

Accounts

Nanocomposites Based on Polytetrafluoroethylene and Ultrahigh Molecular Weight Polyethylene: A Brief Review

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Deficiencies in wear and frost resistance as well as mechanical strength constitute the main causes of equipment failure under the harsh climatic conditions of the Earth's polar regions. To improve the properties of the materials used in this equipment, nanoparticle composites have been prepared from clays such as kaolinite, hectorite, and montmorillonite in combination with polytetrafluoroethylene (PTFE) or ultrahigh molecular weight polyethylene (UHMWPE). A number of techniques have been proposed to disperse silicate particles in PTFE or UHMWPE polymer matrices, and several successful processes have even been widely applied. Polymer nanocomposites that exhibit enhanced mechanical and thermal properties are promising materials for replacing metals and glass in the equipment intended for Arctic use. In this article, we will review PTFE- and UHMWPE-based layered silicate nanocomposites.

Key Words : Nanocomposites, Polytetrafluoroethylene, Ultrahigh molecular weight polyethylene, Arctic use

Introduction

In contrast to other geographical areas, the climatic conditions in the Earth's polar regions are marked by extremely low temperatures that vary widely both daily and annually. For exposed machinery, vehicles, and equipment, these

distinctive weather conditions result in many problems, such as leaking at joints and seals in water and gas pipelines, the loss of elasticity and reduced durability of automobile tires, fluid leakage from the many different valves in mining and industrial equipment, and easy breakage of rings in hydraulic lifts and friction units. Therefore, the extreme winter cold

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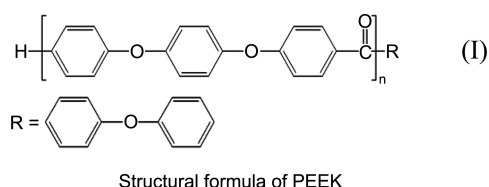
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necessitates that the materials used in exposed equipment exhibit many specific physical and tribomechanical properties, including strength as well as wear and frost resistance.¹ Deficiencies in the latter two properties constitute the main causes of equipment failure in winter. In order to solve such problems, extensive studies on the nanotechnological applications of polymers have been conducted.² Polymer nanocomposites often exhibit enhanced mechanical and thermal properties, which can increase equipment durability.³ Such nanocomposites are promising materials for replacing metals and glass in equipment intended for Arctic use.⁴⁻⁶

Recent studies of polymer–clay nanocomposites, in which the aluminosilicate platelets of a clay such as montmorillonite (MMT) are well exfoliated into a polymer, have suggested a variety of scientific and industrial applications because of anticipated improvements in mechanical properties, stiffness, thermal stability, chemical resistance, barrier properties, and flame retardancy.⁷ Because the polymer matrix plays a significant role in the frost resistance of such composites, the selection of an appropriate polymer is very important.⁸

Among the commonly available engineering polymers, polytetrafluoroethylene (PTFE) meets the requirements for Arctic use. Its antifriction and mechanical properties remain nearly unchanged between 200 and $-150\text{ }^{\circ}\text{C}$.⁹ PTFE is a useful bearing material since it exhibits a low coefficient of friction when rubbed against metallic engineering surfaces.¹⁰ The friction coefficient of PTFE is lower than those of other engineering polymers such as high density polyethylene (HDPE), low density polyethylene (LDPE), nylon, and polyetheretherketone (PEEK).¹¹ However, PTFE cannot be used as an engineering polymer because of its low wear resistance.



Ultrahigh molecular weight polyethylene (UHMWPE) is a well-known thermoplastic polymer that is widely used in a range of industrial applications because of its excellent physical properties, including high toughness, abrasion resistance, and chemical resistance.¹² In particular, note that UHMWPE exhibits better mechanical characteristics and higher wear resistance than PTFE, in addition to similar chemical resistance. Both UHMWPE and PTFE possess higher viscosities above their melting points as compared to other thermoplastics; therefore, their processing for the manufacture of detailed parts is very difficult.¹³ However, nanocomposites based on these materials can mitigate some of the disadvantages of the parent polymers (*i.e.*, their relatively low load-carrying capacity, low wear resistance for PTFE, low melting point for UHMWPE, and low thermal conductivity).^{14,15} Because of their inexpensive fillers and excellent properties (high barrier and mechanical properties, chemical resistance, flame retardancy, and thermal stability),

some of the most common nanocomposites are based on polymer/layered silicate blends. In this article, we will review PTFE- and UHMWPE-based layered silicate nanocomposites.

Historical Review

Since 1950, attempts to prepare polymer/layered filler composites have been described in many articles and patents.¹⁶⁻¹⁹ The major difficulty in fabricating these composites is the dispersion of clay particles in the polymer matrix because of facile clay particle agglomeration, which results from the incompatibility between the hydrophilic silicates and the hydrophobic polymers. The poor clay particle dispersion improves only material rigidity, but does not improve strength and elasticity.²⁰ In 1976, researchers at Unitika Ltd. in Japan tried to solve the agglomeration issue by preparing polyamide-6/layered silicate composites (as opposed to nanocomposites) *via in situ* polymerization of ϵ -caprolactam with montmorillonite.²¹ Another attempt, by Fukushima and Inagaki of the Toyota Central Research & Development Laboratories, Inc. (TCRD) in 1987, successfully replaced inorganic cations in the interlayer space of the native clay with alkyl ammonium species. This method significantly enhanced the compatibility of the clay and the hydrophobic polymer matrix.²² Such modified clays are known as lipophilized, organophilic, or simply, organo-clays. Japanese researchers further discovered that lipophilization promoted the expansion of silicate nanogalleries and the exfoliation of silicate layers into single nanometer-thick sheets. In 2006, Okamoto prepared for the first time an exfoliated polyamide 6/MMT hybrid *via* thorough dispersion of alkylammonium-modified MMT and *in situ* polymerization of ϵ -caprolactam.²⁰

Types of Polymer–Silicate Nanocomposites. The nanoparticle composites discussed in this review are prepared from clays such as kaolinite, hectorite, and montmorillonite in combination with PTFE or UHMWPE. In general, the thickness of the silicate layers in such clays is approximately 1 nm, and the total surface area of the layered silicate platelets is 700–800 m²/g. Small amounts of layered silicates can be dispersed uniformly through a polymer matrix by maximizing the surface area for the polymer–filler interaction. Three different types of polymer–layered silicate (PLS) nanocomposites are thermodynamically favorable.²³⁻²⁵ They depend on the interfacial interactions between the polymer and the layered silicates, which can be modified by different methods. In Figure 1, the three varieties of polymer clay nanocomposites are schematically illustrated. They consist of:

(a) Conventional composites with tactoids: Stacks of modified layered silicates remain after the introduction of the polymer. The initial distance between the layers is about 1.2–1.4 nm. Subsequent interactions between the polymer and layered silicates do not improve the mechanical properties of the composites.²⁶⁻²⁸

(b) Intercalated nanocomposites: Polymer chains intercalate

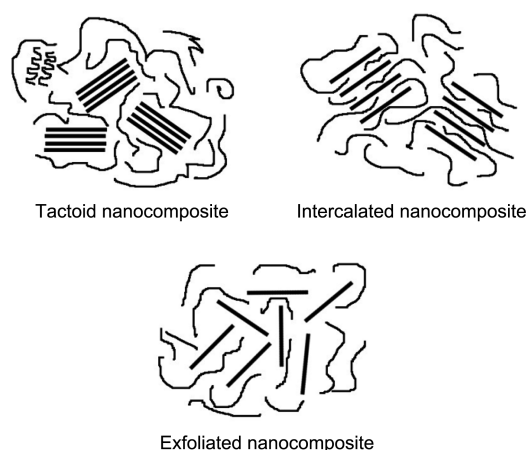


Figure 1. Types of polymer-layered silicate nanocomposites.

into the clay host galleries, but the platelets remain parallel. Only one of the polymer chains can intercalate between the clay platelets.

(c) Exfoliated nanocomposites: The insertion of polymer chains into the clay galleries results in separation of the individual clay layers and further expansion. Before intercalation, the distance between the layers is 1 nm; however, the distance is increased to 8–10 nm after the insertion of the polymer chains into the clay galleries, as shown in the figure. The layers exfoliate individually and distribute uniformly throughout the polymer matrix. This kind of exfoliation can improve mechanical and tribotechnical properties as well as flame resistance, and leads to high-performance nanocomposites.

To characterize such types of structures, two methods are mainly employed. First, X-ray diffraction (XRD) is used to identify the intercalated structures. Nanocomposites having a multilayer structure may be evaluated by the distance between the layers, which can be determined because the repetitive multilayer structure is well maintained. The introduction of the polymer macromolecules between the silicate layers typically increases interlayer distances, which leads to a shift of the diffraction peaks to lower angle values. Values of the angle and distance between the layers may be calculated using the relevant Bragg relationship as follows:

$$n\lambda = 2d \sin\theta$$

where λ corresponds to the wavelength of the X-ray radiation used in the diffraction experiment, d is the distance between the layers, and θ is the measured diffraction or glancing angle (Figure 2).^{29,30}

Intercalation is usually detected by XRD analysis. The lack of silicate basal reflections in the XRD pattern of a nanocomposite indicates the complete exfoliation of the silicate layers in the polymer.³¹ For example, the 001 peak generally corresponds to the distance between silicate layers, and changes in this distance result in a peak shift. Figure 3 shows the XRD patterns of modified and original MMT samples as well as a MMT/UHMWPE nanocomposite.³² The shift of the 001 peak to lower angles reflects the increase

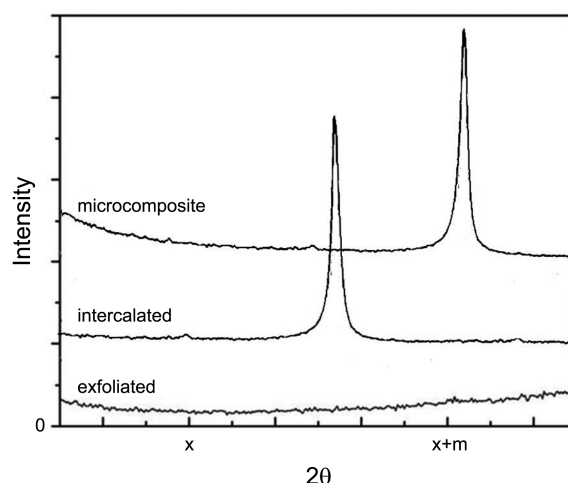


Figure 2. XRD patterns of a phase-separated microcomposite, an intercalated nanocomposite and an exfoliated nanocomposite.³⁰

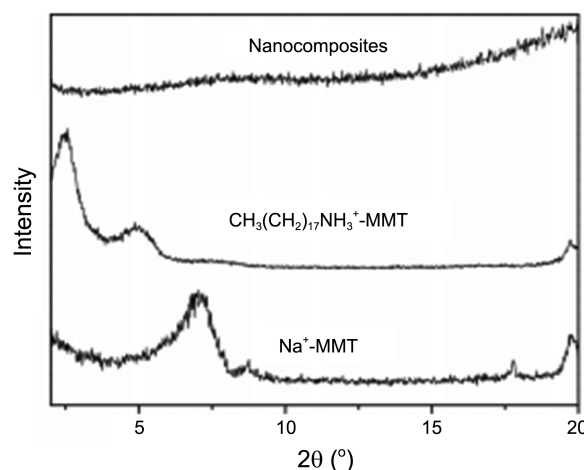


Figure 3. X-ray diffraction patterns of Na^+ -MMT, $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3^+$ -MMT, and a MMT/UHMWPE nanocomposite.³² Reproduced from Park and Hong by Permission of Elsevier B. V.

of the distance between the planes from 12.5 to 36.2 Å. This result shows that the $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3^+$ chain penetrated into the galleries of MMT and increased the distance between the layers of the silicate.³³ The lack of a peak for the nanocomposite indicates its complete exfoliation.

In Figure 4, the XRD patterns of serpentinite and PTFE nanocomposites with or without magnesium aluminate spinel (MAS) are presented.³⁴ Although the peak due to the starting silicate is observed in the composite with 5 wt % serpentinite ($\theta = 2\text{--}12^\circ$), it cannot be seen in the XRD patterns of the composites with both serpentinite and MAS. Thus, the introduction of MAS leads to the disappearance of peaks corresponding to the silicate interlayer space in the XRD pattern, indicating the full exfoliation of the serpentinite layers to monolayers.³⁵

Diffraction peaks in the XRD patterns cannot be detected if the interlayer distance exceeds 6–7 nm or the nanocomposite lacks a crystalline phase. In such cases, transmission electronic microscopy (TEM) is used to characterize the

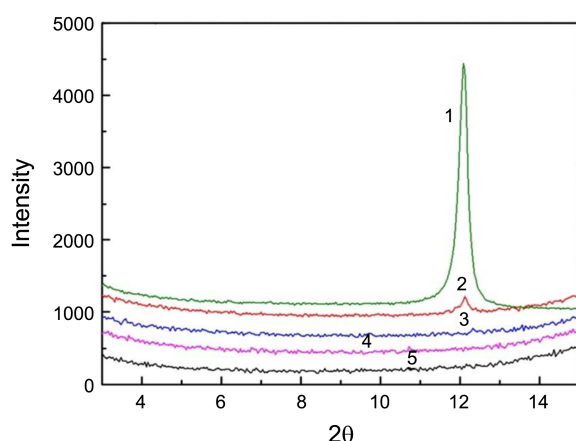


Figure 4. X-ray diffraction patterns of PTFE/layered silicate nanocomposites: (1) serpentine processed in a planetary mill, (2) PTFE containing 5 wt % serpentine, (3) PTFE containing 4.5 wt % serpentine and 0.5 wt % MAS, (4) PTFE containing 4 wt % serpentine and 1 wt % MAS, and (5) initial PTFE.³⁴

nanocomposite morphology. Figure 5 shows TEM micrographs that illustrate both intermediate intercalated and exfoliated nanocomposite structures. Both XRD and TEM methods are used to determine the exact structures of the intercalated or exfoliated nanocomposites, but they must be correlated with each other.^{24,29}

Preparation of Nanocomposites. A number of techniques have been proposed to disperse silicate particles in PTFE or UHMWPE polymer matrices, and several successful processes have even been widely applied. In the plastics industry, the three most popular methods of mixing polymers with nanoparticles are dispersion in solution, *in situ* copolymerization, and melt blending. The main difficulty in effectively dispersing silicate particles in a polymer matrix is their tendency to agglomerate. PLS nanocomposites are usually prepared by *in situ* polymerization, which is useful for polymers such as HDPE, LDPE, and thermosets.³⁶ However, for PTFE, it is difficult to fabricate a nanocomposite in this manner.

Methods of Preparing PTFE-Based Nanocomposites: The chemical resistance of PTFE is similar to those of noble metals, enamels, and special steels, and thus, it can be used for sliding bearings as well as sealing and insulation parts from -269 – 260 °C. Because PTFE has excellent electrical insulating properties over a wide range of electrical frequencies and temperatures, it is a unique dielectric. PTFE shows high strength, toughness, and self-lubricating properties, and

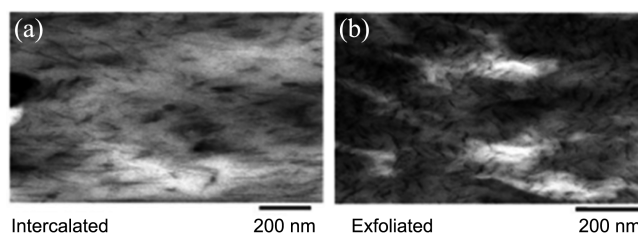


Figure 5. TEM images of two different types of nanocomposites: (a) intercalated, and (b) exfoliated.²⁴ Reproduced from Ray and Okamoto by Permission of Elsevier B. V.

maintains flexibility even at -80 °C. Although PTFE has cold flow ability when loading, this can be mitigated by the incorporation of fillers. In comparison with other plastic materials, PTFE has the lowest friction coefficient against steel (~ 0.04), which results from the ability of PTFE macromolecules to generate films with low shear strength in the polymer–metal contact zone.³⁷

PTFE crystallites melt at temperatures over 327 °C, but the polymer does not transform into a plastic state until its decomposition temperature at 415 °C. In this context, the characteristics of PTFE composites make them very useful for sliding applications. Other disadvantages of PTFE can be corrected by introducing different fillers, depending on the purpose of the materials. The main disadvantage of PTFE is its low durability. Therefore, the friction and wear behaviors of filled PTFE have been extensively investigated.³⁸ For example, Cheng, Xue, and Xie studied the effect of glass fibers on the tribological performance of PTFE-based nanocomposites.³⁹ Table 1 shows friction and wear results for PTFE composites filled with Pb and glass fiber (GF) in dry reciprocating sliding under static loads. The GF was modified with three types of surface modifiers: an alcoholic solution (coded as SGS) of 1.0 wt % *N*- β -aminoethyl- γ -aminopropyltrimethoxysilane coupling agent (*i.e.*, SG-Si900), an alcoholic solution (coded as SGS/RES) of 1.0 wt % SG-Si900 and 0.3 wt % rare earths, and an alcoholic solution (coded as RES) of 0.3 wt % rare earths.

In general, the introduction of an inorganic filler into a polymer increases its durability. Nano- and micro-composites from PTFE are difficult to prepare because liquid phase technologies cannot be used for this material.⁴⁰ The high viscosity and insolubility of the polymer prevent preparative approaches such as the mixing of the nanofillers and the binder solution (or melt), even though a variety of mechanical mixing techniques have been examined.

Table 1. Friction and wear results of the PTFE composites filled with Pb and glass fiber GF in dry reciprocating sliding under static loads (reciprocating sliding frequency, 2.4 Hz; maximum static load, 1000 N)³⁹

Material ^a	Friction coefficient	Wear (mg)
PTFE + 60 wt % Pb + 5 wt % unmodified GF	0.285	83.1
PTFE + 60 wt % Pb + 5 wt % SGS modified GF	0.276	63.5
PTFE + 60 wt % Pb + 5 wt % SGS/RES modified GF	0.249	51.3
PTFE + 60 wt % Pb + 5 wt % RES modified GF	0.227	35.2

The nanosized fillers used to prepare PTFE composites have been studied extensively.⁴¹ The Russian researchers Okhlopkov and Vinogradov studied the effects of various fillers with particle sizes of 40–70 nm on the structure and properties of PTFE.⁴² They obtained significant increases in wear resistance (20–30-fold) with relatively low concentrations (0.5–2.0 wt %) of nanofillers (oxides, nitrides, and carbides of silicon, aluminum, and other metals).^{42–46} Recently, the tribological properties of PTFE composites filled with nanosized zinc⁴⁷ and aluminum oxides³⁸ were investigated. These studies showed some increases in the wear resistance of PTFE upon the introduction of small amounts of nanofillers. The low-filled PTFE composites retain the high physical and mechanical properties of the initial unfilled polymer. This is particularly important in composites for dynamic sealing parts.

There are many kinds of fillers for the polymer composites. One class of well-known fillers consists of the layered silicates, which are particularly effective polymer modifiers. Significant improvements in the performance of polymers with layered silicates have been demonstrated by Kojima and colleagues for nylon/clay nanocomposites.⁴⁹ According to their studies, enhancements included increased modulus, strength, and heat resistance, as well as reduced gas permeability and flammability. Additional performance improvements will be discussed later.

Several methods for producing composites have been developed. For example, composites have been obtained from a mechanically activated mixture of PTFE powder and ultrafine metal or ceramic powders.¹⁰ This method involves the encapsulation of inorganic particles (such as copper) in the fluoropolymer. The composite can be deposited on a metal surface such as aluminum using the cold gas spraying method. The coating of the aluminum surface by the encapsulated copper imparts both the strength and electrical and thermal conductivities similar to the values observed for copper metal, as well as the hydrophobicity and tribological characteristics of the fluoropolymer. This method can be applied to the coating of any large metallic

parts and items.

Another method for PTFE composite preparation uses a slurry of an ultrafine polymer powder in oil.⁴⁰ After transferring the fluoropolymer particles to a fluidized bed surface at elevated temperature, a solution of metal-containing compounds is dripped onto the reactor bed. The metal-containing compounds then form nanoparticles, which would agglomerate under normal conditions. However, in the presence of PTFE, individual nanoparticles of about 10 nm in size, which can function as catalysts, are immobilized on the surface of the fluoropolymer matrix base.

Supercritical CO₂ can be used to create polymer–polymer composites consisting of a core and a shell which differ in composition and physicochemical properties.⁴⁰ The method is based on the stabilization of the paraffin emulsion in supercritical CO₂ fluid through the addition of ultrafine PTFE powder. Spherical particles with 50–300 μm diameters and 10 μm thick fluoropolymer shells are formed. This method can be used to encapsulate material in neutral and non-toxic fluoropolymer coatings.⁴⁰

Methods of Preparing UHMWPE-Based Nanocomposites. The traditional high-performance processing methods and equipment used for polyethylene (*e.g.*, extrusion and injection molding) are unsuitable for processing UHMWPE because of its high viscosity. However, a great deal of research has been devoted to the development and improvement of techniques appropriate for UHMWPE processing and production.⁵⁰ Methods such as hot pressing, sintering, re-extrusion, spraying (in high temperature fire or under electrostatic conditions), and fiber-forming gel formation have been applied on commercial scale.

UHMWPE is highly viscous above its melting temperature. At normal pressure, UHMWPE powder cannot be transformed to the viscous state before it decomposes, which is principally why the processing of UHMWPE powder into products (plates, pipes, seals, *etc.*) is difficult. However, the gel-spinning and drawing-oriented processing of UHMWPE powder is possible and affords high-strength filaments. Many companies such as DSM (Netherlands), Honeywell (USA),

Table 2. Tensile mechanical properties of HDPE/PEgMA/clay nanocomposites⁵¹

Sample composition		Lupolen			Eltex		
		Modulus, E (MPa)	Tensile strength, σ_y (MPa)	Elongation at break, ϵ_r (%)	Modulus, E (MPa)	Tensile strength, σ_y (MPa)	Elongation at break, ϵ_r (%)
HDPE/PEgMA/clay	100/0/0	932 $\pm$ 41	27.7 $\pm$ 0.1	1173 $\pm$ 50	1252 $\pm$ 32	30.5 $\pm$ 0.2	1650 $\pm$ 302
	100/10/0	877 $\pm$ 36	27.2 $\pm$ 0.3	922 $\pm$ 282	1168 $\pm$ 75	30.6 $\pm$ 0.2	1697 $\pm$ 566
Cloisite 15A	98/0/2	934 $\pm$ 18	27.7 $\pm$ 0.5	166 $\pm$ 23	—	—	—
	95/0/5	928 $\pm$ 21	26.0 $\pm$ 0.4	36 $\pm$ 25	—	—	—
	88/10/2	1156 $\pm$ 45	27.8 $\pm$ 0.4	225 $\pm$ 97	1283 $\pm$ 114	29.7 $\pm$ 0.1	1406 $\pm$ 809
	85/10/5	1112 $\pm$ 64	—	14 $\pm$ 8	1379 $\pm$ 85	28.7 $\pm$ 0.1	21 $\pm$ 7
Cloisite 20A	98/0/2	917 $\pm$ 62	28.2 $\pm$ 0.2	172 $\pm$ 18	—	—	—
	95/0/5	975 $\pm$ 87	26.7 $\pm$ 0.3	14 $\pm$ 3	—	—	—
	88/10/2	1147 $\pm$ 40	28.1 $\pm$ 0.2	51 $\pm$ 45	1400 $\pm$ 65	30.3 $\pm$ 0.2	692 $\pm$ 516
	85/10/5	1184 $\pm$ 37	—	10 $\pm$ 2	1341 $\pm$ 75	29.6 $\pm$ 0.7	18 $\pm$ 7

Table 3. Mechanical characteristics of composites based on UHMWPE and mechanically activated kaolinite⁵³

Sample	Elongation at break, ε_r (%)	Tensile strength, σ_y (MPa)
Pristine UHMWPE	310–320	30–35
UHMWPE + 0.5% kaolinite	390–400	35–40
UHMWPE + 1% kaolinite	360–370	35–40
UHMWPE + 2% kaolinite	310–320	30–35
UHMWPE + 5% kaolinite	300–310	20–25

and Mitsui (Japan) currently employ these technologies.¹⁰

Selyutin and others succeeded in the manufacture of an UHMWPE film by application of an electrostatic field, creating a coating of UHMWPE on a prepared metal surface.⁴⁸ They utilized a processing temperature below 220 °C to manufacture a continuous film of UHMWPE, forming a smooth uniform coating that was 30–50 μm thick on the metal surface.

As is well known, bulk products such as bars, pipes, and plates can be obtained by extrusion. In the case of UHMWPE, plasticizers or a polymer powder with a minimum melt viscosity are used. The extrusion pressure is determined by the molecular weight and melt viscosity of the powder. The most common method of UHMWPE powder processing for a bulk product is hot pressing in special molds. The first stage of hot pressing occurs by pressing at relatively low temperatures (< 100 °C) for 5–10 min under pressures of up to 10 MPa. Air must be removed during this stage in order to fill the entire volume with polymer particles. The second stage, the hot pressing cycle, is carried out at 180–230 °C. The pressing time is determined by the thickness of the resulting products, because it is important to fill the entire volume. Air bubbles that remain in the polymer matrix are difficult to remove. The cooling process must be carried out under pressures close to 10 MPa. After cooling, the decrease in UHMWPE volume is 4–8%. The degree of shrinkage and the hot pressing conditions may be modified significantly by the addition of various fillers. These differences are primarily due to the changes in the heat conductivity of the particles and the nature of the interactions between the polymers and fillers.⁵¹

Properties of Composites. Polyolefins have been increasingly used in recent years to create nanocomposites based on clays. Pegoretti, Dorigato, and Penati investigated the structures and mechanical properties of two types of high-density polyethylenes filled with synthetic clays, as shown in Table 2.⁵¹ They prepared samples using two types of organo-modified clays through the melt compounding of HDPEs with different melt flow rates. The relative amount of the polyethylene grafted was changed by the addition of a maleic anhydride (PEgMA) compatibilizer. The intercalation process was more effective when the matrix melt viscosity was reduced; that is, at a higher melt flow rate, the clay interlayer spacing increased as the compatibilizer amount increased. The relative stiffness of the nanocompo-

Table 4. Mechanical characteristics of composites based on UHMWPE and kaolinite which has been modified using 0.005–0.05 wt % cetyltrimethylammonium bromide as a surfactant depending on filler loading⁵³

Sample	Elongation at break, ε_r (%)	Tensile strength, σ_y (MPa)
Pristine UHMWPE	310–320	30–35
UHMWPE + 0.5% kaolinite	435–445	36–41
UHMWPE + 1% kaolinite	410–420	35–40
UHMWPE + 2% kaolinite	435–445	35–40
UHMWPE + 5% kaolinite	395–405	31–36

Table 5. Mechanical characteristics of composites based on UHMWPE and kaolinite which has been modified using polypropylene⁵³

Sample	Elongation at break, ε_r (%)	Tensile strength, σ_y (MPa)
Pristine UHMWPE	310–320	30–35
UHMWPE + 0.5% kaolinite	320–330	30–35
UHMWPE + 1% kaolinite	310–320	32–37
UHMWPE + 2% kaolinite	290–300	31–36
UHMWPE + 5% kaolinite	295–305	30–35

sites also increased with the addition of clay, but the relative yield stress enhancement was limited. When the compatibilizer was added to the plastic blend, better intercalation was observed without concurrent improvement of the tensile mechanical properties. The creep resistance was also enhanced by the addition of clay. The PEgMA compatibilizer provides creep compliance to the composite, and this efficiency is decreased by the addition of clay to polyolefin composites.

UHMWPE is a more attractive polymer than conventional polyethylene because of its high mechanical characteristics, low friction coefficient, and frost resistance.⁵² The physical and mechanical properties of UHMWPE modified by mechanically activated kaolinite in amounts of 0.5–5.0 wt % have been evaluated.⁵³ Compared with the original polymer, Table 3 shows that a 15% increase in tensile strength and 20% increase in elongation at break were observed. Filling with 0.5–1.0 wt % kaolinite afforded the best results. Thereafter, as the kaolinite loading in the composite increased, the physical and mechanical characteristics deteriorated.

UHMWPE can also be modified with kaolinite filler in the presence of cetyltrimethylammonium bromide as a surfactant or polypropylene as a compatibilizer, as opposed to mechanically activating the kaolinite. Surfactants and compatibilizers are widely used to eliminate the agglomeration of particles which have high surface energies and areas.⁵⁴ Such modifications enhance the adhesion interactions of the interfacial layers in the heterogeneous system and eliminate the agglomeration of kaolinite particles. In another approach, a mechanochemical method of kaolinite surface modification was used. Liquid technologies for surface modification

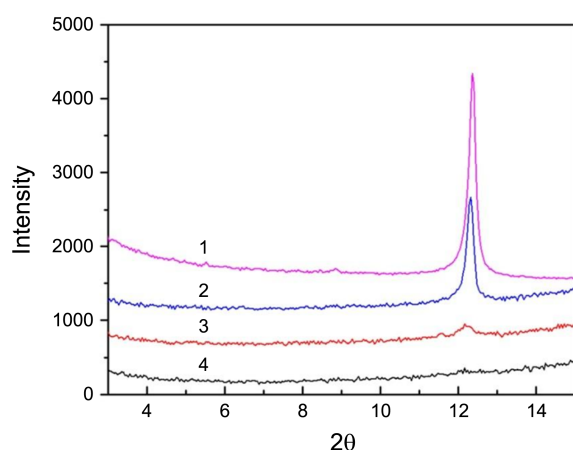


Figure 6. XRD patterns of composites based on UHMWPE and kaolinite filler with a compatibilizer or a surfactant: (1) mechanically activated kaolinite, (2) PCM containing 5 wt % mechanically activated kaolinite, (3) PCM containing 5 wt % kaolinite with a compatibilizer (polypropylene), and (4) PCM containing 5 wt % kaolinite with cetyltrimethylammonium bromide as a surfactant.⁵

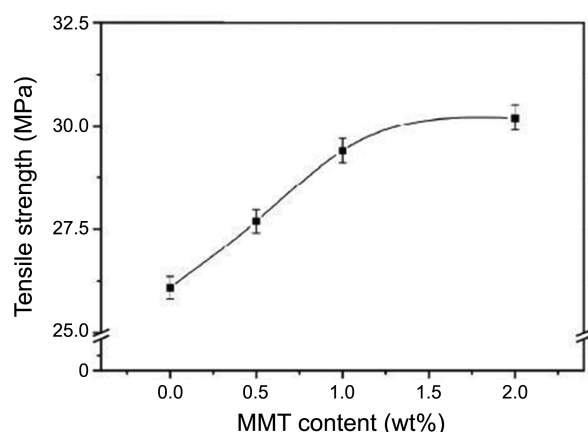


Figure 7. Tensile strengths of MMT/UHMWPE nanocomposites.³² Reproduced from Park and Hong by Permission of Elsevier B. V.

cannot be used in this case because there are no free cations in the interlayer space of the clay. Because a surfactant is both hydrophobic and hydrophilic, we employed it as a surface modifier. Composites prepared using 0.005–0.05 wt % cetyltrimethylammonium bromide as a surfactant depending on filler loading revealed a 17 wt % increase in strength and 33% increase in elongation at break, as shown in Table 4.⁵³ This can be explained by an increase in the adhesive interaction between the filler and polymer matrix in the interfacial layers. We also observed that the deformation and strength characteristics were increased by 5–10% in composites using a compatibilizer. However, Table 5 shows that an increase in the filler content in the polymer does not decrease the strength properties over the entire concentration range, unlike the mechanically activated kaolinite.⁵³

We studied the XRD patterns of the composites in order to explain the property variations of UHMWPE with small amounts of kaolinite.⁵³ The kaolinite peak disappeared in the diffraction pattern when 0.005–0.05 wt % cetyltrimethyl-

Table 6. Tribotechnical characteristics of composites based on PTFE and serpentinite⁵⁵

Composite	The rate of mass wear, I (mg/h)	The friction coefficient, f
PTFE	78	0.04–0.2
PTFE + 2 wt % S	1.8	0.018
PTFE + 5 wt % S	1.2	0.019
PTFE + 10 wt % S	1.5	0.021
PTFE + 2 wt % S act	0.18	0.017
PTFE + 5 wt % S act	0.3	0.019
PTFE + 10 wt % S act	1.5	0.020
PTFE + 1 wt % S + 1 wt % MAS	0.13	0.032
PTFE + 1.5 wt % S + 0.5 wt % MAS	1.07	0.033
PTFE + 1.8 wt % S + 0.2 wt % MAS	2.23	0.044
PTFE + 4 wt % S + 1.0 wt % MAS	0.03	0.041
PTFE + 4.5 wt % S + 0.5 wt % MAS	0.03	0.026
PTFE + 4.8 wt % S + 0.2 wt % MAS	0.27	0.033

Note: S, serpentinite; S act, activated serpentinite; MAS, magnesium aluminate spinel.

ammonium bromide as a surfactant depending on filler loading was used, as shown in Figure 6. This observation may result from the intercalation of the polymers in the interlayer spaces of the kaolinite and exfoliation of the clay sheets into the polymer matrix.³² As is well known, the presence of exfoliated silicate layers leads to a more pronounced effect of the filler on the formation of composite materials.⁵⁴

For comparison, Park and colleagues prepared organically treated MMT/UHMWPE nanocomposites through a melt intercalation technique.³² XRD analysis indicated that the nanocomposites were formed upon exfoliation of the MMT in the polymer matrix, as shown in the top pattern in Figure 3. The nanocomposites showed higher tensile strengths than pristine UHMWPE, as shown in Figure 7. They explained the increase in tensile strength by the dispersion of MMT at the nanoscale level in the UHMWPE matrix.

Tests by the authors showed that modification of a PTFE polymeric matrix by layered silicates resulted in considerable improvement of the composite's tribotechnical characteristics, as shown in Table 6.⁵⁵ The mass wear rate decreased up to 2,500 times in comparison with the unmodified polymer. In addition, the composites exhibited lower friction coefficients than the polymer before modification. Composites containing magnesium aluminate spinel (MAS) showed the highest values of wear resistance while retaining high values of strength and strain characteristics. One of the reasons for the wear resistance of these materials may be the intensification of the adhesion interaction of the components. This indicates the effective participation of MAS in the formation of interfacial layers on the boundary layer of the polymer-serpentinite.

Decreases in the friction coefficient can be related to the change in the structure of the composite surface layer during friction and wear. For example, highly oriented structures

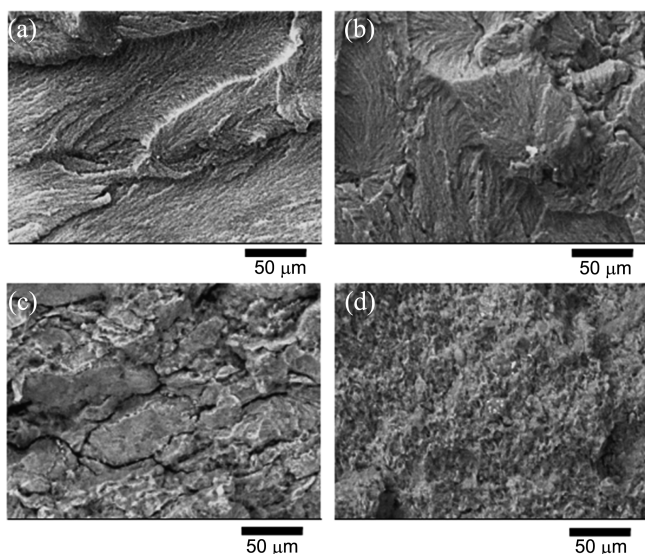


Figure 8. SEM images of brittle split surfaces of (a) PTFE and its composites filled by (b) 1, (c) 10, and (d) 20 wt % commercial carbon, $\times 500$ magnification.⁵⁶

with increased crystallinity compared to the starting polymer can form as a surface layer on a composite, which results in a lowered contact area and concomitant reduction in the friction coefficient. In the case of a layered silicate such as graphite, self-lubricating materials are formed, and consequently, the friction coefficient decreases.

Another way in which the friction coefficient can be reduced is through the formation of a transfer film on the contacted metallic surface during wear.⁴⁷ The film consists of polymer tribodestruction products. During the process of wear, the first run-in period takes place in the maximum wear resistance range (1–5 wt %), and then, a film of transfer forms on the counter metallic face. Only after these stages occur does the friction coefficient significantly decrease. These visible films can be observed by the weight difference of the counter body. During the run-in period, the composite wearing products exist as 1–2 mm flakes. Most of the smaller particles having irregular spherical shapes are separated from the composite wearing products because friction is transferred to the stationary stage.

The nature of the supramolecular structure is related to its wear resistance and friction processing. Most thermoplastic

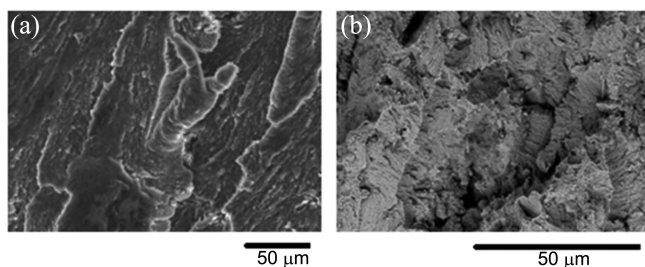


Figure 9. Microphotographs of supramolecular composite structures: (a) pristine PTFE and (b) PTFE containing 5 wt % serpentine.³⁴

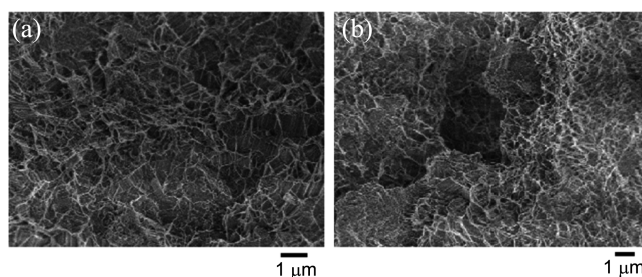


Figure 10. Microphotographs of supramolecular structure of PTFE composite (a, b) containing 4.5 wt % serpentine and 0.5 wt % MAS.³⁴

polymers are characterized by spherulitic structures. Changes in these structures alter the friction coefficient. Small spherulitic structural units provide both a low friction coefficient and low wear.

Structures of PTFE composites have been investigated by scanning electron microscopy (SEM) to determine the effects of various fillers on structure formation and reasons for the property changes.⁴⁸ In Figure 8 are shown the SEM images of PTFE and its composites with various loadings of carbon material.⁵⁶ The split surface of the composite is heterogeneous at a 1 wt % of commercial carbon (Figure 8(b)). The structure contains lamellas in the same direction as in the initial PTFE (Figure 8(a)) and irregular polygons corresponding to spherulitic supramolecular structures (SPS). As the content of the filler increases to 10 wt %, the similarity between the SPS of the composite and the initial PTFE disappears (Figure 8(c)). The average size of the observed irregular polygons is smaller than in the composites with 1 wt % filler, and abundant crystallization centers are evident, although the borders between them become more diffuse. At the maximum degree of filling, the average size of the SPS is further reduced and the number of small micropores is increased (Figure 8(d)). Traces of large 10-micron inclusions, which are most likely coarse filler agglomerates, can even be observed.

We also found that, although pristine PTFE has a typical lamellar structure, a composite sample containing 5 wt % serpentine is quite different, as in Figure 9.³⁴ The morphological analysis of the composite containing serpentine reveals long fibrillose bodies with transverse lamellas wherein chains are in folded configurations. In Figure 10, photomicrographs present the supramolecular structure of a composite containing 4.5 wt % serpentine and 0.5 wt % MAS.³⁴ The polymer composite material (PCM) structure has homogeneous structural elements in which silicate particles are distributed uniformly in the polymer. The polymer and silicate plates bind to each other to form fibrils (Figure 10(b)) as a result of the influence of MAS.

Conclusions and Perspectives

Nanoparticle composites can be prepared from clays such as kaolinite, hectorite, and montmorillonite in combination with PTFE or UHMWPE. The nanosized fillers used to

prepare PTFE composites have been studied extensively. A great deal of research has been devoted to the development and improvement of techniques appropriate for UHMWPE processing and production. Beneficial physicomechanical properties have been achieved by using various surfactants and compatibilizers. The exfoliation of clay in a polymer matrix was confirmed by SEM, XRD, and TEM studies on the supramolecular structures. However, many obstacles remain for producing nanocomposites with exfoliated layered silicates. Further investigations into the preparation of nanocomposites based on layered silicates still remains as a worthy research objective. Polymer nanocomposites are promising materials for replacing metals and glass in equipment intended for Arctic use. Although the mining and development of valuable resources in polar regions, including Siberia, are very limited at present, the very predictable demands of the future will necessitate the solving of problems that result from the distinctive Arctic climate.

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