Chapter 7
Hybridization with Polymers

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7.1 Introduction

As natural layered silicates, clay minerals are widely available and cheap; they have been mixed with organic polymers as bulking fillers in the industry. On the other hands, intercalated compounds of layered clay minerals, such as smectite, with organic molecules have been studied in the academic field. The intercalated compounds are expected to have hybridized characters and properties, which are somewhat alike to those of the parent compounds; but different from those of them also.

The organic polymers are widely used because of their easy formability, light weight, and ductility. Fillers have been mixed with polymers to reduce costs and modify the polymer properties, such as increasing the Young modulus, hardness, and heat resistance. However, ceramic fillers in particular adversely affect the formability and increase the specific weight and brittleness. To overcome the trade-off effects, fine and uniform dispersing and surface modification techniques have been developed. The composites of polymers with fine dispersed organic-modified clay minerals are called hybrid materials or nanocomposite materials. We have an excellent example of a hybrid material in metal alloys, in which ductility and high young modulus is realized together. When we compared structures and mechanical properties of the polymer base “hybrid” materials with the metal alloy, we could not call them “hybrid” but they are still mixtures.

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Exfoliation and surface modification have been the key technologies to develop hybrid materials.

Another way to approach hybrid composites is expected in the extension of the intercalation reactions. “Clay” materials, that is, a typical hybrid material of silicate layers with water, are distinguishing and useful rheological characters. Although it seems simple to imagine silicate layers dispersing in organic polymer matrix, to make hybrids by intercalation is not so easy. Polymerization in the interlayer region or solvent assist penetration of organic polymers into the interlayer spacing has been tried. The tendency to infinite swelling in Na^+-montmorilonite with water could not observed in smectites with organic polymers, due to the strong face-to-face cohesion force between the silicate layers and inadequate driving force to penetrate into the gallery spaces. Surface modification is also one of the key factors to approach the hybridization of silicate layers with polymers. Swelling of layered silicates with various molecules, the motive force for the intercalation reaction and the modification of silicate layers for approaching hybridization will be overviewed below.

7.2 Typical Examples of Hybrid Materials; A Goal of Hybridization with Polymers

7.2.1 Clay; A Hybrid of Silicate Layers with Water

We apply the word “clay” to a sticky and deformable agglomerate. The clays are an important raw material for ceramics. They should have an excellent deforming and forming properties which are controlled by water content, addition of organic additives, kneading, aging, and other traditional pretreatments. Raw materials for ceramics are composed of sticky minerals and nonsticky minerals. Typical sticky minerals are layered silicates for example sericite, kaolinite, or smectite. As they are essential minerals for the plastic deformation properties, they are called “clay minerals.” Mixtures of the clay minerals with water are too sticky, and they are not suitable for usual ceramic formation processes. Fine particles of nonsticky minerals, such as quartz, cristobalite or feldspar, are also necessary for plastic formation of ceramics.

Water molecules adsorbed on the surface of silicate layers are polarized due to the negative charge of the silicate or interlayer cations and the polar interaction between the water molecules chain forms an adsorbed water phases as shown in Fig. 7.1a. The interaction with the negative charges of silicate layers and interlayer cations is a driving force to make an intercalated compound of layered silicates with water molecules following an infinite swelling by water [1, 2]. The layered silicates hybridize with water molecules to form the clay (Fig. 7.1b) with characteristic plastic deformation properties. Although an infinite swelling tendency by water was confirmed [1, 2], the card house structure shown in Fig. 7.1b has not been observed.

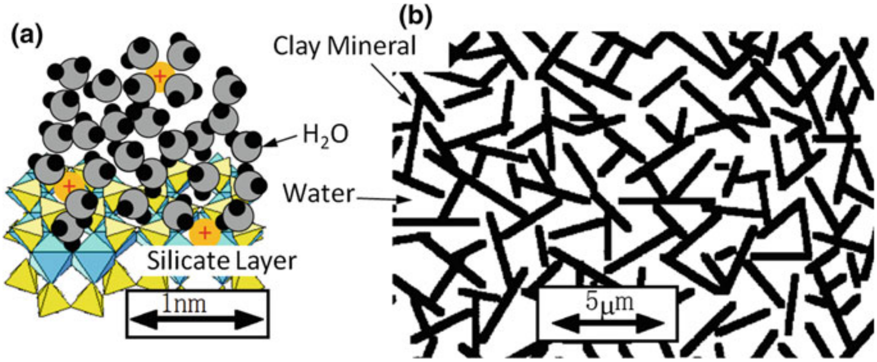
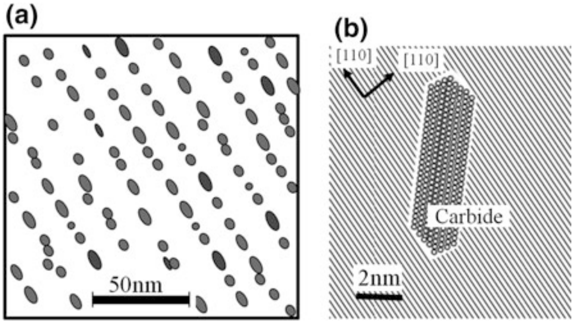


Fig. 7.1 Models of adsorbed water molecule chains on the surface of silicates (**a**), and layered silicates dispersion in plastic clay (**b**)

Fig. 7.2 Sketches of **a** Dispersion of nano-precipitates and **b** Carbide disks in FCC lattice in high performance steel



If we could replace the water phase in Fig. 7.1b with a polymer, we would get silicate layers hybridized with organic polymer.

7.2.2 *Alloys; Good Examples of Ideal Hybrids*

Iron and steel have a long history in our life and through controlled hybridization we have developed ferrite (BCC), austenite (FCC), and metastable phases, carbon, and various carbide precipitates. The continuing challenge in steel for satisfying requests of consumers has been produced high performance steels. A recent severe request for automobile applications brought about a high performance steel; NANO-HEIGHTEN®, in which carbide disks with 2–3 nm size are aligned in a ferrite matrix as shown in Fig. 7.2a [3]. The additive elements and C are dissolved in FCC-austenite at high temperature, followed by precipitation of nano-carbide along the interfaces between FCC-austenite and BCC-ferrite phases during a hot rolling and cooling process. The precipitates are disk shape with FCC structure and

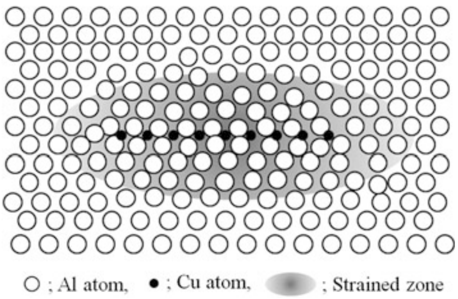


Fig. 7.3 Model for G.P. zone in Al-Cu Alloy

the atomic arrangement on the disk faces fit together with the BCC ferrite matrix as shown in Fig. 7.2b [3]. The high performances of these steels are attributed to the stable nanometer-size carbide dispersion and the well matching of atomic arrangement at the precipitate/matrix interfaces. The hot rolling and cooling process is a key technology for controlling the precipitation and dispersion of nanometer-size carbides [3]. A heat treatment process is also key for aluminum alloys such as Al–Cu–Mg alloy.

An age hardening process at low temperature of supersaturated solid solution of Al with Cu following quenching from high temperatures (at about 500 °C) produced a high performance material [4]. Based on this discovery, the Durener Metallwerke Inc. commercializes this aluminum alloy as “duralmin.” A high temperature aging higher than 200 °C precipitates a stable $CuAl_2$ (θ) phase with cubic structure which does not fit the matrix phase at interfaces. The hybrid with stable θ-phase precipitation does not have good performance but shows brittle behavior. During aging at temperatures lower than 150 °C, Cu clusters are formed in a supersaturated solid solution. These clusters are precursors of an intermediate phase (θ′) in the form of plates with CaF_2 structure. Guinier [5] and Preston [6] confirmed the precursor was one atom layer of Cu with a distortion of the Al arrangement around them as shown in Fig. 7.3 [7]. The high performance of the Aluminum alloys is attributed to the nanometer-size thin precursor G.P.-zone. This alloy, “duralmine,” has been used in the aerospace industry [8]. A dispersion of nanometer precipitates and the interface structure between the precipitates and the matrix are again the key factors for the good performance of the hybridizations.

7.3 Intercalation Reaction of Sheet Silicates with Organic Compounds

The process of precipitation in solutions, which has been successful in the development of the metal alloys, has not been applied for the hybridization of clay minerals with polymers. Silicate layer stacking clay minerals are dispersed in water, and the smectite group (montmorillonite, nontronite, beidelite, saponite, hectorite) clay minerals are swollen by water. Single silicate layers constituted by two tetrahedral sheets and one octahedral sheet can be dispersed [1, 2]. Linear uncharged or cationic polymers dissolved in the aqueous matrix adsorbed on silicate layers and flocculate dispersed silicate layers [9]. The flocculation involves interparticle or interlayer bonding including an intercalation reaction. Polymers were added to soil in agriculture to form hybrids with clay minerals and water in soil as conditioners to increase the mechanical strength of soil aggregates [9]. Long linear chains of polymers have adsorbed parts on silicate layer surfaces and also have hydrated parts with water molecules. Adsorption enthalpies of normal chain aliphatic compounds on silica-gel at room temperature [10] (36.8 kJ/mole for n-C_5H_{12}, 43.7 kJ/mole for C_6H_{12} and 59.4 kJ/mole for n-C_8H_{18}) suggested that the attractive force of the single methylene (–CH_2–) with the silicate surface is about 7 kJ/mole. Although the attractive forces between the silicate surface and single segments of polymers are weak, the total energy would be large because of the multi-point attachment. The polymer additives for soil reinforcement are a good example of the hybridization of silicates with organic polymers, but they are not nano-hybrids. Water molecules are essential for the excellent properties of soil hybrids, which could not be applied to most engineering uses.

The smectite clay minerals form intercalated compounds with organic compounds, in which the organic molecules penetrate interlayer spaces and these spaces are increased to form intercalated nano-hybrid compounds. Interlayer water molecules exchange for polar organic monomers such as acrylamide, vinyl acetate or amino acid, which can be polymerized to form intercalated hybrids of clay minerals with organic polymers. The attractive force of polar parts should be comparable with water molecules, that is about 15 kJ/mole, but additional hydrophilic interaction estimated at about 50 kJ/mole is enough for penetration of the guest organic molecules into interlayer spacing or driving off adsorbed water molecules to form intercalated compounds. The attractive driving force for the intercalations makes hybrid compounds in which the guest gallery aligned single or double molecular layers. Polymerization of interlayer monomers makes intercalation type hybrids of organic polymers with silicate layers. Usually, gallery spaces; Δd, are 0.2–0.8 nm, which corresponds to single and double molecular layer thicknesses as shown in Fig. 7.4a and b [11]. Except the amino acids and poly amino acids which formed triple molecular layer compounds shown in Fig. 7.4c [11], penetration was limited to double layers because of inadequate driving force to further increase space.

Polymerization enthalpies were expected to have enough force for increasing interlayer spaces to make compounds with wider gallery spaces. However, even when the monomer contents in clay mineral/monomer mixtures were increased, excess monomers polymerized outer spaces to form mixtures of polymer and intercalated compounds with double or triple polymer layers in interlayer spaces. Although the intercalated compounds with polymers were expected to have a high affinity with similar polymers, the limited swelling compounds were not suitable as fillers due to tight aggregations of intercalated compound particles.

Nonpolar monomers, such as styrene, could not penetrate into the interlayer spaces. When exchangeable interlayer cations in the smectites were exchanged for

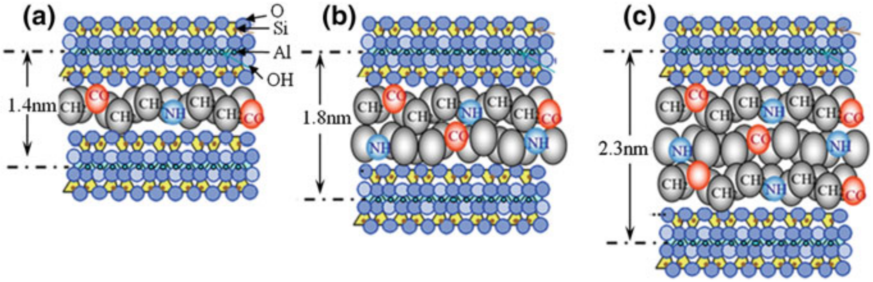


Fig. 7.4 Models for polyamide/montmorillonite intercalated compounds: **a** mono-amino acid layer, **b** double-amino acid layer, and **c** triple-amino acid layer

tri-methyl alkyl ammonium $[(CH_3)_3\text{-N-}(NH_2)_{n-1}CH_3\ n = 12\text{–}18]$, the monomer molecules could go into the interlayer spaces by hydrophobic interaction with the methyl group in the organic cation. The cation exchanged clay minerals for organic surfactants are called organo-clays and research is continuing to apply these organo-clays as fillers for polymers. The interlayer space; Δd, of the intercalated compound of the organo-montmorillonite with polystyrene was 3.7 nm [12]. An attractive force between the silicate layers with $\Delta d = 3.7$ nm was estimated about 1/1000 of that with $\Delta d = 0.2$ nm and about 1/10 of that of $\Delta d = 0.8$ nm. The weak attractive force between the silicate layers suggested easy exfoliation by shear stress during mixing and exclusion process with polymer melts. Unfortunately poly-ethylene was not suitable for the matrix with silicate layers, but a good electric insulator character was expected for the hybrid [12].

7.4 Nylon-Clay Mineral Hybrids (NCH) by Toyota R&D Lab

In early stages of the development of inorganic filler with organic polymer in Toyota R&D Labs in the early 1980s, the combination of smectite and polyamide (Nylon) was decided. Nylon, which has been widely used as an engineering plastic, is a most suitable matrix because of the plentiful polar segments to interact with the surfaces of inorganic additives. An infinite swelling of Na-montmorillonite with water has been confirmed and a similar swelling was expected for smectites and organo-smectites with suitable guest molecules.

Amino acid-6 $[NH_2(CH_2)_5COOH]$ formed an intercalated compound with montmorillonite cation exchanged with $NH_3^+(CH_2)_5COOH$ and polymerized to 6-polyamide by heating at 250 °C. Although the interlayer spacing was increased by increasing the amino acid content to form single, double, and triple polymer layers as shown in Fig. 7.4, the interlayer distance was not increased more than

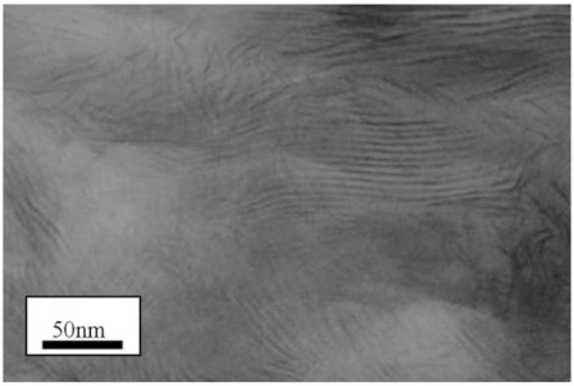


Fig. 7.5 TEM images of 81.8 wt% 6-polyamide/montmorillonite compound

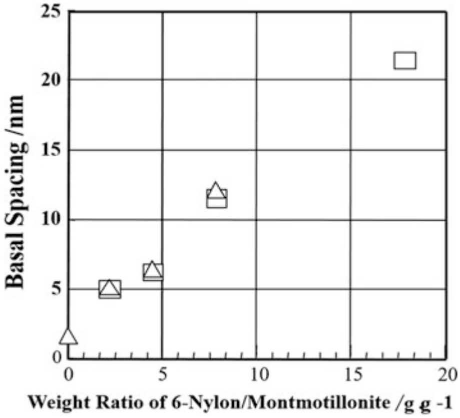


Fig. 7.6 Interlayer distance of 6-polyamide/montmorillonite compounds. *Open triangle*; by X-ray diffraction, *Open square*; by TEM

2.3 nm [11]. An attractive force between the amino acid molecules and the dehydration polymerization enthalpy were not enough for infinite swelling.

A ring molecule ε-caprolactam (NH–CO–$(NH_2)_5$) is also a monomer of 6-polyamide. The ε-caprolactam formed an intercalated compound with the cation exchanged montmorillonite for $NH_3^+(CH_2)_{11}COOH$ whose interlayer space; Δ*d*, was 3.9 nm [13], at 100 °C, about 32 °C higher than the melting point of ε-caprolactam. A following heating at 250 °C made ring-opening type polymerization to form 6-polyamide. The interlayer space; Δ*d*, of X-ray diffraction peaks at *d* = 5.2, 6.9, and 10 nm, which correspond Δ*d* = 4.2, 5.9, and 9 nm respectively, were observed for the compounds with 68.5, 81.8 and 88.7 wt% of 6-polyamide [14]. A TEM image of 81.8 wt% 6-polyamide/montmorillonite shown in Fig. 7.5 also confirm the black line of silicate layers were dispersed in the polyamide matrix [14]. The interlayer distance shown in Fig. 7.6 was increased with increasing the polymer contents and the results of X-ray diffraction and TEM observations were in good agreement. These results suggested the tendency of infinite swelling like water/Na-montmorillonite was also observed for 6-polyamide/montmorillonite compounds. The driving force for the swelling was not the interaction between the silicate layer surface and guest molecules. The –COOH part in the interlayer cation initiated open ring polymerization, followed by the polymerization in the interlayer regions. The polymerization enthalpy of the ε-caprolactam; about 14 kJ/mol, is sufficient to promote the swelling. Pre-swelling of the cation exchanged clay with liquid ε-caprolactam at above the melting point, 68 °C, encouraged the subsequent swelling. The tendency to indefinite swelling after polymerization was also observed for montmorillonite with other exchangeable cations, $NH_3^+(CH_2)_5COOH$, Al^{3+}, H^+, and Cu^{2+}, which had the polymerization initiation effect, but they were not swollen by liquid ε-caprolactam at 100 °C [13]. The increase of interlayer spaces before the polymerization was not an essential condition, but the initiation site in the interlayer region was essential for infinite swelling.

The compounds in which the silicate layers had separated more than 5 nm could disperse in a 6-polyamide matrix during subsequent mixing, excluding and forming processes. They have excellent mechanical properties, heat resistivity, high transparency, and gas barrier effects [15, 16]. They were commercialized and named NCH.

7.5 Exfoliation Process for Clay-Polymer Nanocomposites (CPNs)

Following the development of NCH, dispersing the silicate layers in engineering plastics has been investigated, these materials are the clay-polymer nanocomposites (CPNs). As polyolefin is one of the most widely used engineering plastics, the challenge to get well dispersed CPNs has been concentrated on nonpolar polypropylene nanocomposites with polar clay minerals. Modifications of clay minerals to increase an affinity with nonpolar polymers and to decrease the attractive force of face-to-face stacking of silicate layers and the following exfoliation processes are common methods for developing engineering plastics.

Distearyldimethylammonium $[(CH_3)_2N^+((CH_2)_{17}CH_3)_2]$ cations covers the polar surfaces of silicate layers. Polypropylene oligomer modified with maleic anhydride has polar groups to mediate the intercalation process with the cation exchanged montmorillonite [17]. Expanding the interlayer gallery by intercalation facilitated exfoliation of the modified silicate layers. These exfoliated layers are dispersed in a melted polypropylene matrix during the melt mixing and excluding processes. The obtained clay-polypropylene hybrid wherein many fractions of silicate single layers were exfoliated exhibited good mechanical properties [17].

7.6 Polymer Processing and Optimization of Properties for CPNs

CPNs have been prepared by various molding processing methods in the past. Almost all of the processes are conventional, such as injection molding, extrusion, blow molding or film formation, and so on. On the other hand, much effort in the field of CPN has been focused toward increasing the mechanical strength, barrier property, and flame retardency of the composites using clay nanosheets. The next topic is the development of nanocomposites that have practical levels of flame retardency, rigidity, and moldability while using the morphology control technique by changing the melt-compounding procedures.

In terms of environmental conservation, the use of nonhalogen compounds for flame-retardant plastics is already receiving a lot of attention. When CPNs burn, the dispersed nanoparticles in the polymers form a char layer on the surface. In the plastic electronic field, UL94 recognition (a plastics flammability standard developed by Underwriters Laboratories in the USA) is required, and in many cases the standard required for parts is UL94 V0. In conventional nonhalogen techniques for attaining the UL 94 V0 standard, it was needed to blend more flame retardant even though they achieved V0 flame retardancy. Consequently, we tried to prepare 66-polyamide (PA66) nanocomposites containing small amounts of melamine-modified clay (MelClay) and melamine cyanurate (MC) by changing the compounding procedures [18].

The compounding procedure includes a single- and a multi-stage kneading process which enables control of the dispersion of MelClay (Fig. 7.7). In the single-stage kneading, the raw materials, PA66 and MelClay, are integrally placed

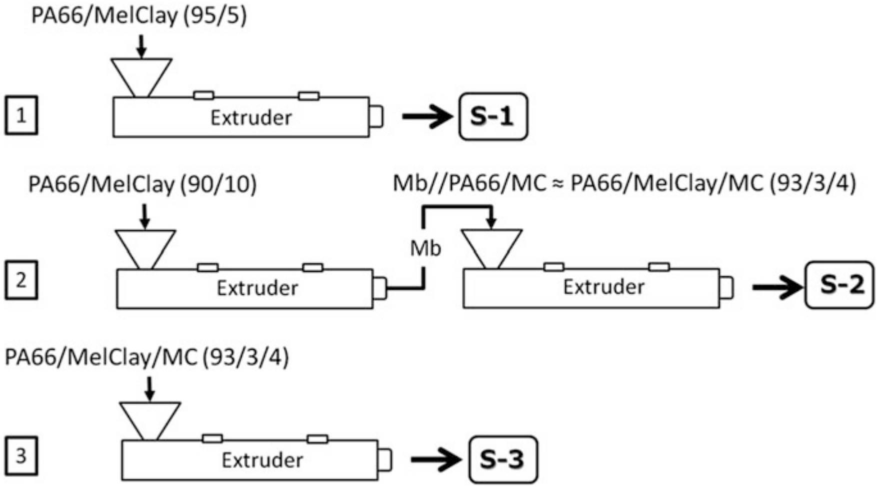


Fig. 7.7 Schematic illustration of the melt-compounding procedures using extruder

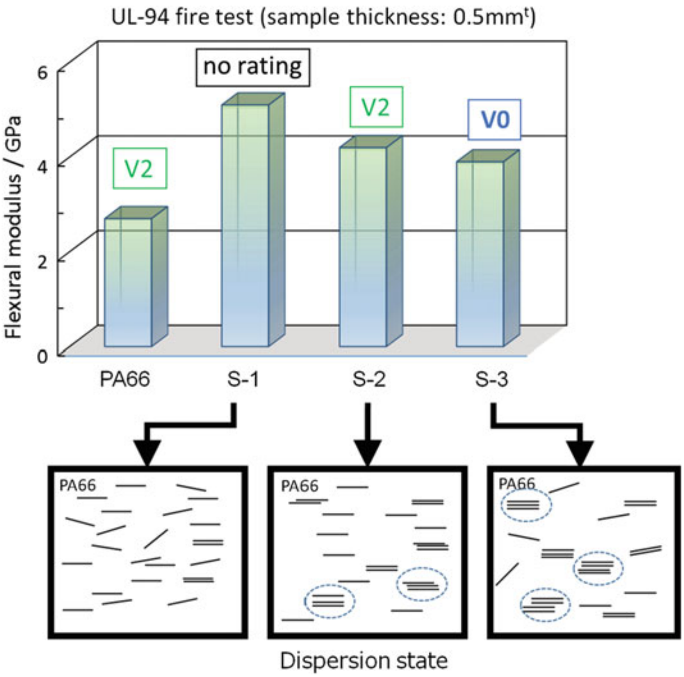


Fig. 7.8 Correlation between the dispersion state of the clay mineral layers and flame retardancy. S-3 has good flame-retardant properties and high mechanical performance

in the kneader (sample: S-1). The multi-stage kneading method comprises, as a first step, the production of a 10 wt%-MelClay master batch (Mb) by mixing and kneading of the PA66 pellet with MelClay, and, as a second step, production of the final compound by mixing and kneading the Mb and MC with PA66 as a diluents (sample: S-2). Samples of MelClay with different dispersion states were obtained by changing the melt-compounding procedures for PA66, MelClay, and MC (sample: S-3). In the experiment, we also found a correlation between the dispersion state of the MelClay layers and flame retardancy in this system.

Ultimately, the S-3 nanocomposite manufactured by one-stage kneading together of PA66, MelClay, and MC was given a UL94 rating of V0 (Fig. 7.8). The flame retardancy in dripping particles during combustion was found to be due to the uneven dispersion of MelClay in the PA66 matrix. The nanocomposites also have high mechanical performance. Additionally, the material shows good workability due to its low viscosity, resulting from the addition of significantly less flame retardant, and can be used to manufacture thin-wall products.

Finally, let us move on to another topic. Electrospinning is a technology that uses electric fields to produce nonwoven fabrics comprising small fibers with diameters that average from a few tens of nanometers to microns (Fig. 7.9). Electrospun nonwoven fabrics can be used in a variety of applications, such as

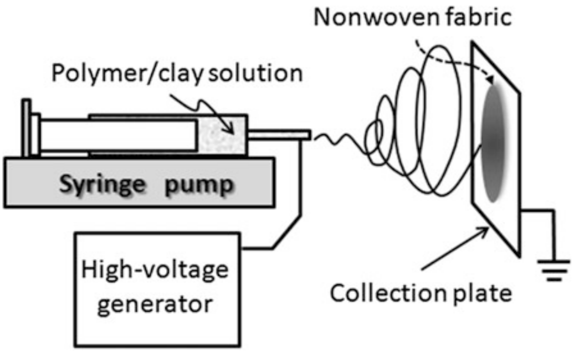


Fig. 7.9 Illustration of electro-spinning apparatus. A fibrous material is formed from the released raw material by electrostatic drawing phenomenon and collected by a collection plate

filtration, tissue engineering, fuel cell membranes, catalytic systems, and sensors. New functional nonwoven fabrics might be obtained by applying this technique to CPNs. For example, to create electrospun nanofiber membranes for direct contact membrane distillation (DCMD) applications, membrane pore wetting consisting of poly(vinylidene fluoride) (PVDF) blended with clay nanofiller has been investigated [19]. The effect of clay on the contact angle of the PVDF–clay nanocomposite membrane was clearly identified to be increasing as the clay concentration increases. Additionally, the melting point of the nanocomposite increased with the increasing concentration of clay particles since the clay particle influenced the crystallization process of the nanocomposite membrane.

In the CPN electro-spinning technique, a solvent capable of dissolving the polymer and swelling the clay have to be selected. Therefore, even if an enthalpy gain is insufficient in the system, an entropy-driven intercalation might be expected to occur due to favorable interactions between the polymers and the surface of the clay layers. One key factor might be the need for high-energy mixing that often was accomplished with sonication. The development of polymer processes in which components are mixed will become more and more important in the future.

7.7 Progress in the Development of New Hybrids

Some clays form smooth gels when mixed with sufficient water. By utilizing this nature, research on hydrogels containing clay nanosheets have been reported. In earlier studies, Haraguchi et al. synthesized nanocomposite gel (NC gel) through in situ free-radical polymerization of N-isopropylacrylamide (NIPA) in the presence of inorganic clay in aqueous solution [20]. The NC gel possesses very large deformability, amazing toughness, and high optical transparency [21], because the material could be prepared using a covalent cross-linkage between the clay surface and the polymer. This NC gel has upset the existing common knowledge that polymer gels are brittle and weak, and carved out new growth investigation areas.

In contrast, a clay-dendrimer hydrogel which is formed only by noncovalent forces was also reported [22]. The components are water and clay (2–3% by mass), which when mixed with a very small proportion (−0.4% by mass) of organic components quickly form a transparent hydrogel. This material can be molded into shape-persistent, free-standing objects owing to its exceptionally great mechanical strength, and rapidly and completely self-heals when damaged. These new NC hydrogel systems could extend the field of high performance materials beyond traditional applications to encompass new unexpected functionalities.

Incidentally, clay minerals include not only layer structures, but also forms of spherical or round tubular pedestals. Each of them has their unique physicochemical properties including adsorption characteristics and colloidal nature [23, 24]. Here, we also refer to the hybrids with tubular clay. Imogolite, consisting of hollow tubes with an external diameter of approximately 2–3 nm (Fig. 7.10a), is a naturally occurring hydrous aluminosilicate found in soils of volcanic origin with a SiO_2/Al_2O_3 ratio of about 1.0 [25]. It has high aspect ratio and surface area with length runs from several hundred nanometers to micrometers (Fig. 7.10b). However, there are some problems in imogolite nanotechnology that remain to be overcome. These include the uniform dispersion of imogolite inside a polymer matrix, tunability of imogolite dimensions (diameter and length), and interfacial adhesion between nanotube and polymer matrix. However, if these problems are resolved, it is anticipated to have numerous applications as a nanofiller similar to a carbon nanotube.

The affinity at interfaces between the inorganic nano-materials and organic matrix has to be appropriately adjusted when forming the hybrid materials. Sometimes, the incompatibility with the hydrophobic polymer has prompted the need to surface modify the imogolite. Several methods have been investigated to convert the surface property of imogolite by grafting with organic modifiers such as organosilanes, and organophosphonic acids [26, 27]. If water-soluble polymers or hydrophilic polymers were used, what effects are imparted for the improving properties of CPN? Sohn et al. have reported that a nanocomposite hydrogel composed of acrylic acid-modified imogolite by grafting techniques has excellent mechanical properties [28]. It shows great tensile strength up to about 1800% extension, and it recovers its original shape immediately after the release of stress.

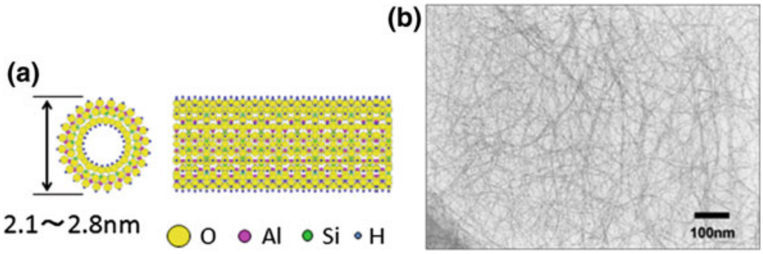


Fig. 7.10 Imogolite images: **a** the molecular structure models of imogolite, and **b** TEM image of synthetic imogolite

Many problems still remain unresolved before it can be put to practical use, however, the unique developments of these new hybrid systems are expected to significantly expand in the future.

7.8 Conclusions

Now, a wide variety of silicate layer hybrids with polymers are available. An approach to intercalation reactions using swelling followed by hybridization was confirmed. Although the subsequent mixing processes with melted polymers offer useful materials, it is not clear if the process is exfoliation or delamination, and if the obtained materials are hybrids or mixtures. The goal of developing hybrid clay materials should be to consider clay characteristics and the assimilation/adaption of metal alloy technology.

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