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National Production of Nanoclay Additives for Polymers: Challenges and Perspectives

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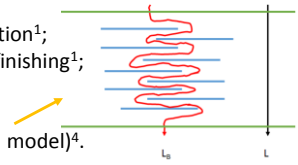
INTRODUCTION

Polymer-layered silicate nanocomposites have attracted a great interest since the Toyota research group developed the Nylon-6/clay material in 1987[1]. These nanocomposites, based on nano-scale organically modified clays (organo montmorillonite – OMMT or organoclay) homogeneously dispersed in polymeric matrix (exfoliated), can greatly improve properties such as:

- Mechanical reinforcement[1];
- Reduces thermal deformation and degradation[1];
- Enhance dimensional stability and surface finishing[1];
- Contribute to flame retardation[2];
- Improve electrical conductivity[3];
- Promote gas impermeability (tortuous path model)[4].



Inorganic cations on the basal planar surface of montmorillite layers makes it hydrophilic in nature. Organophilization is an effective method to replace these ions with organic cationic surfactant molecules which intercalate into the clay gallery expanding the interlayer spacing, increasing the basal spacing, wettability and favoring thermodynamic interactions with organic molecules.

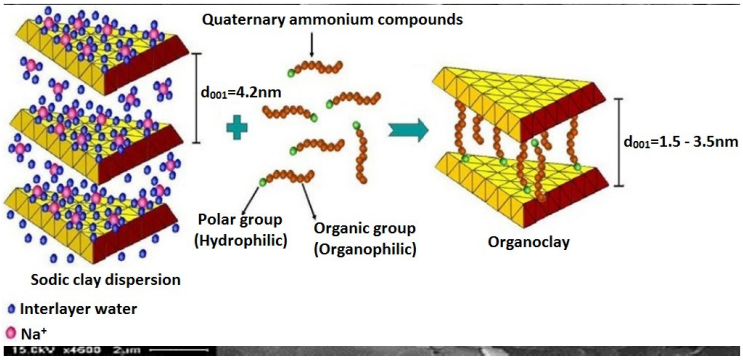
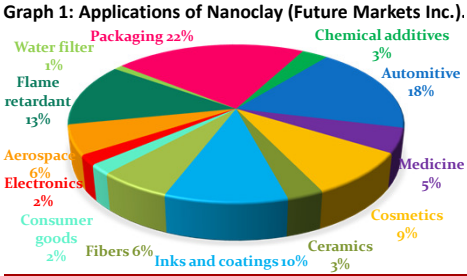


Figure 1: Clay structure and organophilization (Martins, A. B., UFCG 2007).

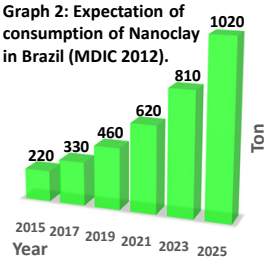
Perspectives

Clays find wide range of applications due to their natural abundance and the propensity with which they can be chemically and physically modified to suit practical technological needs. In Brazil, an study of Ministry of Industry and Foreign Trade (MDIC)[4] indicated that domestic demand of nanofiller for plastic packaging food industry in 2016 will reach 390 tons and can generate revenue of up to R$ 41 million, which would allow the introduction of a local industry of polymeric nanocomposites masterbach.

Graph 1: Applications of Nanoclay (Future Markets Inc.).



Graph 2: Expectation of consumption of Nanoclay in Brazil (MDIC 2012).



Challenges

- High purification of a large quantity of natural clay (industrial scale); ✓
- White clay of low level of iron < 2% (Partnership with Argentina clay mines); ✓
- Intercalation/exfoliation of the organoclay into polymer (melt extrusion); ○
- National marketing for promoting benefits of nanocomposites (consumers). ○

MATERIALS AND METHODS

Materials: Natural policationic clay (Bentonita do Brasil "BdB"); Distearyl dimethyl ammonium chloride aq. in isopropanol (Praepagen WB®) by Clariant.

Clay treatment: Dispersion of BdB clay in distilled water with 0.05% wt. of $Na_6P_6O_{18}$; Centrifugation at 2.500G; Activation of colloidal clay with Sodium carbonate (3.0% wt.); Organophilization of activated clay with Praepagen WB® (100% of CEC) through vigorous stirring; Washing with distilled water and filter pressing. Dried in oven for 12 h at 60°C. Ground into fine powder (< 74 µm).

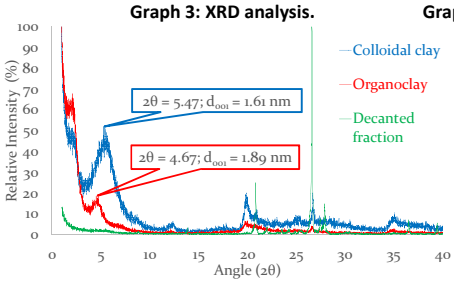
Analysis: Cation Exchange Capacity by Methylene Blue (ASTM C837–14); Swell Index (ASTM D5890–11); X-Ray Diffraction (Philips X'Pert®); X-Ray Fluorescence (PANalytical Epsilon 3$^{X®}$); Particle Size and Distribution (LUMiSizer®).

RESULTS

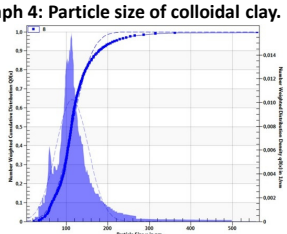
Table 1: XRF, weight loss, CEC and swelling analysis.

Clay sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	CaO	K_2O	wt.% loss at 900 °C	CEC (meq/100g)	Swelling (mL/2.0g)
Wyoming USA (Ref.)	63.0	19.6	4.2	2.3	2.4	1.5	0.5	5.8	67	37
BdB (Natural)	63.3	16.4	5.5	1.8	0.7	0.6	1.9	7.1	48	5
BdB (Colloidal)	53.3	18.8	8.1	2.4	0.2	0.8	1.6	13.1	71	7
BdB (Decanted)	83.4	5.5	0.9	0.4	2.6	0.1	1.8	6.9	0	2
BdB (Colloidal) + 3% wt. Na_2CO_3	50.9	17.9	8.0	2.2	2.3	0.8	1.6	11.5	85	23

Graph 3: XRD analysis.



Graph 4: Particle size of colloidal clay.



10% ≤ in nm	16% ≤ in nm	50% ≤ in nm	84% ≤ in nm	90% ≤ in nm
66,40	79,97	112,8	157,4	179,7

After the organophilization, the basal-spacing (d_{001}) of BdB enhanced from 1.61 to 1.89 nm. X-Ray results of commercial montmorillonite: Cloisite®Na d_{001}=1.17nm and Cloisite®Ca d_{001}=1.55nm. Organoclay Cloisite®30B (alkyl quaternary ammonium salt bentonite) basal-spacing: 1.85nm. Colloidal clay presented a nanometric size and narrow dispersion (pH 8.0).

CONCLUSION

- Purification via centrifugation, followed by activation, can decant mostly of non-smectite phases and greatly enhance CEC and swelling of clay;
- Organic cations between the clay layers can enhance the basal-spacing and chance surface free energy, transforming hydrophilic clays into organophilic;
- These organically modified montmorillonites have potential utility in the preparation of polymer nanocomposites and in other possible applications;
- Other parameters must be tested, for instance varying quaternary ammonium salts (national), proportions of salt (% CEC), time and temperature of reaction.

REFERENCES

1. Pinnavaia, T.J.. Polymer-clay nanocomposites (Wiley 2000).
2. Mouritz, A. P.. Fire Properties of Polymer Composite Materials (Springer 2006).
3. Eftekhari, A.. Nanostructured Conductive Polymers (John Wiley & Sons, 2010).
4. Kalendova, A.. Polymer/clay nanocomposites and their gas barrier properties. Polymer Composites. 34, 9, 1418–1424, 2013;
5. da Silva, P. R.. Estudo de viabilidade de insumos nanométricos (MDIC, RJ 2012).

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