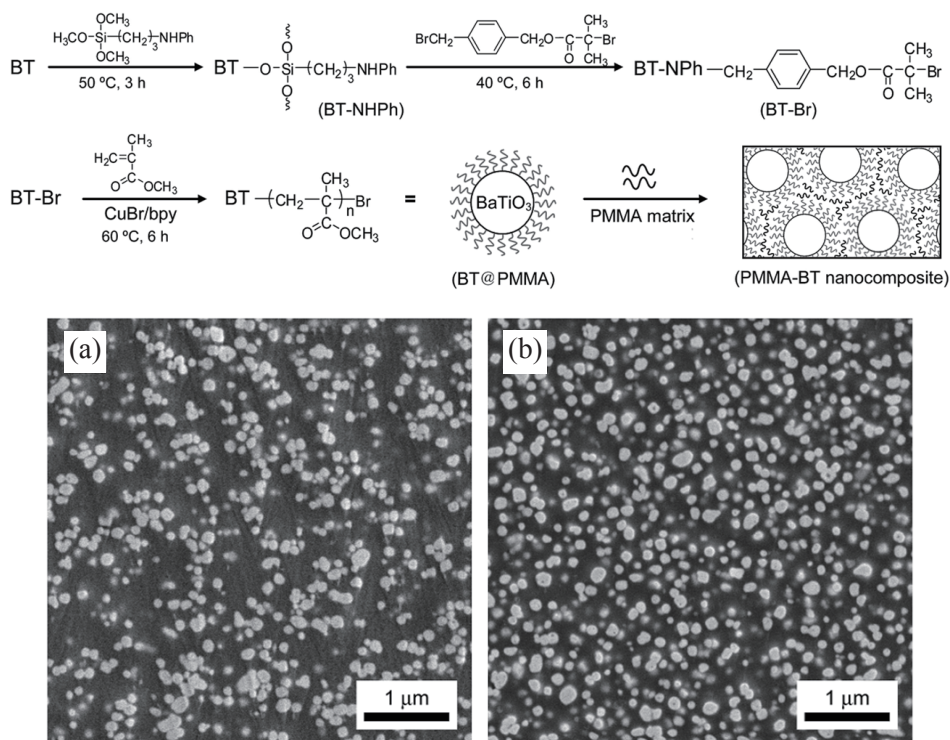
dielectric breakdown strength,  $E_{DB}$ .

By applying the same concept, nanocomposites based on poly(cyclohexyl methacrylate) grafted on multi-walled carbon nanotubes (PCHMA-CNTs) were synthesized.<sup>(53)</sup> PCHMA-CNTs exhibited unique dielectric properties, such as a relatively high  $\epsilon'$  and quite low  $\epsilon''$ ; however, when the volume fraction of the BT particles was  $\Phi_{CNT} > 0.1$ , a very large  $\epsilon'$  was observed at low frequencies, which may be due to the locally enhanced electric field by tunneling conduction. The CNTs were also determined to be five times more effective than BT particles for the enhancement in  $\epsilon'$  of polymer materials. CHMA-CNT/BT composites were fabricated and exhibited much higher  $\epsilon'$  than conventional BT-filled PCHMA composites (PCHMA/BT) with low  $\tan\delta$ .<sup>(54)</sup>

Nanocomposites of CNT and polymers are expected to serve as conductive materials and electromagnetic wave shielding materials. However, these cannot be used for purposes of electromagnetic wave shielding while securing insulation. To realize both functions of electromagnetic wave shielding and insulation,

nanocomposites with core-shell type CNTs with high density grafted PMMA and PMMA exhibited electromagnetic wave shielding performance that was 15 orders of magnitude higher than that of a simple mixture of CNT/PMMA.<sup>(55)</sup> Conventional conductive polymer/CNT composites absorb and shield electromagnetic waves in the low frequency region (0.001-1 GHz). In contrast, a nanocomposite using grafted CNTs resulted in comparative transmission of electromagnetic waves in the low frequency region, while a shielding effect appeared in the high frequency region of 1 GHz or higher.

These highly functional nanocomposites could be realized by making full use of advanced morphology control and synthesis technologies. This evolution, from the simple nanofiller dispersion technology of PCNs to the spatial arrangement control technologies of nanofillers, would enable the production of novel nanocomposites with multifunctionality.



**Fig. 14** Preparation scheme of PMMA-BT nanocomposites and SEM images of (a) PMMA/BT and (b) PMMA-BT nanocomposites with the volume fraction of the BT particle  $\Phi_{BT} = 0.21$ .

## 6. Future Outlook for Nanocomposites

### 6.1 Maximizing the Nano-effect

High-performance nanocomposites with a high reinforcement effect, barrier properties, and several other properties can be created simply using nanofillers with a high strength/elastic modulus and a large aspect ratio while ensuring strong interface adhesion. Although these remain important directions for nanocomposite development, they are limited to composite theories in which the matrix structure and properties remain unchanged. Various unique properties, including the existence of a molten state with a solid phase on the interfaces, unique rheological behavior, abnormal crystallization, and strong orientation effects, have been observed in nanocomposites during processing, especially in NCHs and PCNs, as described in this review. These properties can be attributed to nano-effects. However, they have not yet been completely utilized to realize the full potential of nanocomposites. The key factors would not only include material design but also process design. We should develop a theory for optimizing the process to achieve a high performance unique to nanocomposites based on the nano-effects.

### 6.2 Multifunctionality

With respect to future manufacturing, multifunctional and high-performance materials will be required because of the demand for high-performance, small-sized, and lightweight systems and devices. Nanocomposites are promising materials that can simultaneously exhibit multiple functions and contradictory performances with a high moldability through the addition of functional nanofillers. For example, NCHs realize multifunctionality, including moldability, high heat resistance and elastic modulus, gas impermeability, flame retardancy, and good recyclability. The CNT nanocomposites also realize multifunctionality, including high thermal conduction, dielectric properties, and electrical insulation.

### 6.3 Systematization of the Knowledge Base

It will be necessary to develop novel design methodologies for producing nanocomposites with maximized nano-effects and multifunctionality for future systems and devices within a limited period. As

mentioned in the history of nanocomposites, a large knowledge base with respect to nanocomposites has been created; however, this only contains individual nanocomposite information and data. Systematization of the nanocomposite knowledge base should be pursued by converting individual nanocomposite information and data into a systematic database, followed by the extraction of universal principles and rules from among processes, structures, properties, and functions to construct multiscale simulations and a materials informatics system. Then, nanocomposites will become essential materials in future devices and systems.

## 7. Conclusion

Toyota CRDL, following the invention of NCH in the 1980s, has pioneered nanocomposites and extended this novel field of materials. Simultaneously, several nanocomposites with unique functions and properties were manufactured by researchers worldwide. However, the commercialization of nanocomposites may be limited when compared with their high involvement in research. I believe that there is still high potential for advances and innovations in the field of nanocomposites, which will contribute to a sustainable future and a prosperous society.

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## Table 1

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## Fig. 5

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## Fig. 6

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## Fig. 7

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## Figs. 8 and 9

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## Fig. 10

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## Fig. 11

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## Fig. 12

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## Fig. 13

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## Fig. 14

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