Abstract - The clay-containing polymeric nanocomposite (CPNC) can be treated as a binary mixture of strongly interacting, inorganic, plate-like molecules dispersed in a polymeric matrix. To be successful, one must ascertain the thermodynamic miscibility that controls CPNC structure on the molecular level. There are three basic methods of CPNC preparation: 1) dispersion in polymer solution (followed by solvent removal), 2) dispersion in monomer (followed by its polymerization), and 3) dispersion in molten polymer during compounding. Initially, most commercial CPNC were produced by the second method, but compounding is becoming the preferred alternative. The presentation will focus on the latter method, summarizing extensive comparative tests of compounding using SSE or TSE compounding lines, without or with a static extensional flow mixer, EFM-3 or EFM-N. Furthermore, a wide range of the process variables have been used, viz. compounding strategy (a single pass or double, with pre-compounded master batch) feeding methods, clay content, temperature, screw speed, throughput, EFM gap (controlling the extensional stress), and others. The compounding efficiency was evaluated by a thorough characterization of clay dispersion as well as mechanical performance in tensile, flexural and impact tests.

Introduction

The clay-containing polymeric nanocomposites (CPNC) contain at least two ingredients: polymeric matrix and layered silicates. For the sake of miscibility the layered silicates usually are treated with organic salts (intercalation) and/or compatibilized with functionalized macromolecules. [1, 2] Compounding affects the kinetics of the dispersion process, but rarely miscibility. In the plastics industry the most common compounding machines are single- and twin-screw extruders (SSE and TSE, respectively). Both compounders are mainly shearing devices, while mixing theories show that the extensional flow field is many-folds more efficient. [3, 4, 5] Thus, a static extensional flow mixer (EFM) and its dynamic version (DEFM) have been developed and commercialized. The initial application has been for homogenization of the reactor products (e.g., for the elimination of “fish eyes”) and for the preparation of polymer alloys and blends [6, 7].

Unexpectedly, it has been reported that superior dispersion of organoclays was obtained in several polymers (viz. PET, PA-6, PP, and PS) using a commercial EFM-3 attached to SSE. The dispersion was better than that obtained in TSE with or without EFM. [8, 9] As a result a new mixer (EFM-N) for dispersion of organoclays was designed by modifying flow channels geometry. The elongational
stresses are generated in the gap space between the convergent-divergent (C-D) plates. Thus, to adopt EFM for organoclay dispersion, the geometry of C-D plates had to be optimized. While EFM-3 has the geometry based on the (drop dispersion mechanism) known from microrheology, the EFM-N has another one designed to accommodate a postulated clay dispersion process. A schematic of the static EFM is shown in Figure 1.

![Schematic of the static EFM](image)

Figure 1. The static extensional flow mixer, EFM, with controlled gap height between the convergent-divergent (C-D) plates. Different geometry of the C-D plates is selected for compounding-mixing different polymeric systems (viz. polymer alloying or preparing CPNC).

**Elements of CPNC physics**

The nano-sized clay platelets have > 40% atoms on the surface and their specific surface area is: \( A_{sp} \approx 830 \text{ m}^2/\text{g} \). It is noteworthy that the surface energy of inorganic solids is about 100 times higher than that of organic liquids and that the interaction energy increases with the square of the particle dimension. As a result, the clay dispersion involves energies several orders of magnitude greater than compounding of micron-sized glass fibers or CaCO\(_3\) particles. Consequently, the thermodynamics treats CPNC as a molecular mixture of polymer and clay platelets, most often with an intercalant and compatibilizer(s). The degree of clay dispersion depends on the system miscibility and kinetics – compounding only controls the latter.
Molecular mechanics (MM) often adopts a lattice model, where polymer chains are represented by random walks on numerical lattices, and clay platelets are treated as large molecules. [10] The lattice-based, self-consistent mean field (SCF) approach has been developed by Balazs and her co-workers. [11, 12, 13] Kim et al. extended this two-component 1D model to four-component CPNC (clay, intercalant, polymer, and compatibilizer) such as present in PP-based CPNC. [14] The simulation identified the most influential factors that control the free energy of mixing, demonstrating that exfoliation might be expected only within a limited range of independent variables. The presence of bare clays on the one hand hinders the dispersion, but on the other it provides opportunity for the interactions between clay surface and polar groups of a polymer or compatibilizer. MM computation also suggests that high surface energy of crystalline solids causes adsorption and immobilization of molecules. [15] These results confirmed the experimentally observed reduced chain mobility of molecules or macromolecules. [16, 17] The solidified layers on each side of clay platelet surface is 4 to 6 nm thick, what multiplies the “solid content” by a factor of 9 to 13. Furthermore, the macromolecular mobility exponentially increases with the distance from clay surface, reaching its bulk mobility only ca. 100 nm from its surface, what might seriously hamper clay dispersion.

The adsorption and solidification reduces the free volume of the matrix equivalent to lowering the compounding temperature by \( \Delta T \approx 50^\circ \text{C} \). [10] However, this effect cannot be compensated by increasing compounding temperature. Due to poor thermal stability of the quaternary ammonium intercalants, the Hofmann elimination [18] process starts at \( T \approx 150^\circ \text{C} \), causing its decomposition into volatile amine and vinyl-terminated the longest paraffinic substituent. The latter group might oxidize forming peroxides capable to initiate free radical chain scission of the matrix polymer.

Exfoliation is defined as random distribution of individual clay platelets in the matrix. Assuming monodispersed, circular disks with diameter \( d \) and thickness \( t \), the ratio of the encompassed to actual volume is: \( V_{\text{enc}}/V = 2p/3 \), where for most common montmorillonite (MMT) the aspect ratio is: \( p = d/t \approx 280 \). Thus, exfoliation is only feasible at \( \phi \leq \phi_c \), where \( \phi_c \approx 0.0033 \) (ca. 1-wt% clay loading) is the critical volume fraction for platelet overlap. At higher clay contents the platelets form local stacks with progressively (with \( \phi \)) reduced interlayer spacing.

The above calculations assume that full polymer volume is accessible to clay platelets. However, in semi-crystalline matrix polymer the clay is expelled from the crystalline phase what increases the local clay concentration is the-non-crystalline domains, reduces the degree of clay dispersion and performance. [19]
Experimental

A series of CPNC compounds was prepared with polystyrene (PS) \([20, 21, 22]\), poly-\(\varepsilon\)-caprolactam (PA-6) \([23, 24]\), and polypropylene (PP) \([23, 24]\) matrices. Two compounding methods have been employed: (1) a single-step process (SP), were the matrix polymer is melted, the desired amount of organoclay (and a compatibilizer if needed) is added, and then mixed under blanket of \(N_2\) into the final compound; (2) a two-step process where first concentrated master batch (MB) is prepared, and then it is diluted to the required concentration. For the PP-based CPNC a mixture of two maleated polypropylenes (PP-MA) was used as compatibilizer. The materials characteristics are listed in Table 1.

Table 1. Material characteristics.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name</th>
<th>(M_c) (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>PS</td>
<td>PS-1301</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>NOVA Chemicals</td>
</tr>
<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-MA1</td>
<td>Epolene-3015</td>
<td>47</td>
<td>0.91</td>
<td>162</td>
<td>1.31</td>
<td>Eastman Chemicals</td>
</tr>
<tr>
<td>PP-MA2</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>C10A(^2)</td>
<td>Cloisite(^8) 10A</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>South. Clay Prod.</td>
</tr>
<tr>
<td>C15A(^3)</td>
<td>Cloisite(^8) 15A</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>South. Clay Prod.</td>
</tr>
</tbody>
</table>

Notes: \(^1\) Polymers with other molecular weights than those listed in the Table have also been investigated; \(^2\) C10A = MMT + 2-methyl, benzyl hydrogenated tallow ammonium chloride. \(^3\) C15A = MMT + 2-methyl, 2-hydrogenated tallow ammonium chloride.

The CPNC’s were prepared in a TSE, TSE + gear pump (GP), TSE + GP + EFM, or in a SSE with or without EFM. For comparison, EFM-3 and EFM-N were used with several C-D gap settings, \(h\). For most systems the MB procedure yielded better results than SP, thus mainly MB process has been used. \([25]\)

TSE was a Leistritz-34 mm CORI, L/D = 40, with screw speed \(N = 200\) rpm, and throughput \(Q = 5\) and 10 kg/h. Low and high shear screw configurations were used. Compounding was carried out at \(T = 200^{\circ}C\) for PS, \(T = 180\) and \(200^{\circ}C\) for PP, and \(240^{\circ}C\) for PA-6 systems. GP Model EH 45/28 was from Maag Pump System. SSE was a Flag 63.5 mm machine with L/D = 24, and a two-stage Dry mixing screw. The EFM-3 and EFM-N were used with the C-D gap settings ranging from \(h = 5\) to \(2000\ \mu m\). To be able to place the data for SSE, TSE, and TSE + GP on graphs illustrating the effects of the EFM gap changes, the value of \(h = 4\) mm was arbitrarily assigned to extruder + strand die, and \(h = 3\ mm\) to TSE + GP.

All ingredients were dried in a commercial drying tower. For SP either SSE or TSE extruder could be used, but for MB the first compounding was carried out in TSE with a screw side-feeder, and
then the dilutions to 2 or 4-wt% of organoclay in either SSE or TSE, with or without EFM. For mechanical tests the CPNC specimens containing 0, 2, and 4-wt% organoclay were injection-molded in Engel 150T into end-gated ASTM mold; the central part of the dogbone was used for determining the clay dispersion.

From the XRD spectra of Brüker D8 Discoverer the interlayer spacing, \( d_{001} \), the number of platelets per stack, \( N \), and the percentage of clay platelets absent from the stacks, \( E_x \), were calculated. The high resolution Transmission Electron Microscopy (HRTEM) was Hitachi H9000, while Field Emission Gun Scanning Electron Microscopy (FEGSEM) was Hitachi S4700. The Fourier-Transform Infrared spectrophotometer (FT-IR) was Nicolet Magna 860 FT-IR. The tensile and flexural tests were performed using Instron 5500R and 1125 testers at the crosshead speed of 5 and 15.7 mm/min, respectively. For the notched Izod impact tests at room temperature (\( NIRT \)) Instron 8200 impact tester was used. The reported values were averages of ≥ 10 tests.

**Results and Discussion**

For PS-based CPNC two residence time dependent XRD peaks were observed with the interlayer spacing \( d_{001} \approx 4.5 \) and 1.7 nm (see Figure 2), independent of PS molecular weight. The 1\(^{st}\) peak represents intercalation of organoclay by the macromolecules, whereas the 2\(^{nd}\) evidences the progressive degradation of intercalant and reduction of spacing down to ca. \( d_{001} = 1.35 \) nm. FT-IR confirmed the Hofmann thermal degradation of the ammonium compound. Degradation of organoclays has been reported for \( T \geq 150^\circ C \). \[^{26, 27, 28}\]

---

**Fig. 2.** Interlayer spacing in PS/C10A nanocomposites showing the residence time dependence for the 1\(^{st}\) and the 2\(^{nd}\) peak. \[^{20}\]

**Fig. 3.** EFM gap influence on C15A interlayer spacing in PP + PP-MA matrix, for TSE + GP + EFM, SSE + EFM-3, and SSE + EFM-N at \( Q = 5 \) kg/h. \[^{24}\]

---

*Anais do 9º Congresso Brasileiro de Polímeros*
Table 2. Summary of the XRD scans for PNC’s based on PA-6 [23].

<table>
<thead>
<tr>
<th>C15A (wt%)</th>
<th>Specimen (compounder)</th>
<th>(d_{001}) (nm)</th>
<th>Platelets/stack, (N) (-)</th>
<th>Exfoliation (\text{Ex}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>C15A</td>
<td>3.21</td>
<td>3.34</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>Master-batch (MB)</td>
<td>3.87</td>
<td>3.35</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>TSE</td>
<td>4.44</td>
<td>2.79</td>
<td>52.7</td>
</tr>
<tr>
<td>2</td>
<td>TSE + GP</td>
<td>4.42</td>
<td>2.89</td>
<td>64.7</td>
</tr>
<tr>
<td>2</td>
<td>TSE + GP + EFM-3; (h=5) (\mu) m</td>
<td>4.39</td>
<td>2.78</td>
<td>83.3</td>
</tr>
<tr>
<td>2</td>
<td>SSE + EFM-3; (h=30) (\mu) m</td>
<td>3.65</td>
<td>3.14</td>
<td>89.9</td>
</tr>
<tr>
<td>2</td>
<td>SSE + EFM-N; (h=30) (\mu) m</td>
<td>4.65</td>
<td>2.15</td>
<td>97.1</td>
</tr>
<tr>
<td>2</td>
<td>UBE1015C2</td>
<td>5.33</td>
<td>2.15</td>
<td>80.7</td>
</tr>
</tbody>
</table>

Notes: The listed values are averages. The error of measurements for \(d_{001}\) is ± 0.01, for the number of pellets per stack is ± 0.22, and for the degree of exfoliation is ± 3.5%.

Table 2 summarizes the XRD results for PA-6-based CPNC compounded in TSE or SSE. Judging by the nearly featureless diffractograms, the SSE + EFM-N produced the highest degree of clay dispersion, confirmed by HRTEM. The effect of processing on the interlayer spacing of CPNC with PP matrix is illustrated in Figure 3. By contrast with TSE + EFM in SSE + EFM there was no Hoffman decomposition for C-D gap \(h \geq 30\) mm.

Addition of EFM to the compounding line was found to significantly improve clay dispersion. Better results were obtained for compounding in a SSE + EFM than in TSE with or without EFM. The new EFM-N at a relatively small gap between the C-D plates performed better than the commercial EFM-3. C15A was fully exfoliated in PA-6 matrix. The results in PP/PP-MA matrix were less spectacular, but again the highest degree of dispersion was obtained using SSE + new EFM with a small gap.

Figure 4. Relative tensile modulus and strength of CPNC with 2-wt% C15A with PA-6, or PP + PP-MA as the matrix, plotted as functions of the degree of exfoliation. The samples were prepared in SSE + EFM-N performed better than these in TSE, with or without EFM.
A summary of the tensile tests results is displayed in Figure 4 as relative (re neat polymer) tensile modulus and strength. It is noteworthy that the flexural parameters were linear functions of these from the tensile tests. The significant improvement of the PA-6 performance by addition of 1.1 wt% of clay is related to the thermal degradation of the C15A intercalant, followed by solidification of the matrix on clay surface. This mechanism was not as efficient for PP + PP-MA systems. Evidently interactions between clay and PP are poor, and probability of interaction between clay and maleic anhydride groups is low due to micellization. However, compounding either system in SSE + EFM-N resulted in better dispersion and mechanical performance.

The effect of compounding on the impact strength at room temperature (NIRT) is presented in Figure 5. In well-dispersed CPNC the level of exfoliation, $Ex$, seems to control $NIRT$. As the Figure show, compounding in TSE + EFM resulted in lower values of $Ex$ and $NIRT$ than these obtained for the samples prepared in SSE + EFM. Again, EFM-N performed better than EFM-3. These results also point out that one needs a relatively high degree of exfoliation ($Ex > 70\%$) for good impact performance. The reactively prepared, commercial CPNC Ube 1015C2 had relatively low $NIRT$. Different molecular structures of this CPNC and that of the melt-compounded PA-6/C15A originate from the method of preparation; 1015C2 has clay platelets ionically bonded to the matrix through C$_{12}$ chain, whereas in PA-6/C15A there are delocalized polar interactions between bare clay surface and polar groups of the polymer. Thus, the PA-6/C15A is not as stiff as 1015C2, and tougher than it.

![Fig. 5. Impact strength at room temperature (NIRT) vs. exfoliation for PA-6/C15A; the value for the reactively prepared Ube PA1015C2 is also shown. The mean error of NIRT is 2.04 J/m.](image-url)
Conclusions

The method of compounding, its effects on the degree of clay dispersion and mechanical performance of three CPNC series (based on PS, PA-6 and PP) was outlined. These systems were melt-intercalated in compounding lines consisting of either TSE with GP and EFM, or SSE with EFM. The master-batch (MB) method was found to lead to more consistent and better results.

Several process variables were studied, viz. temperature, screw speed, throughput, method of extruder feeding, composition, organoclays, compatibilizers, pressure inside EFM, gap between the C-D plates, etc. The TSE and SSE compounding lines were compared at the same throughputs of $Q = 5$ or 10 kg/h. Systematically the SSE + EFM-N compounding gave better dispersion and performance than TSE with or without EFM. In spite of shorter residence time, TSE degraded intercalant more than SSE + EFM. Compounding PA-6/C15A in the SSE + EFM resulted in full clay exfoliation – similar in degree of clay platelet dispersion and mechanical performance to those of commercial Ube PA1015C2. From the compounding line: TSE + GP + EFM the dispersion was significantly poorer. The results for the PS or PP-based CPNC’s were poorer than those based on PA-6. However, here also better dispersion was obtained in SSE + EFM than in TSE + GP + EFM. Compounding with newly designed EFM-N led to better dispersion than that with the commercial EFM-3.

Since organoclay is immiscible with PS, PA or PP matrix for improved miscibility a partial elimination of the intercalant from clay surface is needed. The high energy clay surface may interact directly with polar groups of the matrix polymer (such as polyamide or polyester), or with those of a compatibilizer (needed for such non-polar polymers as PP or PS). It is noteworthy that the Hofmann elimination mechanism is always present at $T > 150^\circ$C. Reaction of the bare clay surface with polar groups prevents a collapse of the interlayer spacing, observed in the absence of compatibilizers. When sufficient thermodynamic miscibility and compounding conditions are provided, exfoliation might be obtained for any organoclay with $d_{001} > 1.6$ nm.

The concentration dependence of the tensile modulus for the CPNC with either PA-6 or PP is close to the values calculated from an empirical as well as from the Halpin-Tsai relations, i.e., about 23% increase of modulus at 2-wt% organoclay loading. By contrast, the modulus increase in PS matrix was modest, suggesting a micro- not nano-composite behavior. Furthermore, the tensile strength of the PA-6 and PP based CPNC was higher than predicted by the most optimistic relation. This extra enhancement originates from the increased volume of reinforcing particles, caused by the solidified matrix polymer adsorbed onto the clay surface.
References


8 W. Song, *ITRI publication No. D412KC2P00-8*, Hsinchu, Taiwan, 2002.


