Fibers from polymeric nanocomposites

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The clay-containing polymeric nanocomposites (CPNC) comprise a polymeric matrix and dispersed in it mineral or synthetic clay platelets. The key condition for success is the thermodynamic miscibility of the ingredients at the processing temperature. Toward this goal, the clay is usually pre-intercalated and/or compatibilized with the matrix. The role of melt compounding is to accelerate the dispersion process. Adding an extensional flow mixer to the compounding line accelerates the dispersion. At the organoclay loading of 1-5 wt%, the CPNC show increased (in respect to matrix polymer) rigidity, strength, dimensional stability, barrier properties, flame resistance, etc. The main use of CPNC is in the transport and packaging industries. Fiber spinning of CPNC started about five years ago. The preliminary work demonstrated several beneficial aspects of the technology, e.g. improved spinnability, dyeability, mechanical properties, reduced shrinkage, flame resistance, and others. This review provides a brief outline of the fundamental aspects of CPNC production followed by a summary of publications on the electrospinning, solvent spinning, and melt spinning of CPNC. An effort has been made to focus on the relative effects brought about by incorporation of organoclay.

Keywords: Clay-containing polymeric nanocomposites, Compounding, Extrusion, Nanocomposite, Organoclay, Spinning

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1 Introduction

Polymeric nanocomposite (PNC) is a polymer with dispersed in it particles, whose at least one dimension is smaller than about 10 nm. The particles may be spherical (e.g. metallic or ceramic, for functional applications), fibrillar (e.g. carbon nanotubes) or lamellar – the only nano-sized particles of interest to polymer industry are layered clays, in particular natural (mineral) or synthetic montmorillonite (MMT) or hectorite (HT). The dictionary of terms used in the clay-containing polymeric nanocomposite (CPNC) literature is given in Table 1.

The global CPNC market is > 20 kton/y or ca. $200 M/y, increasing 18.4%/y and projected to reach 550 kton/y by 2009 (ref. 2). The main application is in the automotive and packaging industries with growing demands for appliances, building & construction, electrical & electronic, lawn & garden, power tools, sport equipment, etc. A summary of current CPNC use is given in Table 2.

As shown in Table 2, CPNC has been widely accepted by the industry and its commercialization expands. However, several technological problems still remain and understanding of these systems is superficial. Current industrial production of CPNC is mainly based on the reactive exfoliation, i.e. polymerization of a given monomer(s) in the presence of pre-intercalated clay. This slows down acceptance of these materials by the plastics industry. Only development of a reliable melt compounding technology that shifts the CPNC manufacture from the resin producers to compounders and fabricators will change the situation. The melt compounding will add flexibility; nanocomposites with desired performance characteristics will be prepared where and when needed, accelerating CPNC penetration of the market.

This review discusses the fundamentals that govern CPNC properties and must be respected when preparing these systems, the type of clays, the methods of CPNC preparation, and the use of CPNC in the fiber industry.

2 Fundamentals of CPNC

CPNC have been investigated for about 30 years. At loadings rarely exceeding 4 wt% organoclay, they show significantly improved performance (in comparison to matrix). The principal advantages are: stiffness, strength, reduction of permeability (1000-fold at 5 wt% clay loading) and that of flammability. A high degree of dispersion is essential in applications requiring good mechanical and barrier properties, but it is less important, e.g. for the flame resistance. Thus, the main goal for the researchers and engineers is to ascertain good and stable dispersion. However, before the engineer can put into practice an
Table I—Dictionary of terms used in the polymeric nanocomposite literature

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compatibilization</td>
<td>Process of modification of the interfacial properties in CPNC, resulting in formation of the interphase, creation and stabilization of the desired morphology.</td>
</tr>
<tr>
<td>Exfoliated layered material</td>
<td>Individual platelets dispersed in a matrix with the interlayer spacing: (d_{001} &gt; 8.8 \text{ nm}). Depending on concentration, the platelets may be randomly dispersed or oriented, forming short stacks or tactoids.</td>
</tr>
<tr>
<td>Exfoliation</td>
<td>Converting intercalate into exfoliate.</td>
</tr>
<tr>
<td>Intercalant</td>
<td>Material sorbed between platelets that binds to their surfaces forming an intercalate. Most intercalants are onium (ammonium) salts.</td>
</tr>
<tr>
<td>Intercalated material (organoclay)</td>
<td>Layered material with intercalant molecules inserted between platelets, thus increasing the interlayer spacing between them to at least 1.5 nm.</td>
</tr>
<tr>
<td>Intercalation</td>
<td>Forming an intercalate.</td>
</tr>
<tr>
<td>Layered material</td>
<td>Synthetic or mineral inorganic compound, such as smectic clay, formed of adjacent lamellae with a thickness of 0.3-1 nm each.</td>
</tr>
<tr>
<td>Interlayer spacing</td>
<td>Also known as basal spacing, (d)-spacing or (d_{001}) is the mineral platelet thickness ((\text{in MMT} = 0.96 \text{ nm})).</td>
</tr>
<tr>
<td>Interlayer thickness</td>
<td>Also known as interlamellar spacing or intergallery spacing; (d)-spacing less the mineral lamella thickness.</td>
</tr>
<tr>
<td>Miscible polymeric system</td>
<td>Homogenous down to the molecular level, associated with the negative free energy and heat of mixing, (\Delta G_m = \Delta H_m - T\Delta S \leq 0), and (\partial^2 \Delta G_m / \partial T^2 &gt; 0). A thermodynamically stable CPNC, where the clay platelets are well dispersed in a matrix.</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite; Na-MMT = sodium montmorillonite; H-MMT = protonated MMT.</td>
</tr>
<tr>
<td>Matrix polymer</td>
<td>A polymer in which the intercalate is dispersed to form a CPNC.</td>
</tr>
<tr>
<td>Nanocomposite (NC)</td>
<td>A material (metallic, ceramic or polymeric) having dispersed nano-particles, whose at least one dimension does not exceed 10 nm.</td>
</tr>
<tr>
<td>Nanofibers</td>
<td>Fibers with diameters &lt; 100 nm, whose material properties exhibit size dependence.</td>
</tr>
<tr>
<td>Organoclay</td>
<td>Intercalated clay.</td>
</tr>
<tr>
<td>Platelets</td>
<td>Clay lamellae, individual layers of the layered material.</td>
</tr>
<tr>
<td>Polymeric nanocomposite (PNC)</td>
<td>A polymer or copolymer having dispersed in it nano-sized particles, viz. platelets, fibers, spheroids, etc.</td>
</tr>
<tr>
<td>Short stack or a tactoid</td>
<td>Intercalated or exfoliated clay platelets aligned parallel to each other.</td>
</tr>
<tr>
<td>Spacing</td>
<td>Two measures are used: interlayer spacing and interlamellar spacing. The former comprises the layer plus the platelet thickness. For example, for MMT, (d_{001} = \text{Interlamellar spacing} + 0.96 \text{ (nm)}).</td>
</tr>
</tbody>
</table>

Efficient and commercially successful technology he or she must understand the factors involved – the fundamentals.

Physics is marvelous – its laws have universal validity. For example, the rules governing miscibility of water and alcohol are the same for clay and water or clay and polymer. The best way to regard exfoliated CPNC is to treat it as a solution of 'clay molecules' in molten polymer. In this concept, the 'clay molecules' are equated with individual platelets, characterized by their size and the thermodynamic properties. Similarly like macromolecules, these 'clay molecules' may be treated as composed of a number of statistical segments each with a set of characteristic parameters. This concept has been explored in molecular dynamics (MD) computations, e.g. using the self-consistent field (SCF)\(^\text{10}\) or a cell-hole lattice model, where segments of the "clay molecule" and that of a polymer are placed in the lattice cells of similar size – excellent description of the observed behavior validated the concept for CPNC with PA-6\(^{\text{19}}\), polystyrene (PS)\(^{\text{10}}\), or PP\(^{\text{10}}\) as the matrix. These computations make obvious the key role of thermodynamics for dispersing clay platelets in molten polymer – only when the thermodynamic conditions are satisfied the mechanical exfoliation may be achieved, i.e. the negative free energy of mixing is required:

\[
\Delta G_m = \Delta H - T\Delta S < 0
\]

Since polymer diffusion into the gallery decreases the entropy, \(\Delta S < 0\), the only way to satisfy the condition is for the enthalpy to be strongly negative, \(\Delta H < 0\). Thus, interactions that result in exothermic reactions are needed.

Owing to hydrophilic character of clay, the preparation of CPNC with water-soluble polymers is
Tw o non-exclu sive methods ha ve been used to solve this problem: (i) clay intercalation and (ii) compatibilization of the system.

Historically, the organoclays were developed as thickeners for lubricating oils and greases, thus even today the most common intercalant is a quaternary ammonium ion with paraffinic substituents, e.g. di-methyl di-hydrogenated tallow ammonium chloride (2M2HT, Quaternium-18, C_{36}H_{76}NCl, MW = 567-573 g/mol). Clay intercalated with such a compound becomes miscible (or dispersible) in hydrocarbons, but seldom in polymers. Intercalants with benzyl or ethoxy groups are known and respective organoclays are commercially available. However, the presence of these groups does not provide sufficient thermodynamic miscibility, e.g. Cloisite® 10A (di-methyl benzyl hydrogenated tallow ammonium chloride, 2MBHT) in spite of its benzyl group is immiscible with PS.\textsuperscript{3,11}

As the schematic indicates, the longest paraffinic substituent (R-CH\textsubscript{2}-CH\textsubscript{2}-) is converted into vinyl-terminated compound that in the presence of oxygen forms peroxides, which, in turn, attack the matrix polymer causing a loss of performance. Thus, CPNC must be compounded under blanket of N\textsubscript{2}.

The mathematical modeling leads to the conclusion that macromolecular intercalants (especially
The surface force apparatus was used to study the solidification on the clay surfaces significantly affect the CPNC behavior. The MMT lamellae are 0.96 nm thick, but since the thickness of each solidified organic layer is 5-6 nm, the solidification augments the volume of each exfoliated platelet by a factor of about 12! However, when the system is only intercalated (hence, having the interlayer spacing, \(d_{001}\) < 8.8 nm), the adsorption-\&-solidification turns the intercalated stack into a solid block, making delamination difficult.

The polymer solidification on the clay surface leads to decrease of segmental mobility, and thus a loss of free volume. As shown in Fig. 1, the loss is proportional to the available surface – the largest loss was found for fully exfoliated CPNC having PA-6 as the matrix, the smallest for poorly dispersed organoclay in PS matrix. Thus, at constant organoclay loading of 2 wt\% the loss of free volume (i.e. the reinforcing ability) is a linear function of the interlayer spacing (\(d_{001}\), as measured by the X-ray diffraction), i.e. of the clay surface area available for adsorption.

The large multiplication factor of the adsorbed solid offers explanation for the disproportionate enhancement of performance by addition of small amount of clay. For example, CPNC from Ube, PA1015C2 is reactively exfoliated PA-6 with \(\phi = 0.64\) vol\% of clay, but such a small amount of reinforcement causes tensile modulus to increase by 26\%, strength by 14\%, HDT by 65\°C and permeability to decrease by a factor of two.

The enlargement of clay platelet volume by matrix solidification also affects the flow properties. From the rheological point of view one must distinguish several types of CPNC, e.g. with: \#1 intercalated stacks, \#2 exfoliated organoclay platelets not bonded...
to the matrix (intercalant is miscible with polymer), and #3 exfoliated platelets bonded to the matrix. System #1 follows the pattern of viscoelastic suspensions of anisometric particles. At low clay loading it may show a reduction of viscosity, but when the concentration of stacks exceeds the critical packing volume fraction the system may show a yield stress and high plateau modulus. System #3 displays the distinctive CPNC behavior. For example, the stress growth function in steady shear experiment shows that relaxation of platelet orientation requires about one hour — the system is unusually sluggish. The effect originates in the adsorption- and solidification of the matrix, as well as direct bonding of thousands macromolecules to each clay platelet. The entanglements of macromolecules attached to different platelets engender formation of tri- and higher dimensional structures at the clay volume fraction as low as \( \phi = 0.0016 \). Furthermore, the large clay platelets behave similarly to mesogenic groups in liquid crystal polymers (LCP).

Another evidence of the adsorption- and solidification is more recent and more direct. The tensile strength, \( \sigma_t \), of CPNC with PA-6 and PP matrix was measured\(^2\). Assuming that clay platelets are perfectly aligned in the stress direction and that they perfectly adhere to the matrix, the volumetric rule of mixtures was applied\(^2\):

\[
\sigma_r = \sigma_t / \sigma_m = 1 + \phi_f (\sigma_t - 1); \quad \sigma_c = \sigma_f / \sigma_m \quad \text{...(2)}
\]

In Eq. (2), \( \phi \) is the volume fraction, and the subscripts \( c, m \) and \( f \) stand for composite, matrix, and filler, respectively. Evidently, the assumptions used in deriving Eq. (2) lead to prediction of the maximum possible value of relative strength, \( \sigma_r \).

To calculate \( \sigma_r \) from Eq. (2) for PP and PA-6 systems, the clay tensile strength of mica was used, \( \sigma_t = 240 \) MPa\(^3\), while that of matrix, \( \sigma_m \), was measured. The clay volume fraction in PP and PA-6 systems was: \( \phi_f = 0.0042 \) and 0.0053 respectively. With these values, Eq. (2) highly underestimated \( \sigma_r \). Since the relation should predict the maximum, the only explanation is that there is a larger volume of reinforcing particles in the samples than that of bare inorganic clay platelets. The value of \( \phi_f \) required for Eq. (2) to predict the correct value of \( \sigma_r \) was found to be about 5 and 9 times larger (for PP- and PA-6 CPNC respectively) than that calculated for bare MMT platelets. These numbers are quite reasonable, considering solidification of the matrix in these partially exfoliated systems.

### 3 Mineral vs. Synthetic Clay

While the mineral clays still dominate the market, the synthetic ones constitute a valuable alternative for CPNC. For example, Unitika produces CPNC with synthetic fluorohectorite (FH) dispersed in PA (and in PLA) matrix\(^3\)\(^4\)\(^5\), while Ube uses mineral MMT. The properties of these two commercial CPNC are listed in Table 3.

Synthetic layered silicates are prepared using several methods and might be classified as:

(i) Semi-synthetic—Prepared by modification of such minerals as talc or obsidian, partially replacing Mg\(^{2+}\) by Na\(^+\) or Li\(^+\) in the octahedral layer. For this purpose Li\(_2\)CO\(_3\) and Na\(_2\)SiO\(_3\) may be used. In the fluoro mica (FM), the fluorine partially replaces the -OH groups and thus modifies reactivity.

(ii) Fully synthetic—Here, formation of layered silicate starts with a variety of metal oxides that provide suitable composition, e.g. \((\text{Si}_x\text{O}_{10})\cdot(\text{Mg}_2\text{Li}_3\text{OH})\cdot\text{F}_y\) for crystallizable layered silicates. Two sub-categories are known:

- The low temperature, hydrothermal process starts with aqueous salt solutions, followed by co-

<table>
<thead>
<tr>
<th>Property</th>
<th>CPNC from Ube</th>
<th>CPNC from Unitika</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, kg/cm(^2)</td>
<td>800</td>
<td>810</td>
</tr>
<tr>
<td>Tensile elongation, %</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Flexural strength, kg/cm(^2)</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Flexural modulus, kg/cm(^2)</td>
<td>28.5</td>
<td>29.0</td>
</tr>
<tr>
<td>Impact strength, kg cm/cm</td>
<td>6.5</td>
<td>4.9</td>
</tr>
<tr>
<td>HTD (18.56 kg/cm(^2)), (^\circ)C</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>HTD (4.6 kg/cm(^2)), (^\circ)C</td>
<td>180</td>
<td>175</td>
</tr>
<tr>
<td>H:\O permeability, g/m(^2)\cdot24 h</td>
<td>203</td>
<td>–</td>
</tr>
<tr>
<td>Density, kg/m(^3)</td>
<td>1140</td>
<td>1140</td>
</tr>
</tbody>
</table>
precipitation into slurry, which, in turn is boiled under reflux for 10-20 h to induce crystallization.

- The high temperature process starts with fine powder of suitable salts (e.g., Li2O, MgO, SiO2 and MgF2), mixed in proper proportion, heated at 1300°C for 3 h and then allowed to cool for 10 h. The reaction mass is placed into water, and the solid contaminants sedimented, yielding synthetic hectorite.36

(iii) Tempered synthetic (non-commercial)—Based on organic templates, which after synthesis may be pyrolysed, or left in as intercalants.37

The advantages and disadvantages of mineral and synthetic clays are summarized in Table 4. Owing to non-toxicity, lack of color, reproducible composition and a wide range of available aspect ratios, the synthetic clays may be particularly attractive for the production of CPNC-type nano-fibers.

4 Compounding CPNC

CPNC belong to the category of multi-phase systems (MPS: blends, composites and foams) that require controlled compounding, orientation of the dispersed phase, stabilization of dispersion and orientation as well as optimization of interactions in the solid state. The dispersive mixing is responsible for breaking the minor component domains to desired size, which than are homogeneously distributed within the matrix. Microstructure may be used to describe the dispersive process in the shear or extensional flow field, while distributive mixing may be treated in terms of the laminar flow theory or that of chaotic mixing. Both, the microstructure and laminar mixing, point out the superiority of the extensional flow field.4

Most plastics compounders employ shear, while theories reveal superiority of extensional flow for mixing.38 For example, elongational mixing:

(i) is orders of magnitude more energy-efficient (than shear),
(ii) generates better dispersive and distributing mixing,
(iii) generates low temperature increases; ca. 1-3°C (vs. 70°C in shear),
(iv) does not cause re-aggregation of solid particles (reported in shear), and
(v) may be generated using convergent-divergent (C-D) flow geometry, either in motionless or dynamic mixing devices.

These reasons motivated the development of the extensional flow mixer (EFM) and its dynamic version, DEFM.39 EFM has been designed as an inexpensive mixer to be attached to a single-screw extruder (SSE) for dispersing one molten polymer in another40, i.e. for alloying and blending polymers, homogenization of reaction products, etc.41 Alternatively, a twin-screw extruder (TSE) could be used with EFM. However, this compounder is not only much more expensive than SSE, but also a gear pump (GP) must be used to provide the driving pressure for EFM.42 Addition of GP to the compounding line increases cost and induces additional processing and performance problems.

The blends prepared in SSE + EFM often outperformed those from TSE. These results were expected on the basis of theoretical analysis of mixing, and indeed for melt homogenization and blending, EFM performs well. However, since the principles of dispersing one molten polymer into another are different than those for dispersing solid

<table>
<thead>
<tr>
<th>Mineral clay</th>
<th>Synthetic clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite (MMT)</td>
<td>Fluoro mica (FM)</td>
</tr>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td>Well-established technology</td>
<td>Variability of composition and color</td>
</tr>
<tr>
<td>Availability</td>
<td>Crystallographic defects that prevent total exfoliation</td>
</tr>
<tr>
<td>Lower cost than synthetic</td>
<td>Poor reproducibility of PNC performance</td>
</tr>
<tr>
<td></td>
<td>Difficult removal of contaminants</td>
</tr>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td>Stable composition and shape</td>
<td>Developing technology</td>
</tr>
<tr>
<td>Wide range of platelets aspect ratio: $p = 20-6,000$</td>
<td>Limited and uncertain sourcing</td>
</tr>
<tr>
<td>Reproducible PNC performance</td>
<td>Higher cost than mineral</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>

Table 4—Advantages and disadvantages of mineral and synthetic clays4
aggregates, it came as a surprise that the commercial EFM-3 (Fig. 2a) successfully dispersed organoclay in thermoplastic matrices (polyethylene terephthalate or PET, PA-6, PP, PS, etc.). The theory of mixing suggests that the dispersion of solid particles should be four times more efficient in the extensional flow than in a shear field. PET compounded with organoclay in a TSE + EFM-3 showed the tensile modulus increased by 67%, tensile strength by 70% and impact strength by 80% as compared to the product compounded without EFM. The results encouraged redesigning the EFM.

The new unit (EFM-N) was designed considering the deduced mechanism of clay dispersion. In principle, the flow profile between convergent-divergent (C-D) plates was modified. The material has to pass through a series of C-D elements, each of them having three flow zones: (i) a hyperbolic convergence that orient organoclay aggregates in the flow direction, (ii) controllable gap were the top and bottom clay platelets are peeled off from the aggregate, and (iii) a divergent part that randomizes the flow. The most critical is the balance of the extensional to shear stresses within each C-D element.

Performance of the new EFM-N was examined by preparing a series of CPNC compositions with PA-6 or PP as the matrix. The organoclay was used at 0, 2 and 4 wt% loadings. The PP-based CPNC were compatibilized with a mixture of two PP-MA's. The material characteristics are given in Table 5.

The compounding was carried out using a TSE, TSE + GP, TSE + GP + EFM or a SSE with or without EFM. For comparison, EFM-3 and EFM-N were used with at least four different gap settings between the C-D plates. To ascertain homogeneity of composition, a master-batch (MB) was prepared in a TSE. Dry blending MB with homopolymer, and then mixing in the aforementioned compounding lines resulted in CPNC. The degree of clay dispersion was determined using the X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The performance was assessed measuring the tensile, flexural and impact properties.

As shown in Fig. 3, the use of the new EFM-N resulted in good dispersion of C15A in PA-6. The exfoliation (97.1%) was higher than that determined for Ube PA1015C2 (80.7%) – the material used as a reference. The XRD data were confirmed by HRTEM (Fig. 4).

The results for PP-based CPNC were less spectacular than those for PA. Here, the thermal instability of C15A dominated. TSE caused the greatest reduction of d_{001} as a function of decreasing gap, while in SSE + EFM degradation was evident only at the smallest C-D gap of 15 µm. However, in all three compounding lines the reduction of C-D gap was paralleled by progressive exfoliation. The best dispersion was obtained using SSE + EFM-N with gap of about 30 µm.

5 Use of CPNC in Fiber Industry

The first modern use of clays in a polymeric matrix is credited to Fujiwara and Sakamoto, who in 1976 applied for Japanese patent on the ‘Method for manufacturing a clay-polyamide composite’[^48]. It took additional 20 years before PA-based CPNC became commercially available. The exploratory fiber spinning of CPNC started about five years ago. Three

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[^48]: For more information, see the reference text.
Table 5—Material characteristics

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name*</th>
<th>$M_w$ kg/mol</th>
<th>Density g/mL</th>
<th>$T_m$ °C</th>
<th>MAH wt%</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-6</td>
<td>Ube-PA1015B</td>
<td>21.7</td>
<td>1.14</td>
<td>216</td>
<td>—</td>
<td>Ube Industries</td>
</tr>
<tr>
<td>PP</td>
<td>PROFAX-PDC1274</td>
<td>250</td>
<td>0.902</td>
<td>161</td>
<td>—</td>
<td>Basell Polyolefins</td>
</tr>
<tr>
<td>PP-MA11</td>
<td>Epолнene-3015</td>
<td>47</td>
<td>0.91</td>
<td>162</td>
<td>1.31</td>
<td>Eastman Chemicals</td>
</tr>
<tr>
<td>PP-MA29</td>
<td>Polybond 3150</td>
<td>330</td>
<td>0.91</td>
<td>164</td>
<td>0.5</td>
<td>Crompton</td>
</tr>
<tr>
<td>Organoclay (C15A)</td>
<td>Cloisite® 15A</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>South. Clay Prod.</td>
</tr>
</tbody>
</table>

* C15 is MMT intercalated with excess (1.25 meq/g or 0.78 mmol/g) of di-methyl di-hydrogenated tallow ammonium chloride (Arquad 2HT); it contains 43 wt% of the organic phase and 2 wt% of water

Fig. 3—Interlayer spacing and the degree of exfoliation for PA-6 nanocomposites compounded in a TSE + GP + EFM-3 and in SSE with either EFM-3 or EFM-N. For comparison, the values for Ube PA1015C2 are also shown.

Incorporation of organoclay into matrix polymer is expected to modify the fiber/textile performance. The main effects should be in physical properties, e.g., enhanced tensile modulus and strength, reduction of shrinkage, controlled electrostatic behavior, enhanced abrasion resistance, etc. In addition, the presence of hydrophilic clay might enhance moisture absorption (but at a slower rate), dyeability, biodegradability and chemical resistance. Since clay platelets block the UV irradiation, the CPNC textiles should have better weatherability. Furthermore, the inherent tendency of clay to reduce the burning rate and form char is expected to enhance applicability of these fibers in the domestic and transport applications.

The mineral MMT clay platelets used in most commercial organoclays have the aspect ratio $d = 286$, which means that the average ‘diameter’ is $d \approx 300$ nm. However, the clay platelets fracture mainly along straight lines, thus $d = 2 \sqrt{a_1 a_2 / \pi}$.
where $a_1$ and $a_2$ are the width and length of rectangular flake. If the rectangle has sides whose length ratio is 1.3, the width and length of such a flake would be about 150 and 450 nm respectively. Thus, for smooth surface, the fiber diameter (longitudinally elongated flake) should be $> 150$ nm. However, when polymers are end-tethered to the clay platelet, on stretching the latter gets oriented in the transverse to stress (or fiber) direction. In consequence, the surface of sub-micron fibers might be rough, especially when the organoclay is not fully exfoliated. Alternatively, one may mill the organoclays or use synthetic clays with low aspect ratio, viz. $p = 20-50$. These clays offer additional advantages, e.g. selection of chemical composition to control conductivity, dyeability, etc. Furthermore, since synthetic clays are colorless, they allow generating bright and consistent colors (the mineral MMT is contaminated with Fe[3], coloring the CPNC from light yellow to brown red).

5.1 Electrospinning

In most reports where electrospinning was used, the fibers were produced from solutions containing ca. 10-wt% of polymer or CPNC. The method resulted in the production of neat polymer fibers with diameters ranging from about 70 nm to 1000 nm (refs 49,50). The CPNC technology adds extra dimension to the range of applications of fibers and nanofibers. Evidently, suitable CPNC for the fiber manufacturing must possess several criteria, including the type, geometry, and concentration of nanoparticle, high degree of clay dispersion, miscibility of polymeric matrix and organoclay in selected solvent(s). During electrospinning, fibers are formed from an electrically charged polymer liquid jet in the presence of electric potential. Accordingly, the electrospinnability may be defined as the ability of forming stable and continuous jet in the presence of an electric field.

Fong et al.31 are credited to demonstrate electrospinnability of CPNC first. The authors prepared CPNC by melt compounding of PA-6 with Cloisite® 30B (C30B; MMT intercalated with methyl tallow di-ethoxy ammonium chloride, MT2ETOH)—the system known to yield well-dispersed nanocomposite. For electrospinning, the compound was dissolved in hexafluoro-isopropanol (HFIP). Addition of di-methyl formamide (DMF) was found to aggregate C30B, pointing out the need for selection of solvent(s) miscible with all CPNC components. Highly oriented fibers were produced with diameter ranging from about 100 to 500 nm, but in addition 100-200 nm thick and 10,000 nm wide ribbons were obtained. The orientation of MMT platelets was perpendicular to the fiber axis. Thus, since the fiber surface was smooth, one must infer that the longest dimension of MMT platelets in the product was less than 100 nm, which may indicate attrition either before or during processing. Unfortunately, the authors did not comment on the relative merits of C30B presence in the electrospun polymer.

Similarly, polylactic acid (PLA) and PLA with 3-5 wt% C30B were electrospun from CHCl3 solution.52 Again, smooth fibers with uniform diameter ranging from 100 to 500 nm were reported. Incorporation of organoclay resulted in formation of $\beta$-PLA, reduction of the melting point by 10°C (to 140°C) and significant decrease of PLA crystallinity. The plasticating effects of C30B intercalant might be responsible for these changes.

More recently, electrospun fibers were prepared from DMF solutions of emulsion polymerized poly(methyl methacrylate-co-methacrylic acid) copolymers (PMMA-MA) or their nanocomposites.53 In the latter case, Na-MMT (Cloisite®-Na) or sodium fluorohectorite (Na-FH; a magnesium silicate with aspect ratio: $p \leq 6,000$) was dispersed in emulsion of the monomers. After polymerization, the MMT platelets were well dispersed, whereas FH formed tightly packed ($d_{eq} = 1.04-1.19$ nm), randomly dispersed stacks. Several observations were made: (i) The presence of clays improved the electrospinnability through increased extensional viscosity and strain hardening (SH); (ii) Addition of clay resulted in reduction of fiber diameter, viz. 550, 350 and 320 nm for neat PMMA-MA, that with MMT, and that with FH respectively; (iii) MMT was well dispersed and fiber surface was smooth; (iv) FH platelets were poorly dispersed and protruded from fibers; (v) The exfoliated MMT clays increased the glass transition temperature and thermal stability as well as reduced flammability and improved self-extinguishing properties through char formation.

These preliminary reports on CPNC electrospinnability point out that organoclay must be well dispersed (preferably exfoliated) and miscible (internally and with the solvent). Addition of organoclay that interacts with the matrix is expected to increase the elongational viscosity and SH[1]—both desirable for improved spinnability and elimination of polymeric beads (observed on fibers from neat
polymers). However, when organo clay is immiscible with matrix, the effect on flow is small, and the strain hardening is absent. For electrospinnability, the source of layered silicate might be important. Owing to variability of natural clay composition (from different geographic locations as well as from local strata), the MMT dielectric properties vary, which, in turn, may affect the CPNC electrospinnability.

5.2 Solution Spinning
These days the conventional solution spinning method is seldom used. However, for CPNC with water-soluble polymers the method may be attractive as it is non-toxic, non-polluting and inexpensive. Water-soluble polymers include: polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), polyglycols (e.g. ethylene or propylene: PEG or PPG), polyacrylic acid (PAA), etc. Additional advantage is that in water, the clay (e.g. Na-MMT) may be fully exfoliated by adjusting pH and, thus avoiding the cumbersome and expensive pre-intercalation. Evidently, these comments are also valid for electrospinning – the smallest diameter nanofibers (ca. 70 nm) were obtained from aqueous solutions.

The solution spinning was used to prepare fibers of PVAI with Na-MMT. The latter compound was first dispersed in water at room temperature and then PVAI was dissolved. The nano-suspension was filtered and spun. Fibers could be obtained only when MMT concentration was < 2 wt% (on the total mass of CPNC). While the degree of clay dispersion is not given, the reported properties were improved. However, drawing (to unknown ratio) reduced the relative values, viz. tensile modulus from 1.95 (as spun) to 1.11 (drawn), strength from 1.11 to 1.10 and elongation-at-break from 0.81 to 0.66. The CPNC fibers showed improved thermal stability.

5.3 Melt Spinning
Melt spinning is the most common method. However, owing to large number of parameters involved, it is the most difficult to draw conclusions from. The CPNC for spinning may be prepared by different methods: in many cases the vital information (e.g. the clay concentration, level of clay dispersion, spinning parameters, the draw ratio) is not provided. The melt spinning is carried out at different temperatures and speeds using diversity of equipment and procedures.

The most consistent set of information originating from a single laboratory is available for fibers melt spun from CPNC with thermoplastic polyester (PEST) matrix. The early work involved thermoplastic LCP56 compounded with 2-6 wt% of Cloisite® 25A (C25A; MMT pre-intercalated with di-methyl hydrogenated tallow octyl ammonium salt, 2MHTL8) in internal mixer at 190°C, i.e., within the nematic zone. The fibers were produced using a capillary rheometer with 0.75 mm diameter die. Even at 2 wt% loading, TEM showed presence of clay stacks. In spite of poor dispersion, there was a significant enhancement of the tensile modulus and strength.

Similar results were obtained for CPNC based on polybutylene terephthalate (PBT)57, PET58 or polytrimethyl terephthalate (PITT). The relative modulus, $E_R$, and relative strength, $\sigma_R$, was found to depend on the clay content, w, and draw ratio, DR:

$$E_R = \frac{\sigma_R}{\sigma}$$

As the data in Fig. 5 demonstrate, the incorporation of C25A enhanced performance of LCP. However, the dependencies in Fig. 6 are more interesting. They show that as DR increases, the performance of CPNC fibers falls below that observed for neat matrix (relative values < 1). Drawing usually enhances crystallinity of the polymer. However, in the case of PBT with organoclay, it resulted in CPNC softening and reduction of tensile strength. The most likely reason is the immiscibility of intercalant with the matrix, which provides a stress releasing interphase – the phenomenon well-known for polymer blends.

![Fig. 5—Relative tensile strength, $\sigma_R$, and relative tensile modulus, $E_R$, of LCP as a function of Cloisite® 25A content at draw ratio: DR = 1 (ref. 56).](image)
A better miscibility of organoclay with PET or PTT matrices was achieved using an aromatic phosphine intercalant: dodecyl tri-phenyl phosphonium, DD3PhP. In addition to improved miscibility the organoclay (MMT-DD3PhP) was more thermally stable – an important aspect when the processing temperature is 280°C.

Equation (3) fitted to the relative modulus, \( E_R \), of CPNC with PTT as the matrix gave the following parameters: \( a_0 = 1.006 \pm 0.051 \); \( a_1 = 0.133 \pm 0.016 \); \( a_2 = 0 \); and \( a_2 = 0.198 \pm 0.036 \). The goodness of fit can be judged by the standard deviation, \( \sigma = 0.044 \) and the correlation coefficient squared, \( r^2 = 0.9993 \). Since all parameters of Eq. (3) are non-negative, the relative modulus is always larger then \( a_0 = 1.006 \pm 0.051 \), thus \( E(\text{CPNC}) > E(\text{PTT}) \). For the relative strength, \( \sigma_R \), \( a_0 = 1.24 \pm 0.33 \); \( a_1 = -0.12 \pm 0.23 \); \( a_2 = 0.026 \pm 0.038 \); and \( a_3 = 0.030 \pm 0.051 \); \( \sigma = 0.063 \) and \( r^2 = 0.998 \). Thus, the clay concentration has a secondary effect to drawing, which reduces the CPNC tensile strength.

However, the reason for incorporating clay is not limited to tensile properties. For industrial applications, e.g. hot rinsing in the pulp-&-paper industry, the heat shrinkage of a PET fiber is important. It was reported\(^6\) that the incorporation of 1.5 wt% MMT (pre-intercalated with PVP) into prepolycondensation reactants reduced the heat shrinkage of PET-based CPNC by ca. 12%.

Owing to a wide use of polyamides in the fiber industry, several research groups investigated the effect of organoclay addition on PA fiber properties.\(^6\)\(^4\) In most cases PA-6 has been the matrix (PA-12 in ref. 62). The CPNC were prepared by melt compounding PA-6 with a variety of pre-intercalated MMT and probably by reactive intercalation (refs 61,62). The concentration of organoclay ranged from 1 to 5 wt%. At the high limit, the fibers showed surface roughness and irregular variation of diameter, indicating the presence of organoclay aggregates of different size and properties.\(^6\) Most organoclays had intercalants with paraffinic groups, thus immiscible with PA matrix. As one of the consequences, the PA-6 crystallinity either was unaffected or reduced by organoclay. In spite of that, the tensile modulus was enhanced, e.g. at 3 wt% of organoclay by 40 % (DR not specified).\(^6\)

Similarly as it was the case for CPNC with PEST matrix, the absolute and relative values of tensile modulus and strength of CPNC fibers with PA matrix changed with DR. PA macromolecules can be bonded to clay platelets either covalently or by virtue of strong polar-polar bonds. When such bonding takes place, drawing is expected to be more beneficial for CPNC than neat polymer fibers.

For example, PA-6 was compounded with 1 wt% of organoclay (MMT pre-intercalated with 2M2ODA = di-methyl di-octadecyl ammonium) in a TSE and then spun at 260°C, i.e. well above the limit of thermal stability of 2M2ODA.\(^6\) At DR = 1, 1.5 and about 3, the relative modulus \( (E_R) \) was respectively 0.90, 1.02 and 1.13. Furthermore, incorporation of organoclay increased the flame retardance and thermal stability (over that of PA).\(^6\) This encouraging information notwithstanding, the relative merit of clay incorporation into PA matrix awaits the systematic, well-planned studies.

PP-based nanocomposites also have been melt-spun.\(^6\)\(^0\)\(^6\)\(^5\) The CPNC was prepared by melt intercalation in a TSE, followed by melt spinning from a SSE. The composition comprised PP (MFR = 44 dg/min), 2 wt% PP-MA, 5 wt% unknown organoclay and 1 wt% PS.\(^6\) Good spinnability was reported. The XRD and TEM indicated the presence of organoclay stacks (intercalation). The organoclay was found to nucleate crystallization of PP, increasing the crystallization rate and total crystallinity, but without affecting the crystal form. Considering the high clay content, it was not surprising that the CPNC fiber surface was rough with many flaws and grooves.

However, this, in turn, improved the moisture absorption as well as dyeability of the PP fibers. The latter aspect is of particular importance, considering

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**Fig. 6**—Relative tensile strength, \( \sigma_R \), and relative tensile modulus, \( E_R \), of PBT with 3 wt% organoclay as a function of inverse draw ratio, 1/DR (ref. 57).
the well-known problems associated with dyeability and printability of PP. Recently, it was found that the presence of organoclay (Cloisite®15A = MMT–2M2HTA; C15A) facilitates bonding of acidic and dispersed dyes. The dye adsorption increased with the amount of organoclay in the system as well as with the degree of dispersion. However, the latter term refers mainly to ball milling C15A prior to dispersing it in xylene solution of PP by means of ultrasonication. Two red mono-azo dyes (both having amino groups), Acid Red 266 and Disperse Red 65, were used. Milling C15A improved color uniformity of dyed specimens.

From the fundamental point of view, the basic conditions for ascertaining that composites have high modulus and strength are: good adhesion between the reinforcing particles and the matrix, as well as filler orientation in the stress direction. Translating these to CPNC fibers, the desired elements are: exfoliation, miscibility of the clay intercalant with the matrix and platelets orientation in the fiber direction. To satisfy all three criteria is difficult, and the difficulties increase with the processing temperature. For example, melt spinning of polyetherimide (PEI) requires 345°C. At this temperature, even the high temperature organoclay is not stable. The latter was prepared by intercalating Na-MMT with HCl salt of amino phenoxy benzene (APB):

![Diagram of APB](image)

In the produced CPNC, the clay dispersion was poor and the mechanical properties of CPNC fibers (with 3 wt% organoclay) were not improved; the modulus slightly increased at a cost of loss of strength and elongation.

6 Conclusions

The main reasons for incorporating organoclay into polymeric fibers are: improved spinnability, stiffness, strength, heat deflection temperature, weatherability, biodegradability, moisture and dye absorption as well as reduced shrinkage, electrostatic charge, and flammability. These enhancements are achieved with a small increase of density and cost. At present, the use of CPNC for fiber spinning is in a preliminary, exploratory stage. Electrospinning, solution spinning and melt spinning of a variety of CPNC were reported. Most work was carried out on nanocomposites with polymeric matrix of interest to fiber industry, viz. polyamides and thermoplastic polyesters.

It is imperative to recognize that for good performance of CPNC fibers, the basic material must be prepared observing the fundamental rules of CPNC manufacture. The key to CPNC performance is a high degree of clay dispersion, governed by the thermodynamics and clay concentration-exfoliation is only possible when the platelets can freely rotate in the matrix, e.g. below about 1.2 wt% of clay with aspect ratio of 300. Incorporation of organoclay was found to improve spinnability, via the increase of elongational viscosity and strain hardening, SH. The mechanism for generating SH involves enhanced chain entanglements engendered by strong interactions between clay and the matrix.

The role of melt mixing or compounding is to accelerate the thermodynamically driven process of ‘dissolution’ of organoclay into a matrix. Recent progress in the extensional flow mixing offers a new technology for rapid clay dispersion.

In addition to natural clays, there are several synthetic clay manufacturers offering layered silicates with well-controlled and reproducible geometry and composition. Their use in the CPNC fiber application should be explored.

**Abbreviations and symbols used**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>2M2HT</td>
<td>di-methyl di-hydrogenated tallow ammonium chloride</td>
</tr>
<tr>
<td>2M20DA</td>
<td>di-methyl di-octadecyl ammonium chloride</td>
</tr>
<tr>
<td>2MBHT</td>
<td>di-methyl benzyl hydrogenated tallow ammonium chloride</td>
</tr>
<tr>
<td>2MHTL8</td>
<td>di-methyl hydrogenated tallow octyl ammonium salt</td>
</tr>
<tr>
<td>APB</td>
<td>amino phenoxy benzene</td>
</tr>
<tr>
<td>C15A</td>
<td>Cloisite® 15A</td>
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<tr>
<td>C25A</td>
<td>Cloisite® 25A</td>
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<td>C30B</td>
<td>Cloisite® 30B</td>
</tr>
<tr>
<td>C-D</td>
<td>convergent-divergent (plates, flow geometry, etc.)</td>
</tr>
<tr>
<td>CPNC</td>
<td>clay-containing polymeric nanocomposites</td>
</tr>
<tr>
<td>DD3PhP</td>
<td>decyl tri-phenyl phosphonium</td>
</tr>
<tr>
<td>DEFM</td>
<td>dynamic extensional flow mixer</td>
</tr>
<tr>
<td>DMF</td>
<td>di-methyl formamide</td>
</tr>
<tr>
<td>DR</td>
<td>(fiber) draw ratio</td>
</tr>
<tr>
<td>EFM</td>
<td>extensional flow mixer</td>
</tr>
<tr>
<td>EFM-N</td>
<td>new EFM for dispersing nanoparticles</td>
</tr>
<tr>
<td>FH</td>
<td>synthetic fluorohexiphite</td>
</tr>
<tr>
<td>FM</td>
<td>fluoro micu</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GP</td>
<td>gear pump</td>
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HFIP hexafluoro-iso-propanol
H—MMT protonated MMT
HRTEM high-resolution transmission electron microscopy
HT hectorite
HTD heat deflection temperature
LCP liquid crystal polymer
MAH maleic anhydride
MB master-batch
MD molecular dynamic
MFR melt flow rate
MMT montmorillonite
MPS multi-phase systems (blends, composites and foams)
MT2EtOH methyl tallow di-ethoxy ammonium chloride
Na—MMT sodium montmorillonite
PA polyamide
PA-12 polyamide-12, or poly(dodecanedioamide)
PA-6 polyamide-6, or poly-e-caprolactam
PAA poly(acrylic acid)
PA-mXD6 semi-aromatic poly(m-xylene di-amine and adipic acid-co-caprolactam)
PARA aromatic polyamide
PBD polybutadiene
PBT poly(butylene terephthalate)
PE polyethylene
PEG polyethylene glycol
PEI poly(ether imide)
PEST thermoplastic polyester
PET polyethylene terephthalate
pH negative logarithm of the effective H+ ion concentration
pK negative logarithm of the ionic constant K
PLA poly(lactic acid)
PMMA poly(methyl methacrylate)
PMMA-MA poly[(methyl methacrylate-co-methacrylic acid) copolymer
PNC polymeric nanocomposites
PO polyolefin
PP propylene
PPG poly(propylene glycol)
PP-MA maleated-PP
PPT poly(propylene terephthalate) (also, polytrimethylene terephthalate PTT)
PS polystyrene
PTT poly(trimethylene terephthalate) (also, polypropylene terephthalate, PPT)
PVAJ polyvinyl alcohol
PVP poly(vinyl pyrrolidone)
SCF self-consistent field
SSE single-screw extruder
TEM transmission electron microscopy
TSE twin-screw extruder
UV ultraviolet irradiation
XRD X-ray diffraction
\(\Delta G_m\) free energy of mixing
\(\Delta h\) loss of matrix free volume
\(\Delta H_m\) enthalpy of mixing
\(\Delta S_m\) entropy of mixing
\(E_p\) relative tensile modulus
\(T_m\) melting point
\(a_1, a_2\) width, length of rectangular clay flake
\(d\) clay platelet average ‘diameter’
\(d_{dd}\) interlayer spacing
\(e^2\) aspect ratio
\(R^2\) correlation coefficient squared
\(w\) clay content in wt%
\(z_{bi}\) thickness of solidified polymer on clay surface
\(\phi\) volume fraction
\(\phi_f\) filler (clay) volume fraction
\(\gamma_p\) surface energy per unit area, or surface tension
\(\alpha\) standard deviation
\(\sigma\) CPNC tensile strength
\(\sigma_f\) filler (clay) tensile strength
\(\sigma\) matrix tensile strength
\(\sigma_{f}/\sigma_m\) ratio of filler-to-matrix tensile strength
\(\sigma_{f}/\sigma_m\) relative tensile strength of CPNC

References
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