



## Research paper

# X-ray diffraction and rheology cross-study of polymer chain penetrating surfactant tethered layered double hydroxide resulting into intermixed structure with polypropylene, poly(butylene)succinate and poly(dimethyl)siloxane



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## ABSTRACT

A series of layered double hydroxides interleaved with surfactant using saturated alkyl chain carboxylate anions  $\text{CH}_3(\text{CH}_2)_m\text{COOH}$ , even number  $m$  between 6 (C8) and 16 (C18), obtained by coprecipitation method was dispersed by melt polymer extrusion into polypropylene (PP), poly(butylene)succinate (PBS) and polydimethylsiloxane (PDMS). The hybrid LDH materials were investigated by means of X-ray diffraction and Fourier transform IR spectroscopy resulting in the presence of contracted basal spacing over the entire variation of  $m$ . Dispersion into polymer was found to yield intermixed polymer structures regardless of either the polymer or of the alkyl chain length. PP polymer chain was able to diffuse into the interlayer space, long alkyl chains ( $m \geq 14$ ) were found to reinforce while shorter chains ( $m \leq 12$ ) induced a plasticizing effect. For PBS and PDMS, a chain-extender-type behavior was observed.

The relative change in viscosity within the frequency sweep stress linear response was visualized by the Cole-Cole representation. The molecular weight change relative to polymer free of filler and obtained from the power-law of the zero-shear viscosity  $\eta'_0$  was found to be linearly dependent of the basal spacing increase in the three cases. Such cross-study using XRD and melt polymer rheology was able to unravel the attritive or plasticizing role of the organoclay as function of the basal spacing expansion in the intermixed polymer structure, and to respond whether LDH interleaved platelets were of interest for polar and non-polar polymer and finally to predictively monitor the interfacial attrition by the alkyl chain length of the surfactant molecule tethered to the LDH platelets.

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## 1. Introduction

Surfactant-based clay minerals are known to compatibilize the inorganic platelets by mimicking the olefin chain, providing attrition between filler and continuous polymer phase as well as endowing the whole with barrier properties (Jancar et al., 2010; Paul and Robeson, 2008; Utraki et al., 2007). Therefore it is of interest to investigate the effect of the comb-like morphology resulting from the surfactant molecules tethered to the inorganic platelets and to possibly rationalize the resulting viscoelastic properties of the filler/polymer system. Indeed rheological properties of polymer clay nanocomposite in the molten polymer state are generally described by the dispersed fillers developing interfacial interaction with the polymer chains. As a result, a

restriction of the relaxation of the polymer chains is usually observed by an increase of the elastic and viscous moduli as well as by an increase of the glass transition temperature (Solomon et al., 2001).

Among the possible strategies to modify the interfacial interaction between surfactant-based clay minerals and polymer chains, layered double hydroxide-type framework has been extensively investigated due the tunable layer charge and chemical versatility (Leroux and Taviot-Guého, 2005; Newman and Jones, 1998). Layered Double Hydroxide materials also called “anionic” clay in comparison to smectite-type materials are built from edge-sharing octahedra forming sheets, this in association with a substitution between the divalent cations by trivalent cations from the brucite-type composition  $\text{Mg}(\text{OH})_2$ . The resulting cation composition  $\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2$  with  $x$  being the relative substitution rate generally ranging as  $0.20 < x < 0.33$ , endows a positive charge to the sheet which is counterbalanced by the presence of anion in the interlayer space.

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A linear LDH interlayer space expansion yields layered structure as a function of the alkyl chain length (Xu and Braterman, 2007, 2010). A series of saturated fatty acid  $\text{CH}_3(\text{CH}_2)_m\text{COOH}$ , even number  $m$  between 6 and 16 and hereafter called  $\text{C}_8\text{--C}_{18}$  was interleaved between LDH platelets by coprecipitation method. As previously reported, the basal spacing of the related intercalated compound was directly related to the alkyl chain length by adopting a mono- or bi-layer accommodation (Kopka et al., 1988; Meyn et al., 1990, 1993).

LDH platelets due to their structural anisotropy and their chemical versatility were extensively studied as flame retardant and thermal stabilizer (Feng et al., 2012), as pigments (Tang et al., 2012), as active fillers for biodegradable polymers and in food packaging applications (Costantino et al., 2012) as well as for polymer coating (Leroux et al., 2012).

To probe the attritive force resulting from the diffusion of polymer chain in between the tethered alkyl chains, intercalated polymer nanocomposite structure were here preferred to exfoliate case, the latter being rather difficult to characterize due to the loss of structural information. Therefore the contracted surfactant LDH hybrid series, which was complete over  $\text{C}_8$  to  $\text{C}_{18}$ , was here considered rather than the expanded one. Moreover to get a more critical issue, three different polymers were selected because of the recent relevance of the associated LDH nanocomposite polymer derivatives: polypropylene (PP) (Marchant and Jayaraman, 2002; Sun et al., 2009), poly(butylene)succinate (PBS) and polydimethylsiloxane (PDMS). LDH PP nanocomposite and in particular using  $\text{C}_{12}$ -type surfactant modified LDH was largely studied for fire retardant application (Ardanuy and Velasco, 2010; Ardanuy et al., 2010; Du et al., 2009; Manzi-Nshuti et al., 2009; Wang et al., 2010, 2011a, 2011b; Zhang et al., 2009) as well as for anti-oxidation (Lonkar et al., 2010, 2013). PBS synthesized by polycondensation of 1,4-butanediol with succinic acid presents some drawbacks for a practical end-use application such as low hydrolysis resistance, softness, tensile, gas-barrier properties. Additionally the melt-viscosity is not sufficient for processing. The dispersion of filler such as silica was employed (Han et al., 2008; Ray et al., 2003; Shih et al., 2007) as well as more recently LDH filler (Coehlo et al., 2012a,b; Sisti et al., 2013). Finally PDMS based LDH nanocomposites were scarcely reported only but the potential is great (Pradhan et al., 2012).

From organo-modified surfactant LDH/ $\text{C}_n$  (OMS-LDH) filler extruded with PP, PBS and PDMS, the polymer nanocomposite structure was scrutinized, and more precisely the inorganic layer expansion. Paradoxically an exfoliation was here not wished, and filler loading between 5 to 10 % w/w was used to guarantee the filler structure to diffract once dispersed. Melt polymer rheology was used to characterize the interaction and more precisely the Cole-Cole formalism to give the apparent molecular weight associated to the variation of the zero-shear viscosity (Colby et al., 1987; Fox and Glory, 1951; Friedman and Porter, 1975). Even if the relationship between structure and properties was largely addressed to understand the behaviors and performances, studies regarding complete series were scarcely reported. Using a cross-study between X-ray diffraction and melt polymer rheology, a structure-properties relationship was tentatively performed onto intercalated polymer nanocomposites. The attritive versus plastizing role of the organoclay was rationalized as a function of the intercalated polymer composite structure, in order to respond whether LDH interleaved platelets are of interest for polar and non-polar polymer (Nambo et al., 2008).

## 2. Experimental Section

### 2.1. Materials

Surfactant molecule, sodium octanoate (sodium caprylate,  $\text{H}_3\text{C}(\text{CH}_2)_6\text{COONa}$ , Fluka, 99%), decanoic acid (capric acid,  $\text{H}_3\text{C}(\text{CH}_2)_8\text{COOH}$ , Sigma, 98%), dodecanoic acid (lauric acid,  $\text{H}_3\text{C}(\text{CH}_2)_{10}\text{COOH}$ , Aldrich, 98%), tetradecanoic acid (myristic acid,  $\text{H}_3\text{C}(\text{CH}_2)_{12}\text{COOH}$ ,

Fluka, 98%), hexadecanoic acid (palmitic acid,  $\text{H}_3\text{C}(\text{CH}_2)_{14}\text{COOH}$ , Riedel-de-Haën, 98%), octadecanoic acid (stearic acid,  $\text{H}_3\text{C}(\text{CH}_2)_{16}\text{COOH}$ , Acros organics, 98%) were used as received. Sodium hydroxide (NaOH, Acros organics, 98%), aluminum chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , Acros organics, 98%), and zinc chloride ( $\text{ZnCl}_2$ , Acros organics, 98%) were used as received. The surfactant counter anion was hereafter called  $\text{C}_n$ , for instance stearate anion was labeled as  $\text{C}_{18}$  and its LDH inorganic derivatives  $\text{C}_{18}\text{-LDH}$ . The isotactic polypropylene PP was obtained from Borealis 8 MFI (homopolymer HD601CF), PBS (CAS#25777-14-4) EnPol G-4560 (MI = 1.5 g/10 min,  $T_m = 115^\circ\text{C}$ ) was provided by Ire Chemicals Co. Korea and the silicone PDMS was obtained from Blue Star Silicones.

### 2.2. Preparation of the hybrid hydrophobic phases LDH/ $\text{C}_n$

The cation LDH composition was  $\text{Zn}_2\text{Al}$ , and the preparation of the hydrocalcite-like hybrid materials were performed using the so-called coprecipitation method. Experimentally, solution of carboxylic fatty acid ( $2 \cdot 10^{-2}$  M) was prepared, and 250 ml solution of the salts (Zn;  $2 \cdot 10^{-2}$  M and Al;  $1 \cdot 10^{-2}$  M) were added dropwise to the previous solution. During the addition, the reaction was kept under nitrogen atmosphere in order to avoid contamination by carbonate and the pH was kept constant at  $\text{pH} = 9.5 \pm 0.1$  with the addition of NaOH. The slurry was aged in the mother liquid and separated by centrifugation. The resulting powders hereafter named as  $\text{Zn}_2\text{Al}/\text{C}_n$  was washed several times with distilled water and finally dried at room temperature.

### 2.3. Preparation of polymer filled with LDH/ $\text{C}_n$

Prior to dispersion,  $\text{Zn}_2\text{Al}/\text{C}_n$  organoclays were dried at  $120^\circ\text{C}$  for 2 h as well as PP, while PBS were dried at  $40^\circ\text{C}$  for 48 h in air oven, and PDMS not. LDH additive and polymer were melt-processed on a standard micro-extruder equipment Haake Force Feeder Minilab (Thermo Scientific) at  $180^\circ\text{C}$  (5 ),  $120^\circ\text{C}$  (5 ) and room temperature (15 ) in a twin screw extruder (rotation 100 rpm) for PP, PBS and PDMS, respectively, permitting to prepare about 7 grams of composite. Organoclay loading was from 5, 7.5 up to 10 wt. %. For further analyses, polymer films were prepared by hot pressing.

### 2.4. Characterization of LDHs/ $\text{C}_n$ and polymer nanocomposites

Elemental analysis (S, Al and Zn) was performed at the Vernaison Analysis Center of CNRS using inductive conduction plasma coupled to atomic emission spectroscopy (ICP/AES). The chemical compositions were reported from elemental analyses, Zn and Al at.%.

XRD analyses of the hybrid LDH and polymer nanocomposites were performed on a Siemens D501 diffractometer using  $\text{Cu K}_\alpha$  source (30 mA, 35 kV); data were collected in a step scan mode between  $2.0$  and  $70.0^\circ(2\theta)$  and with a step size of  $0.03^\circ(2\theta)$  and a counting time of 10 s/step. For the low-angle recording, measurements were performed closing the slits from 1 to  $0.3^\circ$  in the  $2\theta$ -range 1 or 0.7 to  $10^\circ$  with a step size  $0.005^\circ$ , and step counting time of 20 s.

Rheological measurements were carried out on a rheometer Rheometric Scientific equipped with a parallel plate geometry using 8 mm diameter plates and using a gap of 1 mm. The dynamic strain sweep measurements were carried out to determine the linear viscoelastic region, and a temperature of  $180^\circ\text{C}$ ,  $120^\circ\text{C}$  and  $30^\circ\text{C}$  was applied on PP, PBS and PDMS and filler composite derivatives, respectively. Experimentally, a decreasing strain from 40 to 3 % was applied when increasing the pulsation from 0.1 to 100 or 500  $\text{rad}\cdot\text{s}^{-1}$ , respectively.

Fourier Transform Infra-Red FTIR spectra were recorded on a Nicolet on the wavenumber domain 400 to  $4000\text{ cm}^{-1}$  with a  $4\text{ cm}^{-1}$  resolution and using KBr pellets in transmission mode.

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