



## Research paper

# Production of montmorillonite/polypyrrole nanocomposites through *in situ* oxidative polymerization of pyrrole: Effect of anionic and cationic surfactants on structure and properties



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## ABSTRACT

Montmorillonite/polypyrrole (Mt/PPy) nanocomposites were prepared through *in situ* oxidative polymerization of pyrrole in aqueous dispersions of unmodified montmorillonite ( $\text{Na}^+$ -Mt) with three different surfactants (dodecylbenzenesulfonic acid (DBSA), sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB)), using iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as an oxidant. In order to investigate the effect of the anionic and cationic surfactants used in the pyrrole polymerization, Mt/PPy nanocomposites were also prepared without surfactant. The anionic surfactants promoted the intercalation and partial exfoliation of the clay, while clay polymer nanocomposites (CPN) prepared with cationic CTAB (Mt/PPy.CTAB) and without surfactant (Mt/PPy.Cl) were partially intercalated. High electrical conductivity ( $10.8 \text{ S cm}^{-1}$ ) was observed for the Mt/PPy.SDS nanocomposites due to the highly site-specific interaction between the protonated PPy ( $\text{N}^+$ ) and the negatively-charged Si–O–Si groups of the Mt. Finally, the thermal stability of the CPN was higher than that found for the corresponding PPy samples, with the exception of the Mt/PPy.CTAB nanocomposite, due to the protective effect of the clay layers.

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## 1. Introduction

Interest in the development of polypyrrole (PPy) clay polymer nanocomposites (CPN) has been increasing recently due to the possibility of obtaining a new functional material with the synergetic properties of the two components. These properties include improved thermal stability, advanced gas barrier, controllable electrical conductivity and good mechanical performance. Conducting CPN are promising materials for important technological applications, such as electrorheological fluids (Kim et al., 2003), cathode materials for oxygen reduction (Rajapakse et al., 2010), metal corrosion protection (Yeh et al., 2003; Castagno et al., 2009; Trung et al., 2014), electrodes for energy storage device (Rajapakse et al., 2008) and fillers for the modification of the physico-chemical properties of insulating polymers (Hosseini et al., 2009; Moučka et al., 2011). Montmorillonite (Mt) has been widely used as a layered inorganic host material for the preparation of

conducting Mt/PPy nanocomposites because of its interesting properties, including large surface area, thermal stability, excellent in-plane strength and stiffness, strong surface activity and high aspect ratio (Kim et al., 2004; Kassim et al., 2007). Several methods have been reported for the production of Mt/PPy nanocomposites. The most extensively studied technique consists of inserting PPy into Mt layers through the chemical *in situ* polymerization of pyrrole (Py) in the presence of Mt suspension with or without surfactant, using an oxidant (Hong et al., 2001; Kim et al., 2003; Bae et al., 2005; Mravčáková et al., 2007; Karim and Yeum, 2008; Han, 2009; Shakoor et al., 2012). Another technique involves the direct intercalation of PPy chains into the Mt layers by mixing the components in solution. In this method, colloidal or water soluble PPy is prepared and then blended with Mt in an aqueous suspension (Bae et al., 2005). The electrochemical polymerization of Mt/PPy nanocomposites on a gold substrate is another way to produce nanostructured materials (Liu and Ger, 2002; Castagno et al., 2009).

Considerable effort has been made to prepare Mt/PPy nanocomposites with an intercalative or exfoliated structure, in which a synergistic combination of the properties of the two components is attained. Although most studies on Mt/PPy nanocomposites have obtained the intercalated structure (Hong et al., 2001; Mravčáková et al., 2007;

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Karim and Yeum, 2008; Han, 2009; Shakoor et al., 2012), the exfoliated samples have better properties (Bae et al., 2005) when compared with Mt/PPy microcomposites and intercalated nanocomposites. It is well known that the extent of exfoliation or intercalation and the electrical conductivity (between  $10^{-7}$  and  $6 \text{ S cm}^{-1}$ ) are dependent on the method and preparation conditions. For example, Kim et al. (2003) reported the preparation of Mt/PPy nanocomposites with an electrical conductivity of  $6 \text{ S cm}^{-1}$  using dodecylbenzenesulfonic acid (DBSA) as a surfactant and ammonium persulfate (APS) as an oxidant. Mravčáková et al. (2006) demonstrated that the electrical conductivity of an organo-modified montmorillonite (OMt/PPy) ( $1.1 \text{ S cm}^{-1}$ ) is two orders of magnitude higher than that of an inorganic Mt/PPy nanocomposite. A fully exfoliated Mt/PPy graft copolymer nanocomposite was obtained through the *in situ* polymerization of pyrrole in the presence of pre-exfoliated water soluble poly(styrenesulfonic acid-co-pyrrolyl methyl styrene) P(SSA-co-PMS)/Mt or through the simple mixing of the two components poly(styrenesulfonic acid-g-pyrrole) (PSSA-g-PPy) and Mt in an aqueous solution (Bae et al., 2005). However, to the best of our knowledge there is no in-depth studies in the literature concerning the effect of the anionic surfactants, such as dodecylbenzenesulfonic acid (DBSA) or sodium dodecyl sulfate (SDS), and cationic surfactant, for instance, cetyltrimethylammonium bromide (CTAB), on the structure and properties of Mt/PPy nanocomposites prepared through *in situ* Py polymerization. In order to obtain an Mt/PPy nanocomposite with functional properties for incorporation into thermoplastic polymers, the aim of this study was to prepare and characterize conducting CPN through *in situ* Py polymerization in Mt aqueous dispersions with three different surfactants (DBSA, SDS or CTAB) using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as an oxidant. Mt/PPy nanocomposite was also prepared without a surfactant under the same method conditions, in order to compare its structure and properties with those of the nanocomposites prepared in the presence of an Mt/surfactant aqueous dispersion.

## 2. Experimental

### 2.1. Materials

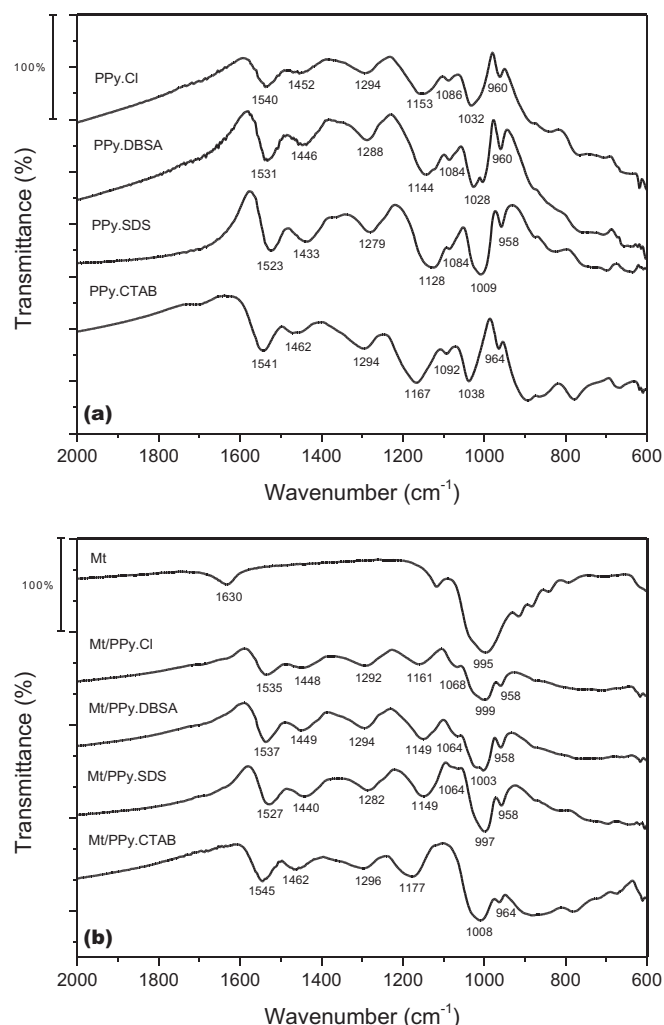
Sodium bentonite ( $\text{Na}^+$ -Mt) (VULGEL CN 45) is a product of Aliança Latina Indústrias e Comércio Ltda (Uruguaiiana, Rio Grande do Sul – Brazil) with high purity, pH of 5.5 and surface area of  $30.73 \text{ m}^2 \text{ g}^{-1}$  (Rossetto et al., 2009). The chemical composition of dry Mt is:  $\text{SiO}_2$  (64.75%),  $\text{Al}_2\text{O}_3$  (17.90%),  $\text{Fe}_2\text{O}_3$  (3.55%),  $\text{MgO}$  (3.00%),  $\text{Na}_2\text{O}$  (2.35%),  $\text{CaO}$  (0.60%),  $\text{TiO}_2$  (0.40%) and  $\text{K}_2\text{O}$  (0.15). The pyrrole (Py) (Aldrich, 98%) was distilled under vacuum and stored in a refrigerator before use. Iron (III) chloride hexahydrate,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Vetec, analytical grade), and the surfactants dodecylbenzenesulfonic acid (DBSA; Aldrich), sodium dodecyl sulfate (SDS; Vetec) and cetyltrimethylammonium bromide (CTAB; Vetec) were used as received.

**Table 1**

Main characteristics of pure MMT, PPy.Cl, PPy.DBSA, PPy.SDS, PPy.CTAB and their nanocomposites.

Samples	Composition (%)			PPy content <sup>a</sup> (wt.%)	Electrical conductivity ( $\text{S cm}^{-1}$ )
	C	H	N		
Mt	0.1 ± 0.1	1.9 ± 0.1	0	0	$(4.3 \pm 0.5) \times 10^{-6}$
PPy.Cl	55.2 ± 0.3	3.7 ± 0.1	16.2 ± 0.2	100	0.5 ± 0.2
PPy.DBSA	63.3 ± 0.5	6.5 ± 0.1	9.3 ± 0.1	100	2.4 ± 0.3
PPy.SDS	59.9 ± 0.4	6.4 ± 0.2	11.0 ± 0.2	100	14.7 ± 0.1
PPy.CTAB	55.6 ± 0.2	3.7 ± 0.1	16.1 ± 0.3	100	0.2 ± 0.1
Mt/PPy.Cl	26.4 ± 0.1	2.6 ± 0.1	7.8 ± 0.2	48.1 ± 0.2	4.4 ± 0.1
Mt/PPy.DBSA	37.5 ± 0.2	4.7 ± 0.2	4.4 ± 0.1	47.3 ± 0.2	1.2 ± 0.3
Mt/PPy.SDS	36.4 ± 0.2	4.4 ± 0.1	6.7 ± 0.1	60.9 ± 0.3	10.8 ± 0.2
Mt/PPy.CTAB	34.4 ± 0.2	4.0 ± 0.1	7.5 ± 0.1	46.6 ± 0.3	0.1 ± 0.2

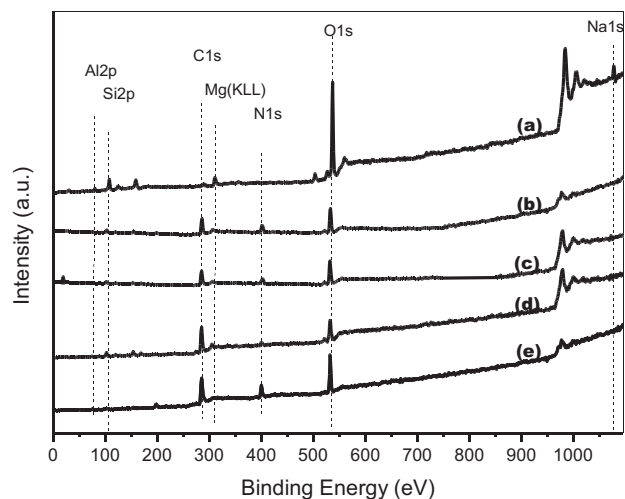
<sup>a</sup> Calculated from elemental analysis.



**Fig. 1.** FTIR-ATR spectra for (a) PPy.Cl, PPy.DBSA, PPy.SDS, PPy.CTAB and (b) neat Mt and nanocomposites (Mt/PPy.Cl, Mt/PPy.DBSA, Mt/PPy.SDS, Mt/PPy.CTAB).

### 2.2. Preparation of Mt/PPy nanocomposite systems

The procedure used for the preparation of the Mt/PPy nanocomposites was based on that described by Mravčáková et al. (2006). The  $\text{Na}^+$ -



**Fig. 2.** XPS spectra for Mt (a), Mt/PPy.Cl (b), Mt/PPy.DBSA (c), Mt/PPy.SDS (d) and Mt/PPy.CTAB (e).

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