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Publisher's version / Version de l'éditeur:

Arabian Journal Science & Engineering -- special issue, 27, 1C, pp. 43-67, 2002-06-01

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CLAY-CONTAINING POLYMERIC NANOCOMPOSITES

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تأثير

تناقش هذه الورقة مركبات البوليمر المدعمة بالطين . ومن مزايا استخدام الطين في البوليمر ، توفّرهُ وقلة كلفته ، ونسبة الطول للعرض ، بينما تتضمن مساوئه خواصه الاسترطابية .

وبعد نشر حبيبات الطين في مذيبات مائية من أحادي أو متضاعف المونومر مهمة سهلة نسبياً ، غير أن تحضير مواد البوليمر المركبة الطاردة للماء ذات الوزن الجزيئي المرتفع مثل البولي بروبيلين يعد من العمليات الصعبة . وللتغلب على هذه المشكلة ، يتوجب التعامل مع مكونات عديمة الذوبان التي تتطلب مزجاً قوياً لنشر الحبيبات الطينية . ومن المواد الطينية المفضلة في هذا المجال المونت مورلونايت (MMT) الذي يُعدُّ أفضلها لاحتوائه على حبيبات صغيرة مكونة من مثلث البلورات الطباقية ذات سماكة (٠,٩٦) نانومتر ، وقطر (١٠٠-٢٠٠) نانومتر . وتقدم خلية MMT الواحدة موقعين للتفاعل بالأيون السليبي على سطح السليكات والهيدروكسيل على الأطراف . وتتطلب عملية مواعمة البوليمر مع المادة الطينية تشكيل رابط أيوني قوي بين سطح المادة والعنصر العضوي من خلال الأيون الموجب ، مثل أونيوم أو الأمونيوم . ولقد تضمنت عملية المواعمة مؤخراً مادة الإيبوكسي على مجمعات الأنهيدريد التي تتفاعل مع مجموعات الهيدروكسيل الطرفية . ونظراً لأن الترابط الداخلي للطبقات الصلبة في (MMT) هي أقوى (١٠٠) مرة من الترابط الداخلي للطبقات السائلة ، فإنه يتوجب عمل رابط جيد بين الجزيئات الطينية والعضوية . وتتضمن الاستراتيجية الأفضل لتحضير البوليمرات المركبة مع المادة الطينية المقشرة اتباع عدة خطوات هي : مزج (MMT) بالماء لزيادة المسافات بين الطبقات الداخلية إلى (١,٣) نانومتر مقارنة بـ (٠,٩٦) في المادة الجافة ، والمزج بالجزيئات العضوية ذات الأيونات موجبة الملازمة الأونيوم أو نوع لويس (Lewis) مما يزيد المسافات إلى (٤) نانومتر . وتؤدي المواعمة التفاعلية بين المادة العضوية والطينية والبوليمر عدد عوامل دقيقة إلى تقشر الحبيبات مما يزيد المسافات الداخلية إلى أكثر من (٨,٨) نانومتر .

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ABSTRACT

In this review we discuss clay-reinforced polymeric nano-composites (PNC). The advantages of using clays are availability, cost, and aspect ratio; the main disadvantage is their hygroscopic character. It is a relatively simple task to disperse clay platelets in water-soluble solvents, monomers, or oligomers. However, preparation of PNC in a hydrophobic, high molecular weight, polymer (*e.g.*, polypropylene) is difficult. The way to approach the problem is to consider the process from the perspective of compatibilization of antagonistically immiscible components and diffusion-controlled mixing. The preferred clay is montmorillonite (MMT) with micron-sized particles formed by stacks of hundreds of layered crystals, each of 0.96 nm thickness and an average diameter of 100–2000 nm. The MMT unit cell offers two types of reactive sites: anions on the silicate flat surfaces and hydroxyl (–OH) groups on the edges. Historically, “compatibilization” involved forming an ionic bond between the clay surface and organophilic onium cation, *e.g.*, ammonium. More recently, “compatibilizers” containing epoxy or acid anhydride groups were reacted with the side –OH groups. Since the solid–solid interactions between MMT layers are about 100 times stronger than liquid–liquid ones, good bonding between clay particle and the matrix is imperative. To prepare PNC with well-exfoliated clay, the best strategy is to do it in multiple steps. Initial swelling of MMT in water may expand the interlayer spacing from the initially dry state of 0.96 to about 1.3 nm. Intercalation with suitable organophilic molecules, onium or Lewis-base type increases it to about 4 nm. Reactive compatibilization of the organo–clay/matrix polymer system under flow results in exfoliation of the clay platelets (interlayer spacing larger than 8.8 nm).

CLAY-CONTAINING POLYMERIC NANOCOMPOSITES

1. INTRODUCTION

1.1. General

Nanocomposites (NC) are materials that comprise a dispersion of nanometer-size particles in a matrix. The matrix may be single or multi-component. It may contain additional materials that add other functionalities to the system (*e.g.*, reinforcement, conductivity, toughness, *etc.*). The matrix can be either metallic, ceramic, or polymeric — only the latter type will be discussed in this review. The nano-particles are classified as lamellar, fibrillar, shell-like, spherical, and others. For the enhancement of mechanical and barrier properties, the anisometric particles are preferred.

From the fundamental point of view, the reinforcing effect of nano-particles is related to the aspect ratio (p = platelet diameter/thickness) and to the particle-matrix interactions. Independently of the actual dimensions, the reinforcing effect is the same for $p > 500$ as of an infinitely large particle. The anisometric particles start overlapping when the volume fraction exceeds the “*maximum packing volume fraction, ϕ_m* ” — above which the platelets are locally oriented:

$$\text{for discs: } 1/\phi_m = 1.29 + 0.0598 p. \quad (1)$$

Since the aspect ratio of exfoliated MMT is $p = 100$ to 2000, the specific surface is in the order of $800 \text{ m}^2/\text{g}$. Thus, a small amount of anisometric particles leads to large effects [1]. On a molecular level, the surface energy of clay particles is high. As a result, adsorbed molecules have a tendency to be strongly bonded in the layer adjacent to the clay surface [2]. This engenders a solid-like behavior of the 2–3 nm thick surface layer and progressive reduction of viscosity with distance to the bulk liquid viscosity at about 15 nm.

1.2. NC with Polymeric Matrix (PNC)

In consequence of these fundamentals, PNC's normally require 1–3 vol% of nano-particles. They behave as a single phase and single component material. PNC's exhibit transparency and low density. They may be easily modified by additives. They can be used as such or as a matrix of traditional multiphase systems (*viz.* blends, composites, or foams), replacing neat polymers and traditional composites. Nanometer-scale structures are frequently found in biological materials with impressive performance [3]. For example, bone has a structure of 4 nm-thick hydroxy apatite crystals dispersed within a collagen matrix.

Three strategies have been developed for producing PNC's with well-defined, tunable nano-architecture. Of these three, only the first will be considered here.

1. Addition of nano-particles, *viz.* nano-fibers, nano-tubes, or nano-platelets. The present review will focus on the latter type of PNC, in particular those with clay.
2. Copolymerization with monomers having bulky side groups, *viz.* the polyhedral oligomeric silsesquioxanes (POSS) [4].
3. Preparation of ordered nano-scale structures using liquid crystal polymer (LCP) technology [5].

PNC's are emerging as a new class of industrially important materials. At loading levels of 2–7 wt%, they offer similar performance to conventional polymeric composites with 30–50 wt% of reinforcing material. Note that high filler loading in the latter materials causes undesirable increase of density, hence heavy parts, decreased melt flow and increased brittleness. Furthermore, the classical composites are opaque with often poor surface finish. These problems are absent in PNC's. Current consumption of PNC is but a few kton per annum, to increase by 2009 to 500 kton/y. Cost differential between the neat matrix and its PNC is about 10%. PNC's main market is in the transport industries, with growing demand for packaging, appliances, building & construction, electrical & electronic, lawn & garden, power tools, *etc.* Their advantages range from enhancement of mechanical performance, to reduction of permeability and flammability, improved optical properties, modified magnetic, electric or light-transmitting performance, biocompatibility, thermochromic effects, *etc.*

Table 1A (in the Appendix) summarizes recent reports on PNC. As Table 2A shows, practically all commercially important PNC's contain exfoliated clays, in particular MMT.

1.3. PNC Definitions

Exfoliated material: individual platelets dispersed in a matrix with the distance between them > 8.8 nm. The platelets can be oriented, forming *Short stacks* or *Tactoids*.

Exfoliation: converting *Intercalate* into *Exfoliate*.

Intercalant: material sorbed between platelets that binds with their surfaces to form an *Intercalate*. Often the intercalant is an onium salt that bonds ionically with platelet anion.

Intercalated material: material with organic or inorganic molecules inserted between platelets, thus increasing the interlayer spacing between them to at least 1.5 nm.

MMT: montmorillonite; *Na-MMT*: sodium montmorillonite; *H-MMT*: – protonated MMT; etc.

Nanocomposite (NC): an oligomer, polymer or copolymer having dispersed *exfoliated* individual platelets obtained from an *Intercalated Layered material*.

Short stack or a Tactoid: *Intercalated* or *Exfoliated* clay platelets aligned parallel to each other.

Spacing: Two measures of spacing are used: *Interlayer spacing*, [also known as *d-spacing*, $d(001)$ or *basal spacing*] and *Interlamellar spacing*. The former comprises the latter plus the platelet thickness. For example for MMT: $d(001) = \text{Interlamellar spacing} + 0.96$ (nm).

1.4. Methods of Characterization

The interlayer spacing, $d(001)$, is commonly determined from the XRD spectrum as arbitrary intensity vs. 2θ . It can be calculated from Bragg's law:

$$d = \lambda / 2 \sin \theta, \quad (2)$$

where λ is the wavelength — most X-ray machines use $\text{Cu-K}\alpha_1$ radiation with $\lambda = 0.1540562$ nm. The dependence given in Equation 2 is shown in Figure 1. It is worth noting that, within the range of interest for PNC ($2\theta = 1\text{--}12^\circ$), there is a straight-line relation between d and $1/(2\theta)$.

XRD resolution decreases at low angles, e.g., for spacing: $d > 8.8$ nm (i.e., $2\theta < 1^\circ$). Furthermore, at such a large spacing, exfoliation reduces the scattering intensity. Thus, the XRD method is not as informative. Within this range (see Figure 2), TEM is used to determine the extent of intercalation/exfoliation.

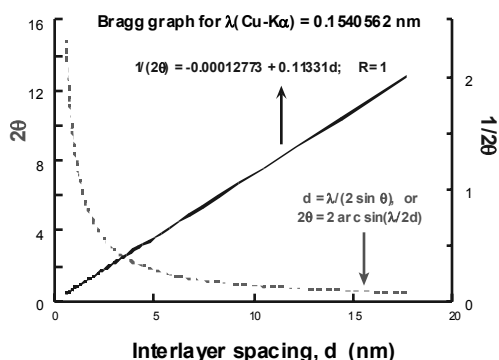


Figure 1. Bragg's law dependencies for $\text{Cu-K}\alpha_1$ radiation. The straight line is given by the empirical dependence shown in the Figure; its correlation coefficient $R=1$.



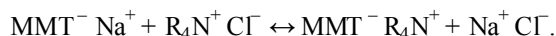
Figure 2. TEM of intercalated epoxy PNC showing limited exfoliation of MMT [6].

To examine the interactions between the clay platelets, the intercalating agent, and polymer, FTIR provides important information. By comparing the experimental and calculated spectra, the type and intensity of interactions can be identified [7]. Solid state ^1H , ^{13}C , ^{15}N , and ^{29}Si Magic Angle Spinning (MAS) NMR spectroscopy at frequencies 100.40, 30.41, and 79.30 MHz, respectively, have been used. The Young's modulus (Y) was found [8] to be proportional to the chemical shift (Cs) of ^{15}N in ammonium-clay complex with the slope: $dY/d(Cs) = 0.1097$ (GPa/ppm). The chemical shifts provide precise information about the degree of clay hydration as well as the interactions engendered by intercalation. MAS-NMR is particularly valuable for the reactive systems, *e.g.*, for PNC's prepared by dispersing intercalated clay into a monomer that is then polymerized. Direct evidence that the reaction involves Si atoms has been reported [9, 10]. Diverse calorimetric studies have been used to characterize PNC, *e.g.*, DSC/DTA to study clay hydration [11] and TGA for the interlayer packing density [12]. Chromatography has been used to determine formation of intercalate complex [13], *etc.* Electrophoretic mobility gives significant insight into variation of the surface charge of clay particles with pH, which is crucial for the intercalation optimization [14].

1.5. Basic Elements of PNC Technology

Intercalation

The most common nano-particles used for the production of commercial PNC are those of MMT. The unit cell (see Figure 3) is $(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{O}^-)_2 + 2$ cations, *i.e.*, MMT behaves as a weak silicic acid. Thus, Na-MMT undergoes ion exchange with an onium salt, *e.g.*, quaternary ammonium chloride: $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{Cl}^-$, to produce hydrophilic or hydrophobic intercalated MMT. The character and the d -spacing depend on the R_i -radicals. In several commercial organoclays $\text{R}_1 = \text{R}_2 = -\text{CH}_3$ and $\text{R}_3 = \text{R}_4 =$ hydrogenated tallow oil. Other radicals used to control interactions with the matrix are benzyl, hydroxy ethyl, 2-ethyl hexyl, *etc.* The intercalation process involves the slow chemical reaction:



Owing to low mobility of the $\text{MMT}^- (\text{R}_i)_4\text{N}^+$, the equilibrium is shifted to the right hand side. The intercalation in aqueous medium at $T = 25\text{--}80^\circ\text{C}$ takes from $t = 10$ min to 8 hrs (in non-aqueous solvent, it may take up to 15 days). It results in a complex of MMT with two ammonium ions and two amines.

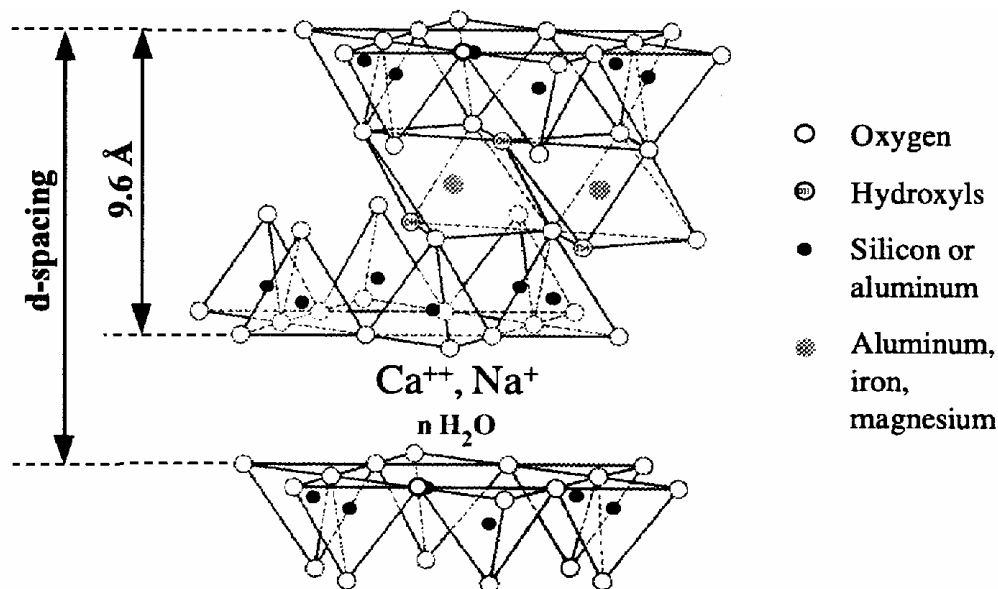


Figure 3. Structure of MMT formed of two tetrahedral sheets fused to an octahedral one. The d - or (001) spacing doubles in water. The interlayer thickness = d -spacing – mineral layer thickness.

Exfoliation

Clay can be dispersed in polymeric matrix as conventional filler with aggregated particles, intercalated clay, ordered exfoliated nanocomposites, or disordered exfoliated nanocomposites. Several methods have been used to exfoliate the intercalated clay during the preparation of PNC.

1. 'In-situ' polymerization in the presence of intercalated clay.
2. Melt compounding of a polymer with suitable intercalated clay complexes.
3. Ultrasonically exfoliating clay particles in a solvent followed by melt compounding
4. Melt compounding polymer with a layered material in a kinetic energy mixer.

The high specific surface of the nano-particles leads to high reinforcement efficiency, high specific modulus, strength, and heat deflection temperature (HDT). In a crystallizable polymer matrix, the clay platelets promote faster crystallization and higher crystallinity [15], which results in improved solvent and moisture resistance. PNC makes it possible to control permeability (see Figures 4, 5). Two elements account for these effects: dispersion of high aspect ratio oriented platelets and reduction of the free volume [16]. The relative permeability coefficient is given by:

$$P_R = P/P_0 = [1 + p\phi/2]^{-1} \quad (3)$$

where ϕ is volume fraction of the platelets and p is the aspect ratio.

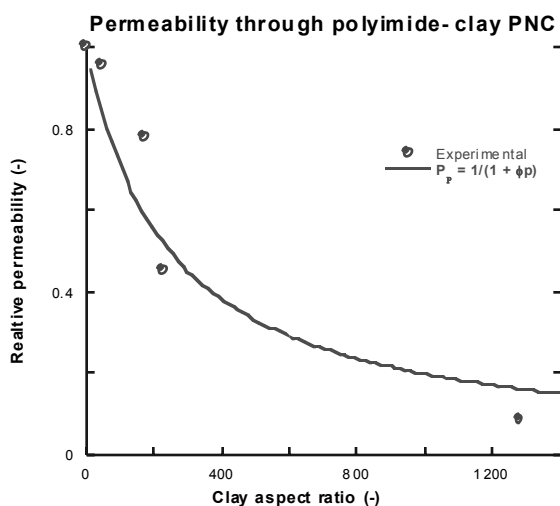


Figure 4. Relative permeability of polyimide with 2 wt% ($\phi = 0.0081$) clay vs. its aspect ratio [16]. Points: experimental, line: calculated.

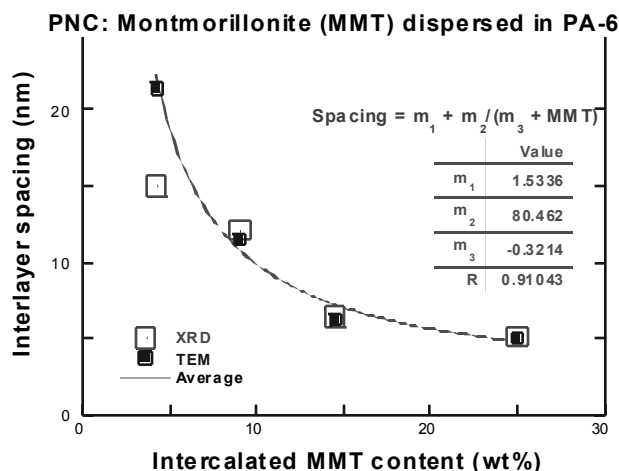


Figure 5. Basal spacing in PNC vs. MMT content as measured by XRD and TEM [17]. Exfoliation is predicted for MMT content below 11.3 wt%.

2. FUNDAMENTAL ASPECTS OF PNC'S

2.1. Modeling of Clay Intercalation

The molecules in the direct proximity of a smooth mica surface have low mobility, resembling that in the solid state [2]. The mobility increases with distance from the solid surface, but it takes up to 12 layers to reach the bulk melt behavior. Molecular modeling of adsorption and ordering at solid interfaces has been carried out [18]. Hackett *et al.* [19] performed molecular dynamics simulation of clay intercalation with alkyl-ammonium salts. Good agreement with the experimental data of interlayer separation was found. The simulation made it possible to propose the intercalated structure presented in Figure 6.

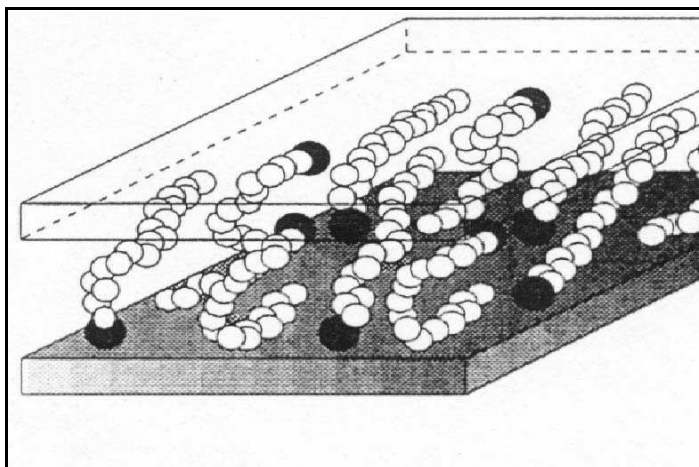


Figure 6. FTIR-based alkyl ammonium model. As the alkyl length increases the short chains in a monolayer on the clay surface are replaced by intermediate quasi-bilayer structure. Finally, long chains are expected to show increased order and multi-layer spacing [12].

Beal [20] described a computational model that can predict the type of intercalate, the d -spacings and the energetics of exfoliation to form a PNC. However, so far, the problem of phase separation caused by immiscibility between the polymer and the intercalant or a coupling agent has not been solved.

2.2. PVT Behavior of Polymers and PNC's

The effects of nano-particles on PNC performance are disproportionate to their content. There is a need to develop a better understanding of the interactions and the structures involved. For this purpose, pressure-volume-temperature (PVT) measurements offer valuable insight.

PVT behavior of PA-6 and its PNC was investigated [21] at $T = 300$ to 560 K and $P = 0$ to 150 MPa. As shown in Figure 7, addition of 2 wt% of organoclay reduces the specific volume of PA-6 by about 1.0 %. Note the excellent agreement between the experimental data and the Simha-Somecynsky theory [22, 23]. As shown in Figure 8, addition of clay reduced the free volume fraction by 14%. This system densification is observed for melts, hence the enhanced crystallinity does not come into consideration. The characteristic parameters extracted from the analysis are presented in Table 1. They reflect the intermolecular interactions and chain flexibility, averaged over the different species present in the mixture.

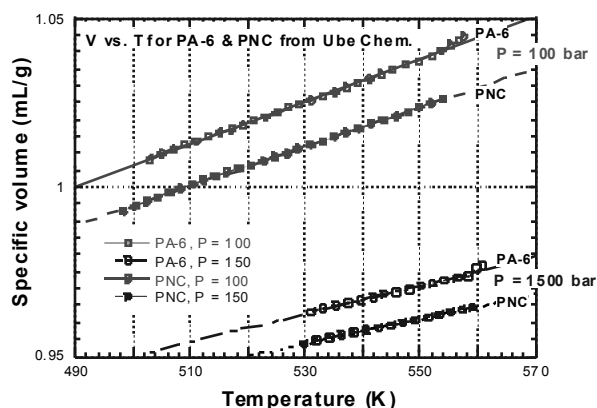


Figure 7. Experimental and computed specific volume vs. T dependencies at 100 and 150 bar for PA-6 and its PNC [21].

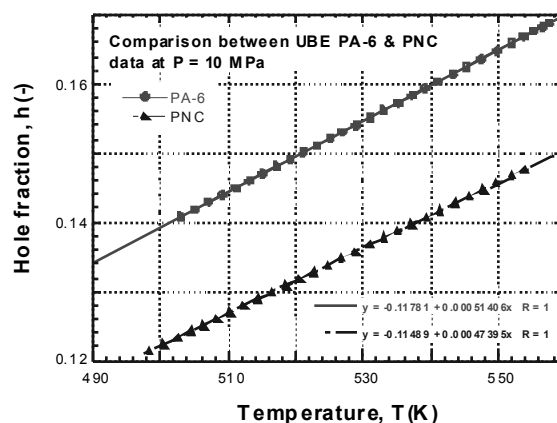


Figure 8. Hole or free volume fraction vs. T for PA-6 and its PNC [21].

Table 1. Characteristic Parameters of PA-6 and its PNC from Ube [25].

Parameter	PA-6	PNC
P^* (bar)	$12\,893 \pm 139$	$12\,198 \pm 102$
T^* (K)	$11\,579 \pm 63$	$12\,411 \pm 61$
$10^4 V^*$	9061 ± 17	9142 ± 14
M_s (g/mol)	27.47	$\langle M_s \rangle = 30.84$
ε_{11} (kJ/mol)	32.09	$\langle \varepsilon^* \rangle = 34.40$
v_{11} (ml/g)	24.89	$\langle v^* \rangle = 28.19$

The Simha–Somcynsky theory is written in terms of the reduced variables [23]:

$$\tilde{P}_i = P_i/P_i^*; \quad \tilde{T}_i = T_i/T_i^*; \quad \tilde{V}_i = V_i/V_i^*; \quad i = 11, 12, 22, \quad (4)$$

where subscript “1” represents the PA-6 segment and “2” that of MMT. For a single liquid, the theory relates the reducing parameters (P^* , V^* , T^*) to the energetic and volumetric interactions, ε_{11} , and v_{11} :

$$P^* = zq \varepsilon_{ii}^* / s v_{ii}^*; \quad T^* = zq \varepsilon_{ii}^* / Rc; \quad V^* = v_{ii}^* / M_0. \quad (5)$$

In Equation 5, zq is the number of intermolecular contacts, s is the number of segments, $3c$ is the number of external degrees of freedom and R is the gas constant. For binary mixtures, the interaction parameters are expressed as averages [24], hence the PNC is treated as a mixture of two components: flexible PA-6 segments and rigid clay “particles”. According to the theory, the hard-core specific volumes of the components are equal: $v_{11}^* = v_{22}^*$. For the binary energetic interactions, the geometric average provides an excellent approximation. Calculations gave the following results for the PA-6-clay and clay–clay interactions:

$$\varepsilon_{12}^* = 9.7707 \times \varepsilon_{11}^* = 313.54; \quad \varepsilon_{22}^* = 95.4676 \times \varepsilon_{11}^* = 3063.55 \text{ (kJ/mol)};$$

$$v_{12}^* = 1.3473 \times v_{11}^* = 33.53 \text{ (ml/mol)}.$$

Thus, v_{12} is larger than v_{11} by 35%. This is reasonable, considering adsorption of the PA-6 layer on the clay surface. The solid–solid energetic interactions between clay particles are 95 times larger than the liquid–liquid ones. Since the solid surface energy is 500–2000 (mN/m), while that of liquids is 20–70 (mN/m), the derived ratio is also reasonable. As the free volume controls flow, permeability, mechanical performance, *etc.*, knowledge of the PVT behavior is critical.

2.3. Rheology of PNC

Polyamide-6 and the PNC based on it (containing 2 wt% of organoclay) supplied by Ube were dried for 48 hrs at 80°C under vacuum, compounded in a twin-screw extruder (TSE) and tested in a Rheometrics ARES at $T = 240^\circ\text{C}$ under a blanket of dry N_2 . Time, strain, and frequency sweeps were carried out [26]. The storage and loss shear moduli (G' and G'' , respectively) increased with time, indicating progressive polycondensation and exfoliation. The rates of change were found to be the same for strains of 10 and 40%, but slightly increased with test frequency. The strain sweeps were carried out at a frequency of $\omega = 6.28$ rad/s within the range $\gamma = 0$ to 100 %. The sweep time was about 600 s. Raw data were corrected for the time effects. All compositions containing 1 to 2 wt% of organoclay showed nonlinear flow behavior. The results were described using KBKZ-type non-linearity expressions [27]:

$$G''(\gamma) = G_0'' / [1 + G_1'' \gamma^2 - G_2'' \gamma^3]. \quad (6)$$

The non-linear least squares fit of Equation 6 to data is shown in Figure 9 for PNC composition containing 2 wt% of organoclay. Good description for all compositions was found.

Even at frequency $\omega = 6.28$ rad/s, the amount of dissipated energy is at least one order of magnitude higher than that stored. For strains $\gamma < 50$ % PNC the shear moduli are independent of strain. At $\omega = 6.28$ rad/s and strains: $\gamma = 0$ and 50% (see Figure 10) the maximum strain effect is for PNC – here the difference between zero-strain and 50% strain is 15 and 7.5% for G' and G'' , respectively.

The frequency sweeps were conducted at 240°C and strains of $\gamma = 10$ and 40%, in the direction from 100 to 0.1 rad/s and from 0.1 to 100 rad/s (see Figure 11). The data were corrected for the polycondensation/exfoliation effects using the rates determined in time sweeps. The specimen structure changes at about $\omega_c = 1.4 \pm 0.2$ rad/s. The relative viscosity vs. composition follows the dependence for suspensions, with the intrinsic viscosity of clay platelets: $[\eta] = 105.5 \pm 22.5$ (see Figure 12).

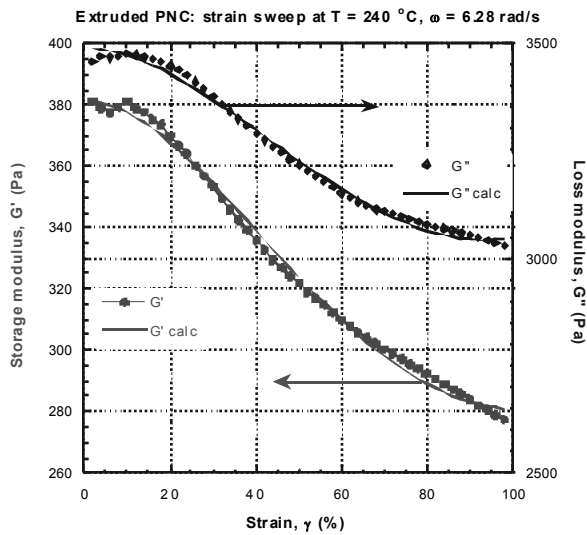


Figure 9. Strain sweep of G' and G'' for PA-6/PNC blends. Points experimental, lines from Equation 6.

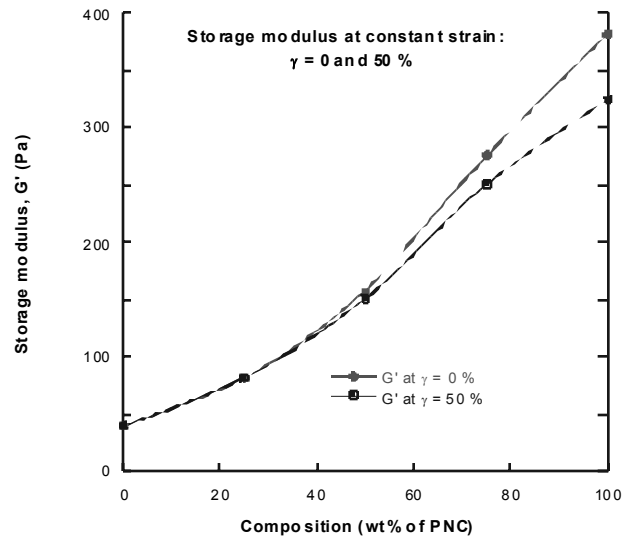


Figure 10. Concentration dependence of G' for PA-6/PNC blends at $\gamma = 0\%$ and 50%.

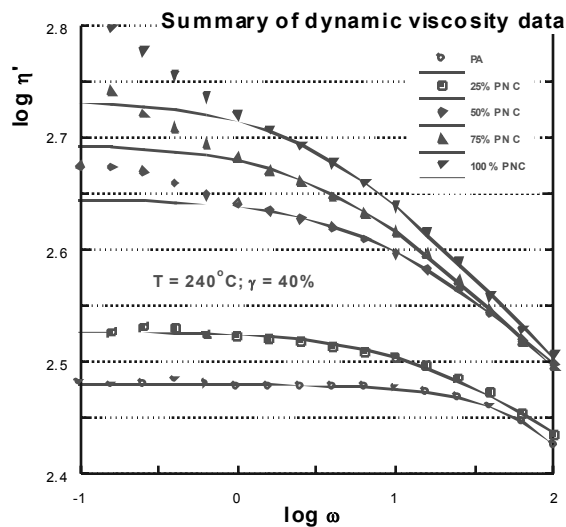


Figure 11. Frequency dependent dynamic viscosity for PA-6 and its mixtures with PNC. Points are experimental at $T = 240^\circ\text{C}$ and $\gamma = 40\%$.

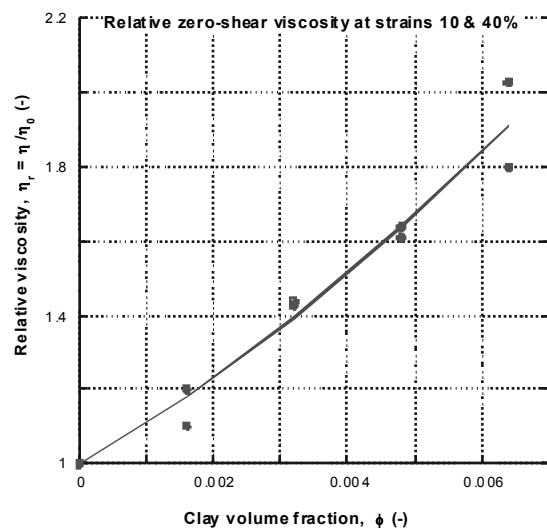


Figure 12. Zero-shear relative viscosity for PA-6 and its mixtures with PNC. Points are experimental at $T = 240^\circ\text{C}$ and $\gamma = 40\%$. Line is theoretical.

For hard sphere suspensions, $[\eta] = 2.5$ was calculated by Einstein; for anisometric particles it depends on the aspect ratio, p , according to the relation [28]:

$$[\eta]_{\text{disks}} = 2.5 - a(1 - p^b), \quad (7)$$

where the parameters are: $a = 0.025 \pm 0.004$, $b = 1.47 \pm 0.03$ with $\sigma = 0.6214$, and $r^2 = 0.9998$. Thus, for the clay particles, $p = 286 \pm 9$. Specifications for PA and PNC from Ube list the moisture permeability as 203 and 106 g/m² per 24 hr, respectively. Theoretically, the relative permeability coefficient is given by:

$$P_r = [1 + p\phi/2]^{-1}. \quad (8)$$

Assuming that morphology of PA matrix in PNC is identical to neat PA, Equation 8 gives $p = 287 \pm 9$. The perfect agreement was unexpected, since a difference between the p -values determined from the melt rheology and from permeability could arise due to such factors as crystallization-induced change of matrix morphology near the clay surface. Finally, from Equation 1, the maximum packing volume fraction of the platelets is: $\phi_m = 0.053 \pm 0.001$, *i.e.*, $w_m \cong 13 \pm 2$ wt%.

2.4. Theory of the Mechanical Behavior

Shia *et al.* tried to explain discrepancy between theoretical modulus predictions and the experimental values [29]. The authors postulated that the difference is caused by imperfect bonding between the matrix/clay interface. A simple model was developed using effective quantities: the aspect ratio and volume fraction of the inclusions. These quantities were assumed to depend only on the interfacial shear stress. For the elastomer-based PNC, by fitting the theory to experimental data, this parameter was found to be in the range of kPa's. Furthermore, the interfacial shear stress was decomposed into intrinsic and frictional part. The former was found to depend only on the inclusion volume fraction, decreasing with an increase of the latter, which was found to increase linearly with strain. Since the mean stress is proportional to the applied strain, the effective coefficient of friction for the PNC under consideration was calculated as 0.0932.

3. PNC TECHNOLOGY

Intercalation of clays started in the 1930's. The dry smectite interlayer spacing of $d = 0.35$ nm, increased in water to $d = 1.2$ – 1.4 nm. In the early 1950s, for hydrophobic applications, clay was intercalated with quaternary alkonium chlorides. *Bentone*TM was commercialized for thickening lubricating greases, paint–varnish–lacquer removers, *etc.* [30, 31].

In 1961, Blumstein reported polymerization of vinyl monomers (*e.g.*, methylmethacrylate) in the presence of intercalated MMT [32]. The first use in polymers of hydrophobic, ammonium-salt intercalated clays was in the mid-1970 at the Toyota Research Corp. [33]. Several US patents followed [34, 35]. The process consisted of caprolactam polymerization in the presence of intercalated clay. The melt exfoliation process for PA-based PNC was developed in the early 1990's at AlliedSignal [36–38]. Thus, a suspension of clay in aqueous solution at 50–90°C was treated with organo silanes, titanates, or zirconates. This increased the interlayer spacing to $d \leq 5$ nm. The dried clay was saturated with monomer, which was subsequently polymerized. Finally, the modified clay was compounded with a matrix polymer until the desired level of exfoliation was reached.

In 1987, Toyota deposited the first patent for polyolefin (PO)-based PNC's [39]. Owing to hydrophobicity and the non-polar nature of PO, preparation of PNC's is difficult. The process involved polymerization in the presence of intercalated clay particles. Next, a general method for preparation of PNC with diverse polymers was disclosed [40]. The process involves three steps: (i) intercalation of clay with an onium ion rendering it compatible with a “guest molecule”; (ii) contacting the organo–clay with the “main guest molecule” at $T \leq 250^\circ\text{C}$; and (iii) the modified clay is either transferred into a reactor during PO polymerization (preferred) or blended with a synthetic resin. For example, maleated PP with high acid value was used as the “guest molecule” that resulted in good exfoliation [41].

PO-based PNC's were also prepared by [42]: (i) intercalation with an organic, polymeric or inorganic intercalant [*e.g.*, $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(\text{OCH}_3)_4$, $\text{Ge}(\text{OC}_3\text{H}_7)_4$, $\text{Ge}(\text{OC}_2\text{H}_5)_4$] that resulted in $d = 0.5\text{--}60$ nm; (ii) after drying or calcination, the intercalated material was dispersed in a monomer or melt-blended until at least 80 wt% of the layers were exfoliated. Another method for the preparation of PO-type PNC's follows the steps [43]: (i) MMT was functionalized in $\text{H}_2\text{O}/\text{EtOH}$ with, *e.g.*, amino ethyl-dimethyl ethoxysilane; (ii) maleated PO was grafted to the functionalized MMT by amine-carboxyl bond; and (iii) 0.1–50 wt% of the modified particles was dispersed in PE or PP.

To avoid thermal instability of ammonium salt, Ellsworth used organophosphonium $\text{R}_1\text{P}^+(\text{R}_2)_3$ cations [44]. The dispersion carried out in a twin-screw extruder (TSE) resulted in $d \geq 3.5$ nm. The product was stable to about 370°C . Another method for PNC preparation uses bentonite intercalated with C_{12} - or C_{16} -ammonium chloride and treated with 2 wt % of epoxy [45]. The compound was added to molten polymer and mixed for up to 2 h. Intercalation and/or exfoliation were not successful for all used polymers. Exfoliation in PE was reported to be slow. The polymers with $\text{MW} > 150$ kg/mol, showed low exfoliation — evidently the process is diffusion controlled.

3.1. Layered Nano-Particles of Interest to PNC Technology

3.1.1. General

The layered materials of interest to PNC technology have an average layer thickness 0.7 to ≤ 2.5 nm. They include:

Smectite clays	Montmorillonite, Beidellite, Nontronite, Hectorite, Saponite, Sauconite, <i>etc.</i>
Other clays	Vermiculite; Illite, Leditite, Attapulgitite, Magadiite
Synthetic clays	<i>e.g.</i> , $\text{MgO}(\text{SiO}_2)_x(\text{Al}_2\text{O}_3)_y(\text{AB})_z(\text{H}_2\text{O})_x$ (where AB is a ion pair, <i>viz.</i> NaF)
Layered hydroxides	<i>e.g.</i> , $\text{Mg}_6\text{Al}_{3-4}(\text{OH})_{18-8}(\text{CO}_3)_{1-7}\cdot\text{H}_2\text{O}$; or $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot n\text{H}_2\text{O}$
Oxides	$\text{H}_2\text{Si}_2\text{O}_5$, V_6O_{13} , HfNbO_5 , $\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$, $\text{W}_{0.2}\text{V}_{2.8}\text{O}_7$, Cr_3O_8 , $\text{MoO}_3(\text{OH})_2$, $\text{VOPO}_4\cdot 2\text{H}_2\text{O}$, $\text{CaPO}_4\text{CH}_3\cdot\text{H}_2\text{O}$, $\text{MnHAsO}_4\cdot\text{H}_2\text{O}$, $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$, <i>etc.</i>
Others	FeCl_3 , FeOCl ; TiS_2 , MoS_2 , MoS_3 , $(\text{PbS})_{1.18}(\text{TiS}_2)_2$; $\text{Ni}(\text{CN})_2$; Graphite, <i>etc.</i>

For PNC, the preferred are 2:1 type clays of the 2:1 type, *i.e.*, in particular **montmorillonite (MMT)**. The layer surface has 0.25 to 0.9 negative charges per formula unit. The amount of nano-material added to PNC is ≥ 5 ppm. The aim is to totally exfoliate the platelets.

3.1.2. Crystalline Clays [46]

Clays are distinctive from hard rocks as they are composed of extremely fine crystals, usually plate-shaped, less than $2\text{ }\mu\text{m}$ in diameter. When wet, they can be easily formed by application of slight pressure and retain the shape after pressure release. They have large specific-surface areas. Clays are physically sorptive and chemically surface-reactive. The synthesis of clays has been extensively studied [47].

Kaolins have the structural formula: $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$. Their lattice consists of one sheet of tetrahedrally coordinated Si (with O) and one sheet of octahedrally coordinated Al (with O and OH), hence a 1:1 or two-layered structure. Kaolin has a cation-exchange capacity, $\text{CEC} < 10$ meq/100 g.

Smectites, partially hydrated in atmosphere, XRD yields basal spacing $d = 1.2\text{--}1.4$ nm. Solvating them in ethylene glycol expands d to 1.7 nm, while heating to 550°C collapses it to 0.96 nm. The DTA curves for smectites show three endothermic and one exothermic peak, within the ranges 150–320, 695–730, 870–920, and 925–1050 $^\circ\text{C}$, respectively. Smectite has $\text{CEC} = 80\text{--}120$ meq/100g.

Bentonite is a rock rich in MMT that has resulted from the alteration of volcanic ash and the intermediate siliceous type. Smectites are 2:1 clays that carry a lattice charge and characteristically expand in water or alcohol, glycol, or glycerol. Typical chemical formulas of the smectite clays are:

Mineral	Chemical composition
Montmorillonite (MMT)	$[\text{Al}_{1.67}\text{Mg}_{0.33}(\text{Na}_{0.33})]\text{Si}_4\text{O}_{10}(\text{OH})_2$
Beidellite	$\text{Al}_{2.17}[\text{Al}_{0.33}(\text{Na}_{0.33})\text{Si}_{3.17}]\text{O}_{10}(\text{OH})_2$
Nontronite	$\text{Fe(III)}[\text{Al}_{0.33}(\text{Na}_{0.33})\text{Si}_{3.67}]\text{O}_{10}(\text{OH})_2$
Hectorite	$[\text{Mg}_{2.67}\text{Li}_{0.33}(\text{Na}_{0.33})]\text{Si}_4\text{O}_{10}(\text{OH},\text{F})_2$
Saponite	$\text{Mg}_3[\text{Al}_{0.33}(\text{Na}_{0.33})\text{Si}_{3.67}]\text{O}_{10}(\text{OH})_2$
Sauconite	$[\text{Zn}_{1.48}\text{Mg}_{0.14}\text{Al}_{0.74}\text{Fe(III)}_{0.40}][\text{Al}_{0.99}\text{Si}_{3.01}]\text{O}_{10}(\text{OH})_2\text{X}_{0.33}$

Note: $\text{Na}_{0.33}$ or $\text{X}_{0.33}$ refers to the exchangeable cation which is typically 0.33 equivalent.

Mica has a 2:1 sheet structure, similar to MMT, except that the maximum charge deficit is in the tetrahedral layers and contains potassium held tenaciously in the interlayer space. A 1.0 nm basal spacing exhibited in XRD is somewhat broad and skewed toward wider spacings. Its CEC \cong 20 meq/100 g

Vermiculites. The interlayer sheet is octahedrally coordinated. Its basal spacing $d = 1.4\text{--}1.5$ nm. CEC is relatively high and it may even exceed that of MMT.

3.2. Intercalation of Clay

Intercalation of clays for applications as rheological additives, catalyst supports or nano-reinforcements has been practiced for nearly 70 years. Significant developments are summarized in Table 3A.

For successful intercalation, the clay should have a CEC = 50 to 200 meq/100 g. Below this range the adsorption of a swelling agent is insufficient. Above it, bonding is too strong for intercalation. Thus, smectites and vermiculites have optimum CEC. As a consequence, MMT, saponite, and hectorite are the preferred clays for PNC's, but since MMT is more abundant and it has the largest aspect ratio, p , (hectorite has the smallest) it became the main nano-filler for PNC.

Several routes have been used to intercalate clay particles. They can be classified as follows:

1. Solvents and low MW solutions, viz. water, alcohols, glycols, or monomer solutions;
2. Organic cations, viz. ammonium, phosphonium, or sulfonium;
3. Inorganic compounds that form inter-layer pillars;
4. Organic liquids, viz. monomers, epoxies, PEG, PVAI, PDMS, PVP, and their solutions;
5. Melt intercalation.

Purification of clay [48]. MMT is ground to 200 μm diameter particles (> 90 wt%), then dispersed in water. The slurry flows through sedimenting blungers into hydrocyclones that remove impurities of a size > 50 μm . Next, MMT in a cation exchanger is converted into $> 95\%$ pure Na-MMT. Finally, the clay is centrifuged to remove particles > 5 μm in size, filtered, then spray-dried, and bagged.

Intercalation by solvents and solutions. The d -spacing of MMT (0.96 nm) increases in aqueous ethylene glycol to 1.7 nm. Intercalation using aqueous solution of glycols, glycerol or sorbitol was reported to be facilitated by the addition of $\text{Mg}(\text{OH})_2$ that changes pH to about 9.4 [49].

Intercalation by organic cations. For over sixty years, the quaternary ammonium cations have been the main intercalants. The d -spacing of intercalated clays depends on the length of the alkyl radical and CEC. As shown in Figure 13, the spacing change is step-wise [50]. Organophilic clays were prepared, e.g., by reacting Na-MMT with methyl benzyl di-hydrogenated tallow ammonium chloride in water at $T = 66\text{--}77^\circ\text{C}$, for 1–60 min, followed by filtering, washing, drying, and grinding. The intercalating cation [51] may be selected from between ammonium, phosphonium, sulfonium quaternary onium salts or their mixture.

Intercalation is improved, if prior to the reaction with onium salt, the clay is subjected to high energy milling, dispersing or grinding [52]. Milling with energy of 30, 51, and 108 HP-hr/ton reduced the smectite clay particle diameter from 475 to, respectively, 391, 277, and 276 nm, hence reducing p . Since the diffusion process is exponential, reduction of the diameter by half reduces the time by a factor of 7.39. The high shear may also pull some platelets out from the stack.

In Jordan's patents [53], clay was pre-blended with mixed cations by mixing the dry materials in a high pressure reaction vessel in the presence of dispersant. The mixed cations comprised at least 5% of each: $X_2R_2M^+$ and XYR_2M^+ , where X is methyl, Y is benzyl and R is an alkyl, derived from saturated tallow oil, and M is nitrogen or phosphorus. The mixture of clay, quaternary salt, and dispersant passed from blender to a auger-extruder with a perforated die. Inside, the mixing blade assembly mixed the material at $P = 20\text{--}55$ MPa and $T \leq 80^\circ\text{C}$. The product was milled to usable particle size.

Frequently, it has been necessary to add to clay low molecular weight polar organics. Such compounds have been called polar activators, dispersants, dispersion aids, solvating agents, *etc.* An organosilane [54] of the type: $R_n\text{SiX}_{4-n}$ is an alternative. In the formula, $n = 1\text{--}3$, R is an organic radical having C–Si link and X is hydrolyzable alkoxy, acryloxy, amino, or halogen group. For example, the new organoclay is the reaction product of Na–MMT (CEC ≥ 75 meq/100 g), quaternary ammonium ion and 0.5–5 wt% organosilane, the same as that used in reinforced plastic manufacture [55], *e.g.*, methyl trimethoxy silane.

The ammonium-modified clay may be used to prepare PNC at $T < 250^\circ\text{C}$. With the exception of some elastomers, there are few polymers that can be processed at these temperatures. The thermal stability of ammonium-modified clay systems may be improved by extracting an excess of the intercalating ammonium salt and/or by reacting it with, *e.g.*, epoxies [56]. In several patents, ammonium, sulfonium, and phosphonium salts are listed [51, 53, 57]. Phosphonium-clay salts are stable to 370°C .

Intercalation by organic liquids. Clay [58] was intercalated using 30–80 wt% of a water-soluble monomer, oligomer or polymer, increasing interlayer spacing to $d = 3\text{--}4.5$ nm. These intercalants must have polar groups (*e.g.*, hydroxyl, carboxyl, amine) or aromatic rings that provide metal–cation complexing. The preferred polymers are: PVP, PVAI, and their mixtures. As shown in Figure 14, the interlayer spacing increases with the amount of sorbed intercalant. Exfoliation can be achieved by shearing the mixture at shear rate of $100\text{--}10\,000\text{ sec}^{-1}$. Some systems exfoliate naturally by heating, or by applying low pressure.

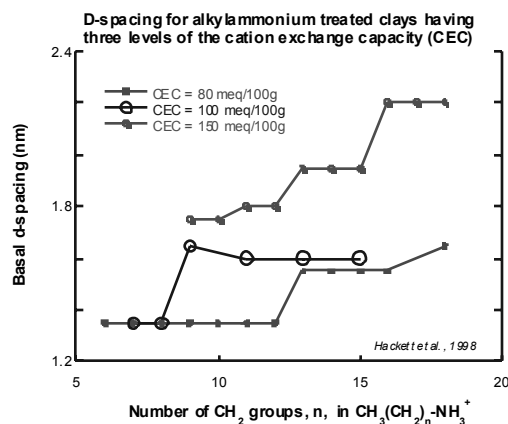


Figure 13. The basal d-spacing of layered materials with CEC = 80, 100 and 150 as a function of the alkyl radical chain length [50].

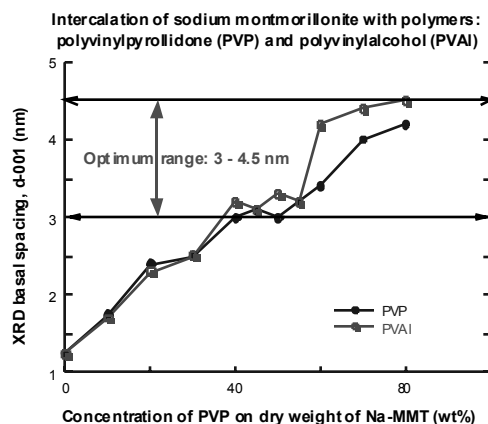


Figure 14. Increase of interlayer spacing as a function of PVP or PVAI concentration in the intercalating suspension (data [58]).

Lan *et al.* [59] treated clay with 30–80 wt% of monomeric organic compound having at least 6 C-atoms in a chain and a polar functionality, *e.g.*, hydroxyl, carbonyl, *etc.* The process does not require onium salts or silane coupling agents and it eliminates the ion exchange process. It can be applied to all commercial polymeric systems, particularly epoxy resins. The presence of polymerizable monomer or oligomer in the galleries of the layered materials makes the layered materials compatible with the matrix polymer. Exfoliation may require mechanical shearing, thermal shock, pressure alteration, or ultrasonics.

Fischer *et al.* prepared PNC's with clay using a compatibilization strategy [60]. Block or graft copolymer with one part that was miscible with the matrix polymer and another one that interacted with clay was used. The interaction was preferably by ionic or hydrogen bonding. It resulted in partial exfoliation.

Inorganic intercalants. In these processes, pillared structures are formed between clay layers. Cations of Al, Zr, Be, Cr, Fe, Ni, Nb, Ta, Ho, and others have been used individually or in mixtures. Since these intercalated clays are subjected to a calcination step at $T \approx 600^\circ\text{C}$ and are mainly used in catalysis, the high temperature stability is of essence [61]. The technology is new and its use in PNC has just begun.

Katdare *et al.* reported that Na–MMT, dispersed in water, was mixed with alumina chlorhydrol and subjected to ultrasonic agitation at 50 kHz for 20 min. After washing, the intercalated clay was calcined at 500°C . Surprisingly, the clay did not show any peak in XRD scan, indicating exfoliation [62]. Hopefully, after some “compatibilization”, these exfoliated clays may be incorporated into a polymer. Nichols and Chou [42] caused the clay to swell in a liquid, then added a polymerizable inorganic intercalant [*e.g.*, a metallic alcoholate, *viz.* $\text{Si}(\text{OR})_4$, $\text{Al}(\text{OR})_3$, $\text{Ge}(\text{OR})_4$]. Hydrolysis leads to an inorganic polymer at $T > 70^\circ\text{C}$. Following intercalation, the clay was centrifuged and dried at $50\text{--}80^\circ\text{C}$ or calcined at $T = 450\text{--}550^\circ\text{C}$. Intercalation increased the inter-layer spacing to $d \leq 60$ nm. PNC could be formed using such intercalated clay either in polymerization, by melt compounding, or by dispersing it in a dissolved polymer.

3.2.1. Melt Intercalation

There is no commercially viable process that would start with dry, unaltered clay powder and thermoplastics melt and produce exfoliated PNC. Attempts of a solvent-less intercalation of Na–MMT or Li–MMT with PEG or PS were reported [63]. For PEG the process was slow, resulting in a modest d -spacing of 1.77 nm [64] and the method failed for PS. Lan *et al.* [59] pointed out that intercalation by a water-soluble monomer, oligomer or polymer requires *ca.* 10 wt% water. Furthermore, it can increase only after a minimum interlamellar distance is created by adsorption of organic cations. Thus, the process labeled as “melt intercalation” must start with pre-intercalated organoclay.

One may speculate that when the monomer molecule is highly polar and sufficiently small, direct intercalation is possible. However, this was not the case for caprolactam, as research at the Toyota Laboratories demonstrated [8, 17, 65]. It was shown that, to produce PA-6 with exfoliated clay particles, Na–MMT must be pre-intercalated. Thus, again pre-swelling and ionic intercalation were found necessary.

3.2.2. Temperature and Pressure Effects on the Interlamellar Spacing

The “standard” intercalation is under mild conditions — ambient pressure and $T = 20\text{--}80^\circ\text{C}$. However, exfoliation of PNC may require more severe treatment. The information on this topic is scarce and system-specific. For example, the temperature effects on the interlayer spacing were found to depend on the ammonium radical and (to a lesser extent) on the type of clay. Information on the effects of pressure is difficult to find, but there are indications that high P causes the interlamellar thickness to decrease [66], the interlayer water is denser ($\rho(\text{interlayer}) = 1.06$) than in the bulk ($\rho(\text{bulk}) = 0.874$ g/ml). Thus, in the vicinity of the clay particles, free volume is reduced.

3.3. Exfoliation of Clays

Exfoliation is the last step in the preparation of PNC. It may be achieved by different mechanisms.

1. Polymerization in the presence of organo–clay.
2. Melt compounding a polymer with a suitable organo–clay complex.

3. Others:

- Combining the organo-clays with latex;
- Ultrasonic exfoliating of organo-clay particles in a low MW polar liquid;
- Melt compounding polymer with layered particles in a kinetic energy mixer;
- Other methods.

Of the above, the first two are of particular importance and will be discussed in some detail.

3.3.1. Polymerization in the Presence of Organo-Clay

The first patent on PNC focused on polyamide (PA) or a mixture of PA with other polymers. The manufacturing process followed three steps [34, 35, 67]:

1. **Intercalation** of Na-MMT in water containing 12-amino-dodecanoic acid and HCl at $T = 80^{\circ}\text{C}$ for 60 min. The complex (abbreviated as 12MMT) had an interlayer distance of 1.8 nm.
2. **Mixing** the complex with ϵ -caprolactam at the ratio of 12MMT:H₂O: ϵ -caprolactam = 1:9:9, which increased the interlayer distance to $d = 3.87$ nm. A base catalyst and an activator may be added.
3. **Polymerization** at 100 and 250°C for 48 h, followed by TSE extrusion. Excellent clay layer dispersion was observed under TEM, with up to two layers visible.

Empirically, the d -spacing was found to decrease with MMT wt%: $d = 1.534 + 80.46/(\text{MMT} - 0.321)$. Thus, exfoliation is predicted for MMT < 11.3 wt%. The product has good dye-affinity and whitening. The method is economic, efficiently producing a PNC with a wide viscosity range, in which every kind of PA matrix may be used. As shown in Table 2, the material has good mechanical properties, heat resistance, improved dye-affinity, and whitening resistance during stretching.

Toyota also was the first to develop a process for producing the polyolefin (PO)-based PNC [39]. Thus, onium salt intercalated MMT was mixed with a vinyl-based monomer and/or oligomer (*e.g.*, ethylene, propylene, butadiene, *etc.*) then polymerized in bulk, in suspension or in solution, *via* radical, cationic, anionic, coordination, or polycondensation reaction. The polymerization takes place in the interlayer space, expanding the interlayer distance to $d > 3.0$ nm.

Heinemann *et al.* [68] reported on PO-based PNC with hectorite intercalated with di-methyl stearyl benzyl ammonium chloride $d = 1.96$ nm. When HDPE was polymerized in its presence, XRD showed a reduction of the peak intensity and shift to $d = 1.40$ nm. Best results were obtained for LLDPE-type ethylene-octene copolymers. Some organo-clays were found to interfere with the metallocene-catalyst.

Table 2. Performance of PA-6 and PNC Based on it with 2 wt% of Organoclay from Ube[25].

Property	ASTM	Units	PA-6	PNC
Tensile strength	D-638	kg/cm ²	800	910
Tensile elongation	D-638	%	100	75
Flexural strength	D-790	kg/cm ²	1100	1390
Flexural modulus	D-790	kg/cm ²	28 500	35 900
Impact strength	D-256	kg cm/cm	6.5	5
HDT (4.6 kg/cm ²)/(18.56 kg/cm ²)	D-648	$^{\circ}\text{C}$	180/75	197/140
H ₂ O permeability	JIS Z208	G/m ² 24 h	203	106
Density	D-792	kg/m ³	1140	1150

A bulk polymerization method was used to prepare PS-based PNC [69] starting with MMT intercalated by vinylbenzyl di-methyl dodecyl ammonium chloride (VDAC). Owing to good miscibility of VDAC with styrene, a uniform dispersion of platelets was obtained. Polymerization for 48 h at 60°C resulted in exfoliation. At 7.6 wt% of clay, the modulus of PNC was about 70% higher than that of PS. PMMA-based PNC was also prepared in bulk polymerization by Okamoto *et al.* [70], using MMT intercalated with either oligo-propylene glycol ($n = 25$) or an ammonium chloride. The clay complex was ultrasonically dispersed in a monomer at 25°C for 7 h. This led to $d = 4.2$ increasing during polymerization to 4.55 nm. TEM showed stacks of platelets, suggesting thermodynamically-driven phase separation.

Translucent acrylic nanocomposites were recently described by Dietsche *et al.* [71] The new material was prepared by polymerization of methyl methacrylate–dodecyl methacrylate copolymer in the presence of 2–10 wt% bentonite intercalated with N,N,N,N -dioctadecyl dimethyl ammonium ions. Addition of n -dodecyl methacrylate improved interactions and accounted for improved stiffness-to-toughness balance, higher T_g , and thermal stability, in comparison to the corresponding copolymer.

Recent patents from Eastman [72, 73] describe PET-based PNC with enhanced barrier properties. MMT is intercalated (with a quarternary onium salt) and treated with an expanding agent (*e.g.*, PEG, PCL) or vitamin E. The organoclay ($d = 2.2$ – 4.2 nm) is incorporated into PET either by polycondensation or by melt extrusion, followed by solid state polymerization. TEM showed mostly individual platelets and few tactoids and aggregates. PC-based PNC was prepared with MMT intercalated with di-tallow dimethyl ammonium cation and cyclomer [74], followed by mixing either in dichloromethane or in the melt ($d = 2.47$ – 3.62 nm). Next, ring-opening polymerization resulted in total exfoliation.

3.3.2. Melt Compounding a Polymer with a Suitable Organo–Clay Complex

Maxfield *et al.* [36] emphasized formation of the γ -phase crystalline PA-6 by compounding with clay. The preferred process involves melt blending in a TSE of PA with a compatibilized organoclay at $T \geq T_m$. A compatibilizing agent, *e.g.*, amino-ethyl amino-propyl trimethoxy silane, was used. The blending was carried out until about 95 wt% of clay was exfoliated. In later patents [37, 38] PA-based PNC was produced by:

1. Reacting MMT with an organo-silane, organo titanate or organo-zirconate, aided by exposure to heat, ultrasonic cavitation, or microwaves. The intercalated MMT is filtered, dried, and ground to about 100 mesh. The interlayer spacing of the MMT should be $d \geq 1.5$ nm.
2. Polymerizing caprolactam in the presence of intercalated MMT to form a PNC. Suitable monomer may be selected such that the resulting matrix is formed of one or more thermosetting and/or thermoplastic polymers or rubbers. The preferred average platelet diameter is $15 \leq D \leq 300$ nm and the interparticle spacing ≥ 5 nm. The particles are uniformly dispersed in a polymer.

Melt compounding was also used by Liu *et al.* to prepare PA-6/orgno-clay PNC [75]. Firstly, Na-MMT was intercalated with octadecyl ammonium chloride. The interlayer spacing increased from 0.98 to 1.55 nm. Dry PA-6 was melt-compounded in a TSE. The processing increased the interlayer spacing to 3.68 nm. Similar results were reported by Dahman from the RTP Co. for melt compounded PA-6 [76].

A simple route to PO-based PNC was described by Usuki *et al.* [40]. Ammonium ion intercalated MMT was first treated in a toluene solution of a polar guest molecule (end-hydroxylated PBD or maleated-PP). Dry clay complex was added to molten PP at 200°C and mixed for 30 min, resulting in $d = 3.82$ nm. As reported by Kato *et al.* [41], intercalation/exfoliation can only be obtained by melt compounding when the acid value (AV) of the maleated PP (MAH-PP) is reasonably high, *viz.* AV = 52 worked quite well, but not AV = 7 mg KOH/g. Good exfoliation depends on strong interaction of MAH-PP with the organo–clay and miscibility of the MAH-PP with the main polymer.

Hudson *et al.* [43, 77] described PNC preparation in three steps. Firstly, a nano-filler (*e.g.*, MMT) was reacted with an aminosilane (2–4 hours at 25–90°C). Then, in xylene, a carboxylated or maleated PO was grafted onto it through an amine-carboxyl reaction (at 120°C in about 30 min). Finally, the modified filler was compounded with a semi-crystalline PO, capable to co-crystallize with the carboxylated or maleated PO.

Serrano *et al.* [78] patented PNC that comprises 40–99.95 wt% EVAL and about preferably >2 wt% of exfoliated MMT. No onium ion or silane coupling agent was required, provided that water-soluble intercalants were used, *e.g.*, PVP, PVAL. The intercalant complexes to the platelet surfaces, covering the Na^+ and shielding the EVAL from its degrading influences. Thus, MMT is mixed in TSE with an intercalant at $T = T_m + 50^\circ\text{C}$. One or more monomers can be intercalated between the platelets. These PNC's may be used as external, heat-resistant body parts for the automotive industry; tire cord; food wrap having improved gas impermeability; electrical components; food grade drink containers, *etc.*

Frisk and Laurent, in patents, described PNC based on polyesters, *e.g.*, PET, COPET or their blends [79]. By dispersing 5 wt% Na–MMT ($p = 100$ to 1500), O_2 permeability was reduced by a factor of 100. The clay also improved HDT and mechanical properties — both important for the “hot-filling” applications. To facilitate dispersion, the clay was treated with a surfactant.

Badesha *et al.* prepared fluoroelastomer-type PNC using mica-type silicate (MTS) [80] intercalated with 5–10 wt% of dimethyl dioctadecyl ammonium salt. The MTS plates are *ca.* 1 nm thick with $p = 50$ –1000. MTS may be exfoliated into fluoroelastomer during milling at 66°C . Ellsworth's method of making PNC [57] is based on melt-blending of *e.g.*, ethylene-tetrafluoroethylene copolymer with 10–80 phr of organophosphonium modified Na-hectorite. The intercalation increases d to ≥ 2.0 nm, making it amenable to exfoliation during melt blending. The modulus has been improved, but at a cost of the elongation at break and (to a lesser degree) of the extensional strength.

3.3.3. Other Exfoliation Methods

The preferred methods for the preparation of PS-based PNC's are emulsion, solution or bulk (co-)polymerization in which an organo-clay is dispersed. Since clay intercalation is usually in water, emulsion polymerization is an obvious choice. However, when intercalation is insufficient, the clay will not be transferred to the monomer phase, leading to a limited improvement. Thus, SBR-based PNC was prepared by emulsion polymerization in the presence of onium-intercalated MMT. The PNC's showed superior barrier and mechanical properties [81]. SAN-based PNC's [82] were prepared in emulsion or solution polymerization. Thermo-gravimetric analysis showed that at 500°C the amount of remaining residue was: 5 wt% of SAN, 20 wt% of solution-type PNC, and 70 wt% of emulsion-type.

Solution polymerization of MMA in the presence of intercalated clay complex was described by Tabtiang *et al.* [83]. Polymerization increased the interlayer spacing from 1.79 nm (determined for the intercalated complex) to $d \geq 8.8$ nm, indicating exfoliation. However, during melt processing, d was reduced to about the length of the intercalant, *viz.* 2.9 to 3.9 nm. Evidently, the radical polymerization did not bond the polymer to either clay platelets or the onium.

3.3.4. Thermoset Nanocomposites

Preparation of PNC with thermoset matrix is simpler, because of low viscosity and high polarity of the monomeric ingredients. The methods comprise two steps: dispersion of clay or intercalated clay, then polymerization. For example, Wang and Pinnavaia [84] reported delamination of an onium-modified MMT in an epoxy, upon heating to $T = 200$ – 300°C . Giannelis and Messersmith prepared epoxy-based PNC [85] by first intercalating MMT with an alkylammonium having functional groups able to react with epoxy, *viz.* bis(2-hydroxyethyl)methyl tallow alkyl ammonium ion. The complex was dispersed in a mixture of epoxy with diglycidyl ether of bisphenol-A and a curing agent. The reaction was carried out at $T = 100$ – 200°C . Exfoliation of clay (d -spacing ≥ 8.8 nm) within the crosslinked epoxy matrix was obtained. Pinnavaia and Lan [86–88] developed clay-epoxy PNC with improved tensile strength and/or solvent resistance. Thus, Na–MMT intercalated with alkylammonium salts was mixed with epoxy at 75°C for 30 min and cured with a polyoxypropylene diamine. XRD indicated exfoliation. The strength and modulus increased nearly linearly (*ca.* by a factor of 10) upon addition of 15 wt % of the organoclay.

Kommann *et al.* [89] produced PNC based on MMT and unsaturated polyester (UP). Na–MMT was intercalated at 50°C in MeOH with methacrylate, then dried. The treated MMT was dispersed in UP (containing 42 wt% styrene) and Co-octanoate. The mixture was cured at room temperature for 3 h then post cured at 70°C for another 3 h. XRD showed no peaks, hence exfoliation was achieved. The optimum concentration of clay in UP was about 3.5 vol%.

In 1998, Wang and Pinnavaia prepared thermoset PU-based PNC [90]. Alkylammonium-intercalated MMT was solvated by polyols commonly used in PU synthesis at $T = 25\text{--}50^\circ\text{C}$ for 12 h. The chain length of the onium ion determined the d -spacing = 3.1–3.9 nm, increasing during curing to 5.08 nm — the clay layers were in tactoids. PU-based PNC was also prepared by Chen *et al.* [91, 92]. Firstly, Na-MMT was reacted with either 12-aminolauric acid (12COOH) or benzidine (BZD), forming the complexes: 12COOH-MMT and BZD-MMT. These were washed, dried under vacuum at 80°C for 12h, then ground and screened. Next, MDI and polytetramethylene glycol (PTMEG) in DMF were heated at 90°C for 2.5 h to form pre-polymer. Then, 1,4-butanediol and organoclay (1, 3, 5 wt%) were added. After degassing the mixture and removing DMF, an elastic film was obtained with d -spacing = 1.7 and 1.54 nm for 12COOH-MMT and BZD-MMT, respectively. However, as TEM micrographs showed these PNC's were exfoliated. The maximum reinforcement was obtained for 1 wt% BZD-MMT.

4. PERFORMANCE

As discussed in the text, addition of clay to polymer results in a reduction of free volume. Melt flow of PNC's show increased viscosity, significant augmentation of yield stress and possible exfoliation during the testing. The flow data can be understood by considering the concentration and the aspect ratio of the dispersed clay platelets. Rheological tests offer information regarding the structure and interaction in PNC, hence constitute important aid for the optimization of these materials. Owing to limited space, in the following parts, few examples of the mechanical behavior and flammability of PNC will be discussed.

4.1. Mechanical Properties of PA- and PP-Based PNC's

It has been reported that the impact strength of crystalline polymers is reduced by incorporation of nano-particles. For example, addition of 2.2 wt% of organo-clay to PA-6 reduced the impact strength by a factor of 4.3. However, recent data suggest that the problem is related to the crystallization kinetics. By proper selection of process variables, the same impact strength of PNC as that of the matrix resin may be obtained [93]. Modification of PA-6 behavior by addition of MMT is illustrated in Tables 3 and 4.

Mechanical properties of PP-based PNC are encouraging [43, 77]. The tensile modulus increases nearly 8-fold with 1 wt% of the nano-filler. The tensile strength also increases, but at least 10% loading is required to achieve a significant result. At this level, the Izod impact strength was reduced. However, even at 30% loading, the impact strength was 28 J/m, comparable to that of PP (30 J/m). Addition of chain-grafted filler particles retarded the rate of crack growth. At 10% loading, the time to failure increased 4.5 times. The new PO-based PNC's are useful as molding resins. They can replace PE or PP when decreased crack growth rates are desired.

Table 3. Properties of PNC from AlliedSignal [36].

Property	Unfilled	0.01 wt% NC	0.05 wt% NC	0.1 wt% NC
Dry PA-6				
Flex strength (MPa)	2770	3070	3130	3160
Flex 5% modulus (MPa)	108	120	124	124
Tensile yield (MPa)	77	83	86	85
Impact strength (J/m)	69	66	64	65
Wet PA-6				
Flex strength (MPa)	417	507	550	546
Flex 5% modulus (MPa)	18	22	24	24
Tensile yield (MPa)	21	27	29	28
Elongation to break (%)	300	280	270	270

Table 4. Physical Properties of PP-based PNC with Modified Clay [43, 77].

#1. Modified clay = 10 wt% silane-treated clay (containing 2 wt% silane) and 90 wt% MA-PP							
Modified Clay (wt%)	0	1	2	5	10	20	30
Isotactic PP (wt%)	100	99	98	95	90	80	70
Tensile Modulus (GPa)	1.9	13	14	16	16	17	18
Strength (MPa)	31	32	32	33	43	50	53
Izod Impact (J/m)	33	31	31	30	31	29	28
#2. Modified clay = 60 wt% silane-treated clay (containing 2 wt% silane) and 40 wt% MA-PP							
Modified Clay (wt%)	0	1	2	5	10	20	30
Isotactic PP (wt%)	100	99	98	95	90	80	70
Tensile Modulus (GPa)	1.9	16	16	18	19	20	23
Strength (GPa)	31	34	35	35	57	64	68
Izod Impact (J/m)	33	31	29	29	27	25	22

4.2. Flame Retardancy of PNC

PA-based PNC's showed a non-obvious aspect of the nanocomposites technology — an improvement of the flame resistance. In 1965, Blumstein [94] reported that the presence of MMT increased the thermal decomposition temperature of PMMA by 40–50°C. Similar results were reported for PDMS and polyimide [95]. Since 1997, several publications from NIST call the PNC “a revolutionary new flame retardant” [96]. Cone calorimetry showed that PNC comprising 5 wt% clay reduces the peak heat release rate by 63%. The PNC structure appears to enhance formation of char through reinforcement by the clay particles. Furthermore, by contrast with customary flame retardants that lower resin performance, in PNC, the other physical properties are improved by incorporation of the clay. In 1997, Nyden and Gilman [97] developed a mathematical model to explain the flame retardant effect of graphite on PP. In agreement with radiative gasification experiments, it was found that the mass loss goes through a local minimum at the interlayer distance of 3 nm. Gilman recently published a review on these topics [98].

The use of PA-6-based PNC's as ablative materials was examined by Vaia *et al.* [99]. It was found that during ablation of PNC containing only 2 wt% of clay, an inorganic char forms that reduces the mass loss at least by one order of magnitude (relative to PA-6). The effect is related to the insulating layer of char formed on the ablated surface. The ablative layer and the role played by O₂ in thermal degradation were recently examined for PA-PNC [100]. During the thermal degradation of PNC, a protective barrier is formed that slows down the fuel diffusion.

5. SUMMARY

1. The most frequently used nano-filler is Na-MMT, having the optimum cation exchange capacity CEC = 90–120 meq/100g. The optimum aspect ratio of exfoliated platelets is $p = 500$ –1000.
2. During intercalation, the intercalant molecules diffuse to the galleries between individual clay layers. The process depends on the balance of forces, gallery size and geometry, the size and shape of the intercalant molecule, the matrix viscosity, *etc.*
3. Intercalation *via* Na⁺ exchange for onium cation is the most common. There is a great diversity of these intercalants, mostly based on the quarternary ammonium. The disadvantage of the ammonium intercalant is its degradability that is quite severe at $T > 250^\circ\text{C}$. Three solutions have been offered:
 - use of phosphonium intercalants that are stable up to 370°C,
 - use of inorganic pillared structures, and
 - use of a monomer as an intercalant, especially for acidified clays.

4. MMT also has hydroxyl groups that can participate in reactions with organo silanes, titanates, or zirconates. This method of intercalation is attractive for melt compounding of PO-based PNC.
5. In PNC's, the clay should be exfoliated, *i.e.*, the distance between individual platelets should be larger than about 8.8 nm, either forming short stacks (tactoids) or randomly dispersed layer by layer.
6. During the preparation of PNC by polymerization, the growing macromolecules should covalently bond to the clay platelet, ensuring exfoliation and preventing platelets to re-aggregate.
7. During the preparation of PNC by melt compounding, the macromolecules must be miscible with the intercalant. The process is diffusion controlled, hence sufficient time must be provided to ensure expansion of the interlayer spacing from about 3–4 nm to > 10 nm. Low melt viscosity and the use of ultrasonics (*ca.* 50 kHz) can help.
8. The recognized advantages of PNC are: increased modulus, strength, and elongation at break, reduced permeability for gases and liquids, as well as increased flame resistance and maintenance of transparency. The disadvantages are related mainly to the melt flow behavior, *viz.* increased viscosity and presence of the yield stress.

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Invited Paper Received 18 March 2001.

APPENDICES

Table 1A. Recent Examples of PNC (in Inverse Chronology)

Polymer	Nano-particles	Process
2000		
PS, PMMA, SAN	Lipophilized smectic clays	Free radical solution or emulsion polymerization
1999		
PP	Ultrasonically intercalated clay	Compounding PP with clay in an internal mixer
PA-6	Montmorillonite	Fiber spinning
HDPE	Treated fluoromica	Z-N polymerization and direct compounding
Dendrimers	Copper sulfide	Complexing and immobilization of dendrimer particles with (CuS) ₁₅
Polyvinylester	Organically-modified clay	Ultrasonic and mechanical agitation
Ionomer	Silicone oxide	Sol-gel process
HDPE	Silver-nano-particles	Solvent casting, extrusion or solid-state drawing; UV-irradiation.
PVC	Cellulose whiskers	Mechanical performance
PEG/PMMA	Exfoliated clay	Direct melt intercalation for controlled electrical properties
	Core-shell latex particles	Emulsion polymerization of nano-thick shell for optical properties
P(tBuA); PE	Evaporated gold particles	Vacuum deposition for optical anisotropy
PET	Intercalated clay	Polycondensation
PA-6, PVP	Clay	Melt intercalation
PA	Aromatic-PA fibers	Polymer blending
Polypyrrole	FeO	Synthesis of conductive NC
PSA	ZnS	Polymerization and precipitation of nano particles of ZnS
PDMS	Zirconia	Sol-gel method
A polymer	Mn-Zn ferrites	Room Temp. synthesis
Polyacrylamide	CdS, ZnS, or PbS	Polymerization into semiconductive NC
Epoxy	Clay	Anhydride curing
A polymer	Fe	Reduction of Fe ⁺⁺ in aqueous Solution
1998		
PVAc	SiO ₂	Sol-gel method
PDMS	Delaminated clay 1×100×1000 nm	Mechanically aligned
Latex	Cellulose whiskers, 5×300 nm	Strong effects of processing on NC performance
1997		
PC copolymer	CdS	Synthesis
Polyacrylonitrile	PbS	Synthesis by gamma-irradiation
Latex	Hard core-soft shell particles	Ordering then shell fusion to give fluorescent NC

Table 2A. Examples of Commercially Important PNC

Matrix	Nano-particles	Properties	Application
Polyamide, esp. PA-6 Major players: Toyota, AlliedSignal, Ube, Nanocor, Unitica, Showa Denko, Bayer, BASF, and Solutia-Dow.	Exfoliated silicates, <i>e.g.</i> , 1–3 vol% Na-montmorillonite. Exfoliation is crucial.	Similar density to PA, transparency, 70°C higher HDT, 70% higher tensile modulus, 130% higher flexural modulus, 1/2 lower oxygen permeability, 70% lower flammability, <i>etc.</i>	Automotive, tool housing, garden equipment, telecommunication, aerospace, specialty application, barrier film for food packaging, <i>etc.</i>
Polyolefins, esp. PP and copolymers. Major players: Montell, GM, Southern Clay Products Inc., Toyota, Ford, Dow Plastics, and Magna International.	Exfoliated smectite clay particles; ≤ 5 wt%. Compatibilizer is needed; <i>e.g.</i> , Toyota uses maleic anhydride modified PP.	Low density (0.91 g/ml), modulus of composites with 35 wt% talc, dimensional stability, low- <i>T</i> impact strength, ductility to -35°C , high heat aging, low flammability, surface finish	Automotive: body panels, door panels, interior trim, instrument panels, pillars, consoles, <i>etc.</i>
PS and blends Major players: Toyota	Surface-treated clay particles; 4.8 wt%.	High strength, tensile modulus increased by 37% (over PS), 43% smaller thermal expansion	Aerospace, automotive
Polyethylene terephthalate Major players: Eastman, Bayer, BASF	Solution-expanded clay particles present during the polycondensation.	Transparency, low permeability, high strength & stiffness, low density	Food packaging (central layer in co-formed beer, juice and soft drink bottles).
EVA Major players: Nanocor, Mitsubishi	Exfoliated smectite clay particles; ≤ 5 wt%.	NC to be the central layer in multilayer, co-formed products.	Packaging films, for moisture and oxygen sensitive foods and electronics.
Acetal (POM) Major players: Showa Denko, Bayer	Montmorillonite (?)	Low warpage, low shrink, high surface quality, HDT increased by 45°, 40% higher modulus	Automotive under-hood applications, electronics, <i>etc.</i>
Polyolefins (PO) Major players: Toyota, Mitsui, Showa Denko, Mitsubishi	Polypropylene columnar crystals	Low density, high rigidity and strength	Automotive

Table 3A. Summary of Intercalation Methods

Clay	Intercalant	<i>d</i> -spacing (nm)	Comments
MMT	None	0.96	Dry clay
MMT	Water	1.3	Ambient humidity
MMT	Ethylene glycol or sorbitol	1.7	Thickener
Clays with CEC = 80 to 150 meq/100 g	Ammonium, phosphonium or sulfonium salts with aliphatic or aromatic radicals	1.3–2.2	Spacing depends on CEC & intercalant size
Na–MMT	Aqueous solution of methyl benzyl di-hydrogenated tallow ammonium chloride	⇒ exfoliation	Thickening of organic solvents
Na–MMT	Aqueous solution of hydroxy-polyoxyethylene-tri-alkyl-ammonium chloride	⇒ exfoliation	Thickening of highly polar organic solvents
MMT	Aqueous solution of PVAI	≈ 2.0	PVAc 88% hydrolyzed
MMT	Aqueous solution of PVP (at least 10% of water is needed)	1.5–11.0; 3–4.5 is optimum	Thickener or for drug-delivery
MMT	Polar, water soluble compounds	⇒ exfoliation	For PNC as well
Smectite	Aqueous solution of $\text{AlCl}_2(\text{OH}) + \text{ZrOCl}_2$	2–6	Rigid pores for catalyst
MMT	Swelling in waterless PEG in 2–6 h	1.77	
Organo–clay	Monomer or polymer	⇒ exfoliation	For PNC
Inorganic layered materials	Inorganic polymer having colloidal particles, <i>e.g.</i> , hydrolyzable metallic alcoholates	1.5–61	For TS, TP or rubber-based PNC
Na–MMT	Aqueous ω -amino- C_{12-18} acid onium ion, with caprolactam	⇒ exfoliation	For PA-based PNC (Toyota)
MMT	Octadecylammonium cation and amino-ethyl amino-propyl trimethoxy silane	⇒ exfoliation	For PA-based PNC (AlliedSignal)
aqueous HCl + Na–MMT	Liquid polybutadiene (PBD)	⇒ exfoliation	For rubber-based PNC (Toyota)
Na–MMT (CEC = 120 meq/100 g)	Aqueous di-stearyl-dimethyl ammonium chloride, then end-hydroxylated PBD in toluene	⇒ exfoliation	For rubber-based PNC (Toyota)
Na–MMT (CEC = 120 meq/100 g)	Aqueous di-stearyl-dimethyl ammonium chloride, then melt-compounding with maleated PP	⇒ exfoliation	For rubber-based PNC (Toyota)
A layered material, <i>e.g.</i> , MMT	Hydrolyzed alcoholates: $\text{Si}(\text{OR})_4$, $\text{Al}(\text{OR})_3$, $\text{Ge}(\text{OR})_4$, <i>etc.</i>	⇒ exfoliation	For PO-based PNC (Dow)
Clay	Amino-functional silane + carboxylated or maleated semi-crystalline PO	⇒ exfoliation	For PO-based PNC
Acidified clay; H^+ MMT	Lewis bases, esp. primary amines	⇒ exfoliation	Explored for epoxy- and PU-based PNC's
Synthetic smectite	Aqueous solution of ethylenediamine + polyol, then oleophilic solution of TEP	Intercalation	Slow intercalation (2 weeks!) to fire-resistant clays