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Publisher's version / Version de l'éditeur:

SPE Plastics Research Online, 2011-03-15

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For SPE Plastics Research Online, 2011

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The clay-containing polymeric nanocomposites (CPNC) are dispersions of clay in a polymer. For good performance, finely dispersed clay (preferably exfoliated) is important. Thus this article focuses on the clay quality and method of compounding.

In the IUPAC nomenclature, the nano-particles must have at least one dimension in the nano-meter range, ≤ 2 nm. For industrial production of structural CPNC crystalline natural or synthetic clays are employed with platelets 0.7 – 1.7 nm thick, having an aspect ratio: p = diameter/thickness = 20 – 6000. [1] The natural clays originate from the hydrothermal alteration of volcanic ashes, deposited in seas and lakes. [2]. Clay contaminants are: (1) organic (*e.g*., humic substances, HS), (2) non-expandable clays (*e.g*., amorphous or kaolin) and (3) particulate minerals (quartz, sand, silt, feldspar, gypsum, orthoclase, apatite, calcite, dolomite, biotite, etc).

Historically, the industrial CPNC production involved polymerization in the presence of clay, but now the emphasis has shifted toward melt compounding in a single or twin-screw extruder (SSE or TSE, respectively) in the shear or extensional flow field. Dispersing in extensional flow is superior since it is more energy-efficient, generates better dispersive and distributive mixing, is performed in a more uniform flow field at lower temperatures and it does not re-aggregates solid particles as the shear field does. Some years back the extensional flow mixer (EFM) and then its dynamic version, DEFM were developed. These devices may be attached to a SSE or TSE, or it may be used as stand-alone mixer. [3] The CPNC mechanical properties will exemplify advantages of clay addition. [4]

1 Clays for CPNC

The natural, semi-synthetic and synthetic clays are being used in production of CPNC. The requirement is the clay ability to exfoliate, related to the ionic imbalance of the crystalline layers, compensated by hydrated ions in the interlayer galleries. The most important (natural or synthetic) exfoliating clays are: montmorillonite (MMT), hectorite (HT), and saponite (SP). These minerals have an octahedral layer (Oc) sandwiched between two tetrahedral (Tc) ones. For example, substitution of Al^{+3} by Mg^{+2} in MMT Oc-layer engenders 0.25 to 1.2 negative charges per unit cell, expressed as the cation exchange capacity, CEC ≈ 0.5 to 2 meq/g.

The synthetic clays are classified as: [5]

1. ***Semi-synthetic,*** prepared in a reaction of a natural mineral with salt, e.g., talc with Na_2SiF_6, at $T \approx 900^oC$.

2. ***Synthetic,*** formed in a reaction of metal salts or oxides, *viz.* in:
    a. Low temperature, high pressure hydrothermal synthesis.
    b. Reaction of *e.g.*, Li_2O, MgO, SiO_2 and MgF_2 at 1300 – 1500°C.
    c. Co-precipitation of di- and tri-valent aqueous ions into layered double hydroxides (LDH).
3. ***Templated***, starting with organic templates, which after synthesis may be pyrolyzed.

In the recent VAMAS TWA-33 project three types of sodium-clays were studied: [6] (1) the natural MMT, Cloisite®-Na^+ (C-Na^+), (2) the semi-synthetic fluoro-hectorite, Somasif ME-100, and (3) the synthetic fluoro-tetrasilicic mica, Topy-Na^+. Their properties are listed in Table 1.

Table 1. Properties of the sodium-clays.

Property	C-Na^+	ME-100	Topy-Na^+
Specific density, g/mL	2.86	2.6	2.6
Interlayer spacing, d_{001} (nm)	1.17	0.95	1.23
Platelets thickness, nm	0.96	0.91	
CEC (meq/g)	0.92	1.2	0.80
Nominal aspect ratio, *p* (-)	280	≤ 6000	≤ 5000

The clays were characterized for platelet shape, size, chemical composition and impurities. The test methodology and results are published in the cited PES article. Briefly, the findings are as follows.

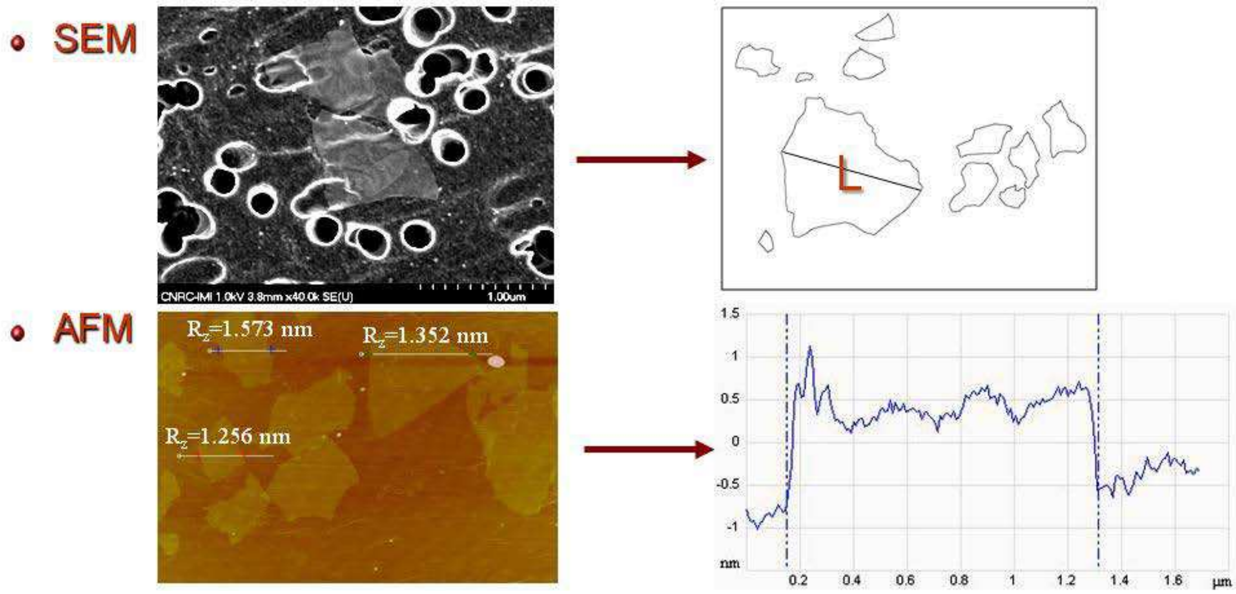

Figure.1. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of Somasif ME-100 platelets. As an example, the platelet length is indicated as L; the width is taken as the largest perpendicular to L platelet size.

Example of ME-100 images is shown in Figure 1. The number and weight average values of the platelet length and the orthogonal width (subscripts *n* and *w*, respectively) are listed in Table 2. The average clay platelet dimensions in three orthogonal directions are: thickness $t \approx 1$ nm, width $W \approx 20 - 4000$ nm, length $L \approx 30 - 6000$ nm, and the nearly universal ratio $L/W \approx 1.5 \pm 0.1$. The distribution of clay platelet size is approximately Gaussian.

Table 2. Statistical analysis of three clays.

Clay	*Length* L *(nm)*		*Width,* W *(nm)*		*Ratios*	
	L_n	L_w	W_n	W_w	$(L/W)_n$	$(L/W)_w$
Natural, C-Na$^+$	*290*	*350*	*183*	*219*	*1.58*	*1.60*
Semi-synthetic, ME-100	*872*	*1097*	*572*	*743*	*1.52*	*1.48*
Synthetic, Topy-Na$^+$	*1204*	*1704*	*761*	*1186*	*1.58*	*1.44*
Error					*± 0.2*	*± 0.2*

Chemical analysis of clays was obtained by the Energy-dispersive X-ray (EDX) analysis in SEM. Since clay particles may have locally different composition, ca. 30 particles were sampled at least five locations, each. Results are listed in Table 3.

Table 3. Elemental composition of C-Na⁺ and ME-100 clays

Source	C-Na$^+$	ME-100
Nominal	$[Al_{3.34}Mg_{0.66}Na_{0.66}](Si_8O_{20})(OH)_4$	$(NaF)_{2.2}(MgF_2)_{0.1}(MgO)_{5.4}(SiO_2)_8$
Found	$[Al_{2.9}Fe_{0.6}Mg_{0.35}Na_{0.72}](Si_8O_{20})(OH)_4$	$(NaF)_{0.94}(MgF_2)_{2.3}(MgO)_{2.7}(SiO_2)_8$
O	21.10 (± 15% error)	22.80 (± 9% error)
Na	0.72 (± 13% error)	0.94 (± 19% error)
Mg	0.35 (± 21% error)	5.00 (± 10% error)
Al	2.90 (± 13% error)	--
Si	8.00 (± 13% error)	8.00 (± 22% error)
Fe	0.63 (± 52% error)	--
F	--	5.50 (± 31% error)

There is large variability of composition both for the natural C-Na$^+$ and semi-synthetic ME-100 clay. There are three principal sources of error: (a) non-uniform atomic substitution in the crystalline cells, (b) reported tendency of natural clays to vary composition with particle size, (c) presence of mineral impurities. Owing to the presence of impurities, in natural clays the scatter of ±15% has been observed. Variability in ME-100 is larger than the error of measurements what may reflect the local variation of composition. The chemical heterogeneity may cause batch-to-batch variability of the mechano-chemical sensitivity during CPNC compounding, degradability, weatherability, sensitivity or lack of it toward antioxidants and stabilizers, etc.

Purification of natural clays into a polymer-grade material is a long process of about 300 steps. The patents specify that the product should contain ≤ 5 wt% (“preferably less than about 2% by weight”) of impurities, > 300 nm large. [7] The identified the following minerals in C-Na$^+$: vermiculite, quartz, cristobalite, rutile, albite, microcline, aragonite, vaterite, dolomite, gypsum, anhydrite, alunite and sylvite. As expected, the semi-synthetic ME-100 contained traces of natural talc contaminants: vermiculite and gypsum. The presence of particulates, incompatible with the matrix polymer, reduces mechanical performance as well as the barrier performance.

2 Compounding CPNC

Principles of clay dispersion in SSE or TSE resembles that of polymer alloys and blends (PAB), thus thermodynamic interactions and complex flow field (shear, chaotic and extensional mixing) are of key importance. [8, 9, 10] In CPNC, the interactions are modified by intercalant, and compatibilizers. However, in CPNC the former high energy clay adsorbs and solidifies ca. 4 – 6 nm thick polymer layer.

3 Mechanical properties

The CPNC tensile and flexural properties (*i.e.*, modulus or strength) are proportional to each other. [11] At low loadings the relative modulus follows:

$$E_R \equiv E_c / E_m = 1 + a_w w(wt\%) \tag{1}$$

(subscripts *c* and *m* stand for composite and matrix, respectively). For CPNC with PA or PP matrix $a_w \approx 0.2$, thus at 5 wt% clay the modulus doubles. In elastomers the effect is larger: $a_w \approx 0.7$. Factorial analyses indicate that E_R is a linear function of the interlayer spacing, d_{001}.

The simplest tensile strength theory predicts that relative strength:

$$\sigma_R \equiv \frac{\sigma_c}{\sigma_m} \leq 1 + \phi_f \left(\frac{\sigma_f}{\sigma_m} - 1 \right) \tag{2}$$

where ϕ_f is clay volume fraction. Because of polymer solidification on clay, from the experimental values of $\sigma_c, \sigma_m, \sigma_f$, for CPNC with PA-6 and PP, respectively, Eq. 2 predicts 9 and 5 times larger ϕ_f than factual. The strength linearly increases with the degree of exfoliation.

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