

# Physicochemical driving forces behind exfoliation process of a synthetic montmorillonite in PDMS polymers

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## ARTICLE INFO

### Article history:

Received 19 March 2010

Received in revised form

23 July 2010

Accepted 15 December 2010

Available online 22 December 2010

### Keywords:

Clay exfoliation

Flow calorimetry

Surface energy

## ABSTRACT

The conditions under which exfoliation of organo-montmorillonite in Poly(dimethylsiloxane) elastomers may occur were investigated via a three approaches: determination of the inter-platelet distance (as measured by WAXS), the surface energy evaluation (via inverse gas chromatography) of the polymer matrix and the clays, and measurement of heat of interaction (using a flow microcalorimeter in heptane) between polymers and the clay. The exfoliation efficiency is estimated by performing dynamic mechanical measurements. The results indicate that compatibilization and geometrical considerations are not sufficient requirements to transform clay particles into platelets. It evidences the determinant role of specific interactions between the reactive polymer end-groups and the filler surface. Polymer conformation on the clay surface and heat of adsorption associating “dispersive or London” forces and hydrogen bonding of respectively trimethyl- and hydroxyl-terminated polymer are evaluated.

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## 1. Introduction

The present development of engineering polymers seeks the reinforcement of the polymer matrix, improving strength, stiffness, thermal stability, barrier properties, toughness and optical properties without complicating too much the processing step. In conventional composites, including macroscopically separated phases, the property enhancement is achieved using a 30–40 weight percent of filler. Without this, a rubbery matrix for instance, is almost useless. During the last two decades, an alternative way was prospected, developing new polymer–clay nanocomposites. Indeed, improvements are already observed, even with a small weight percents of fillers [1]. Moreover, all polymer–clay systems are not necessarily true nanocomposites. If polymers are unable to intercalate between the clay platelets, conventional microcomposites are formed. Nanocomposites are considered exclusively in cases where the mineral is integrated at the nanoscale: *intercalated* when the periodic multilayer structure of the clay is preserved after the intercalation of polymer inside the galleries. The distance between individual layers is simply increased in comparison to the initial value. The nanocomposites are called *exfoliated* (delaminated) nanocomposites when the clay particles are disintegrated into discrete 1 nm thick platelets, randomly distributed in the

polymer. Particles of layered silicates in a pristine state can only be easily dispersed in hydrophilic polymers. Therefore, a “compatibilization” procedure of the silicate has to be applied before the manufacturing of the nanocomposite in a hydrophobic matrix. Generally, the alkali metal ions (such as Na<sup>+</sup>) located inside the interlayer spaces are exchanged with amphiphilic alkyl ammonium salts. Such a procedure renders the hydrophilic clay organophilic and thus simplifies the clay dispersion, and increases, at the same time, the inter-platelet distance facilitating the polymer penetrations. Only then, melt intercalation, solution blending and in-situ polymerization processes can be foreseen as the three main ways for the manufacturing of polymer–clay nanocomposites [2–6].

Melt intercalation is the most relevant approach for rubber blend applications since it requires the same tools used to achieve conventional filled rubbers. Physico-chemical properties of both polymer and clay are among the most important driving forces controlling, in this case, an exfoliation mechanism. In this work, we shall try to establish a relation between the surface characteristics of the two constituents, their affinity toward each other and the accomplishment of the exfoliation process. Therefore, three parameters, considered to play a major role in the exfoliation process, are investigated: the inter-platelet distance measured by X-ray diffraction (XRD), the surface energies of polymers and clays determined by inverse gas chromatography (IGC) and the heat of adsorption of polymer molecules on clays surfaces estimated by flow micro-calorimetry (FMC).

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## 2. Materials

### 2.1. Polymers

Two different series of Poly(dimethylsiloxane) elastomers (PDMS) were purchased from GELEST-ABCR: silanol-terminated and trimethylsiloxy-terminated elastomers. The molecular weights (MW), the concentrations ( $c^*$ ) of polymer solutions and the radius of gyration ( $R_g$ ) of the polymers are displayed in Table 1.

### 2.2. Clay synthesis

A synthetic layered silicate, montmorillonite  $\text{Na}_x(\text{Al}(2-x)\text{Mg}_x)\text{Si}_4\text{O}_{10}(\text{OH})_2$ ,  $x = 0.3$ , was prepared in our laboratory using a hydrothermal method in a fluoride media [9]. According to the elemental analysis, its unit cell formula is:  $\text{Na}_{0.26}\text{Si}_{4.06}\text{Al}_{1.70}\text{Mg}_{0.20}\text{O}_{10}(\text{OH}_{1.85}\text{F}_{0.15})$ . The negative charge of such a silicate layer is compensated by  $\text{Na}^+$  ions located in the interlayer galleries and the total Cation Exchange Capacity (CEC) of the clay was determined by elemental analyses [10] and methylene blue titration [11] and found to be approximately 71 meq/100 g. The fine structure of the synthesized montmorillonite was confirmed by wide angle XRD as reported elsewhere [9] and shown in Fig. 1.

The organophilic treatments were made by dispersing pristine clay in an aqueous solution (at 60 °C) of Octadecyltrimethyl ammonium bromide (ODTMABr,  $\text{C}_{21}\text{H}_{46}\text{NBr}$ , MW = 392.52 g/mol), purchased from Fluka. The suspension was left under stirring during 24 h before centrifugation and extraction of the excess reactant using distilled water. The amount of ODTMABr was varied during treatment in the 1–3.5 CEC range and the amounts of ODTMABr retained in the organoclay were determined by elemental (bromine and carbon) and thermogravimetric analysis. Elemental analyses were performed at the “Service Central d’Analyse de Solaize” CNRS using silver nitrate titration for bromine and a combustion technique for Carbon.

### 2.3. XRD

The characterization of the different clays was performed on crushed and sieved powders. Only the 100–400  $\mu\text{m}$  fraction was considered. The same fraction was used for other investigations throughout this paper. The wideangle X-ray diffraction, WAXS, measurements were carried out at 25 °C in reflection with an X’PERT diffractometer from Philips using the  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ nm}$ ).

### 2.4. IGC [12]

The Inverse gas chromatography apparatus is a FISONS’ chromatograph GC 8000. Injectors, columns oven and ionization flame

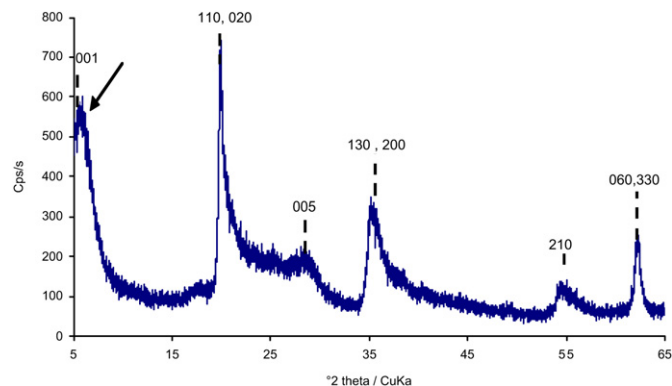
**Table 1**

MW, heptane concentrations ( $c^*$ ) and gyration values ( $R_g$ ) of polymers [7,8].

Silanol-terminated PDMS				Trimethylsiloxy-terminated PDMS			
Specimen	MW g/mol	$c^*$ <sup>a</sup> g/l	$R_g$ <sup>b</sup> nm	Specimen	MW g/mol	$c^*$ g/l	$R_g$ nm
OH-800	780	483	1.0	CH <sub>3</sub> -4000	4000	131	2.4
OH-5100	5150	107	2.7	CH <sub>3</sub> -9430	9430	66	3.7
OH-18000	18400	39	5.2	CH <sub>3</sub> -29000	29000	27	6.5
OH-23000	23500	32	5.9	CH <sub>3</sub> -49000	49000	18	8.5
OH-44000	44400	19	8.1	CH <sub>3</sub> -91700	91700	11	11.6
OH-47000	47200	18	8.3	CH <sub>3</sub> -139000	139000	8	14.3
OH-49000	49000	18	8.5	CH <sub>3</sub> -420000	420000	3	24.8
OH-77000	77000	12	10.6				
OH-139000	139000	8	14.3				

<sup>a</sup>  $c^*$  estimated according to the results of Lapp et al.:  $c^* \#k \text{ MW}^{-4/5}$ .

<sup>b</sup>  $R_g$  estimated according to the Flory’s equation:  $R_g^2 = n \cdot b^2 / 6$  with  $n$ , the number of monomer units and  $b$ , the statistical length of the polymer segments ( $b = 0.561 \text{ nm}$ ).



**Fig. 1.** XRD pattern of pristine MMT at the wide angles. Arrow points to the  $d_{001}$  reflexes corresponding to an inter-platelet distance of about 1.3 nm (interlayers spacing from 0.3 nm).

detector (FID) are computer controlled, data integrations are made using AZUR software. Helium is used as vector gas at a flow rate of about  $15 \text{ cm}^3/\text{min}$ . The columns are made of stainless steel of 2 mm interior diameter and a length of 200 mm. Powders were prepared as mentioned in the XRD section. The homogeneity of the stationary phase has been assured by vibration in order to reduce the space died between the grains. Columns were stabilized by heat treatment above the highest measurement temperature under a helium flow for 12 h. Measurements were made in the 120–160 °C temperature range. A series of  $n$  alkanes (C1–C16) was used as probes. The dispersive or London component,  $\gamma_S^D$ , of the surface energy, was estimated according to the Dorris and Gray equation [13]:

$$\gamma_S^D = \frac{(\Delta G_a(\text{CH}_2))^2}{4 \cdot N^2 \cdot a_{\text{CH}_2}^2 \cdot \gamma_{\text{CH}_2}^2} \quad (1)$$

The free energy  $\Delta G_a^{\circ}(\text{C}_n\text{H}_{2n+2})$  is based on the experimentally determined slope of the equation

$$\Delta G_a^{\circ}(\text{C}_n\text{H}_{2n+2}) = -RT \cdot \ln(V_n) + C(T) \quad (2)$$

where  $V_n$  is the net retention volume,  $R$ ,  $T$  and  $C$  are the gas constant, the temperature (K) and a constant depending of the reference state respectively.  $\Delta G_a(\text{CH}_2)$  is the free energy increment by of methylene group. The theoretical base of the IGC and the experimental procedure are detailed elsewhere [13]

### 2.5. Surface area

The powder surface areas were estimated from low temperature nitrogen adsorption isotherms and application of the BET equation [14]. Adsorption isotherms were determined using a Micromeritics ASAP 2020 apparatus.

### 2.6. FMC

Adsorption enthalpies were determined at 20 °C in heptane (Spectrosol, 99.9%, chromatography grade), a good solvent for PDMS, using liquid flow micro-calorimetry (FMC, Microscal with a Perkin–Elmer Totalchrom Workstation integrator). It was verified that heptane does not dissolve the ODTMABr used in the clay modification, and therefore, does not harm the organoclay structure during the FMC measurements. The effluent flow rate was maintained constant at 3.3 ml/h. The amount of powder required to fill up the measurement cell depends on the powder density: for pristine clay this amount was around 110 mg. FMC measurements

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