



## Research paper

# Preparation and characterization of polyacrylamide-modified kaolinite containing poly [acrylic acid-co-methylene bisacrylamide] nanocomposite hydrogels



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## ABSTRACT

Novel nanocomposite hydrogel structures based on cross-linked poly(acrylic acid) (PAA) and kaolinite (Kaol), modified with different loadings of polyacrylamide (PAAm), were prepared by inverse dispersion polymerization. Ceric ammonium nitrate as an initiator in the presence of nitric acid was used to graft PAAm from the Kaol surface. The surface-modified Kaol showed enhanced interactions between the filler and the PAA matrix, through interactions between amino (–NH<sub>2</sub>) from PAAm and carboxylic groups (–COOH) from PAA. The XRD and TEM measurements confirmed the exfoliated nanocomposites with the Kaol filler. The swelling degree (SD) of the swollen hydrogel nanocomposite was increased following the addition of polyacrylamide-modified Kaol particles into the hydrogel structures. Rheological characterization showed that an increase in the storage modulus ( $G'$ ) could be a consequence of a good dispersion of Kaol particles in the polyacrylic acid matrix, thereby leading to enhanced interactions and furthermore to improved mechanical properties of the final hydrogels.

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## 1. Introduction

Hydrogels are cross-linked polymer materials with high water-retaining capacity (Peppas, 2004; Sandu et al., 2013). In the last few decades these materials have found innovative applications in many areas, especially in medicine (Hoffman, 2002; Kashyap et al., 2005; Langer and Peppas, 2003) and agriculture (Rudzinski et al., 2002; Teodorescu et al., 2009). The major disadvantages of simple hydrogels include high production costs and low gel strength, leading to restrictions in agricultural and horticultural applications (Kabiri and Zohuriaan-Mehr, 2004; Lee and Chen, 2004; Liang and Liu, 2007). The use of an inorganic reinforcing agent, mainly clays, can represent a way of reducing production costs and improving the mechanical strength of hydrogel nanocomposites (Zhang et al., 2006). Nowadays, the preparation of hydrogel nanocomposites is intensively studied due to their superior properties in comparison to plain hydrogels. Most research on hydrogel nanocomposites has focused on the incorporation of clay particles into the polymer structure of hydrogels (Theng, 2012), in order to improve mechanical, physical, and chemical properties. Moreover, the incorporation of these clay

particles into the hydrogel structure also leads to reduced swelling capacity and swelling rates (Sirousazar et al., 2012; Wu et al., 2011; B. Zhang et al., 2007; J. Zhang et al., 2007). Kaolinite (noted hereafter Kaol) is the most abundant clay mineral, with about 20 million tonnes being produced every year (Harvey and Lagaly, 2006). Very strong interlayer interactions through Van der Waals and hydrogen bonding between the Al–OH and Si–O groups from adjacent sheets make Kaol a unique layered material and a very important raw ceramic material. Because of its excellent properties and its low price it is used extensively in almost every branch of the chemical industry for plastics, paints, and fire-resistant materials (Ianchis et al., 2012). Furthermore, Kaol is known to exhibit much lower cation exchange capacity (CEC = 1–15 meq/100 g) compared to other, much more expensive clay minerals (montmorillonite, vermiculite, CEC = 80–150 meq/100 g) (Harvey and Lagaly, 2006; Ianchis et al., 2011; Sirousazar et al., 2012; J. Zhang et al., 2007). Therefore, it is very difficult to exfoliate/intercalate the layers. The intercalation of Kaol has been performed through the introduction of a small polar molecule between the layers, in order to increase the interlayer space, followed by the intercalation of an organic compound, which was successfully grafted onto the interlayer space in a process known as the “displacement method” (Gardolinski et al., 2000; Sugahara et al., 1988; Tunney and Detellier, 1996). Tonlé et al. (2007) reported a series of

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new organo-Kaol nanohybrid materials based on Kaol and organosilanes (such as 3-aminopropyltriethoxysilane). Polymer synthesis into the interlayer space of clay minerals was recognized in early studies in this field (Sugahara et al., 1988). In recent years, Kaol polymer nanocomposites have been reported to enhance the mechanical (rigidity, strength), thermal, electrical, and insulating properties of several polymer matrices (Bahramian and Kokabi, 2011; Elbokl and Detellier, 2006; Sugahara et al., 1988; Xia et al., 2003). According to the literature, a variety of polymers such as polyacrylonitrile (PAN) (Sugahara et al., 1988), polyethylene glycol (PEG) (Tunney and Detellier, 1996), and poly(hydroxybutyrate) (PHB) (Gardolinski et al., 2000) have been employed in the Kaol intercalation process. In all of these methods Kaol–polymer intercalation was achieved by employing the displacement method, in which ammonium acetate (Sugahara et al., 1988) or dimethyl sulfoxide (Gardolinski et al., 2000; Tunney and Detellier, 1996) was used as precursors. The mechanism involves polymer chains interacting with the Kaol interlayer through hydrogen bond formation, since the C≡N (from PAN) group as well as C=O and –O– are acceptors (Sugahara et al., 1988). The present paper deals with the synthesis and characterization of novel exfoliated hydrogel nanocomposites containing poly(acrylic acid) (PAA) cross-linked with N, N' methylenebisacrylamide, and surface-modified Kaol. Firstly, the polymerization of acrylamide (AAm) into Kaol interlayers was performed, in order to obtain an intercalated Kaol structure. The modification of Kaol was achieved by adapting an old method—cerium-initiated polymerization (Gupta and Khandekar, 2006; Mino and Kaizerman, 1958)—which in this case was the first time it had been applied to the intercalation of Kaol. Furthermore, the polymerization of acrylic acid (AA) was achieved, in order to obtain the exfoliated Kaol structure.

## 2. Experimental

### 2.1. Materials

Acrylic acid (Aldrich, 99%) was distilled under vacuum conditions and stored in the refrigerator. Potassium persulfate (KPS, Acros Organics, 99%), sodium metabisulfite (MS, Acros Organics, 97%) and N, N'-methylenebisacrylamide (MBA, Sigma-Aldrich, 99%) were used without further purification. Paraffin oil (PO, Stera Chemicals, technical product—an ingredient prevalent in the cosmetic industry) and cyclohexane (Fluka, 99%) were used as received. Acrylamide and other chemicals not mentioned above were supplied by Sigma-Aldrich. Distilled or double distilled water was employed in all experiments involving water. The Kaol was also supplied by Sigma-Aldrich and was used as received.

### 2.2. Preparation of the polyacrylamide-modified Kaol through cerium ion-initiated polymerization

Kaol (22.8 g) was mixed with H<sub>2</sub>O (577.2 mL) in a 1 L round-bottom flask equipped with a condenser. The mixture was stirred at room temperature for 1.5 h and thereafter heated at 80 °C for 1 h. The mixture was allowed to cool to room temperature while very fine particles formed in the aqueous phase. The dispersion was used after preparation without further purification. The Kaol dispersion (78.9 g, containing 3 g of Kaol) was added to a round-bottom flask, diluted with H<sub>2</sub>O (66 mL), and pH was adjusted to pH = 7 with HNO<sub>3</sub>. Acrylamide (AAm, 12 g, 0.17 mol) was added to the dispersion, which was then bubbled with nitrogen for 1 h. Concentrated HNO<sub>3</sub> (0.93 mL, 1.31 g, 0.015 mol) and Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (0.54 g, 0.001 mol) were added under nitrogen atmosphere, and the dispersion was heated at 30 °C in an oil bath for 25 min. After polymerization, the reaction was quenched by cooling to 0 °C in an ice bath. The dispersion was filtered (0.4 μm cellulose filter) and the solid was washed with copious amounts of H<sub>2</sub>O and freeze-dried to deliver the product as a powder (K<sub>PAAm</sub>(X), where X represents the loading in mass-% PAAm determined by thermogravimetric analyses).

### 2.3. Preparation of the poly [acrylic acid-co-methylene bisacrylamide] nanocomposite hydrogels containing polyacrylamide-modified Kaol through inverse dispersion polymerization

Polymerization was performed under a nitrogen atmosphere in a three-necked round-bottom flask fitted with a mechanical stirrer. The aqueous phase/paraffin oil ratio was 1:7, in order to minimize crust deposition or the agglomeration of hydrogel particles on the stirrer and/or flask walls. Thus, a stock solution was prepared in a 20 mL glass vial from the appropriate amounts of polyacrylamide-modified Kaol [K<sub>AAm</sub>(X)], acrylic acid [AA], and N, N'-methylenebisacrylamide [MBA] in 3 mL of distilled water. For a better dispersion of polyacrylamide-modified Kaol particles, the mixture was stirred for 1 h on a magnetic stirrer. After appropriate time intervals, the corresponding solutions of the redox initiation system, consisting of [KPS]/[MS], were added to the mixture. The reaction mixture was kept under magnetic stirring for 2 min, and then the resulting dispersion was added via a syringe to the three-necked round-bottom flask fitted with a mechanical stirrer under a nitrogen atmosphere. After 2 h of reaction time, at room temperature, the heating was stopped and the reaction mixture was filtered using a G1 filtering crucible with filter paper. The newly obtained nanocomposite hydrogels were washed with an appropriate amount of cyclohexane, in order to remove traces of paraffin oil, and they were then dried in an oven at 50 °C to acquire constant mass. Hydrogel nanocomposites were designated as K-PAA, in the case of samples with non-modified Kaol particles, and as K<sub>AAm</sub>(X)-PAA in the case of xerogel samples with modified Kaol. All xerogels contained 5 mass% K, while the molar concentration of AA in distilled water was 4 mol/L. The employed molar concentrations of the [MBA] and [KPS]/[MS] were 1 M% relative to [AA]. The difference between the samples consisted in using modified Kaol with different [PAAm] loadings. For an accurate reference, the polymerization of AA in the same conditions was achieved, albeit without Kaol or modified Kaol particles.

### 2.4. Determining the swelling degree

The swelling degree (SD) of the new nanocomposite hydrogel structures obtained by polymerization was determined as follows: A disc-shaped piece from each of the synthesized nanocomposite hydrogels was submerged in a glass vial with distilled water and kept for five days at room temperature (the water was changed daily). The hydrogel nanocomposite, including water, was taken out, blotted with filter paper, and weighed ( $w_{\text{hydrogel}}$ ). It was then dried in an oven at 30 °C for 16 h in a vacuum (15 mm Hg), following which the mass of the dry (xerogel) polymer ( $w_{\text{xerogel}}$ ) was determined.

The SD was calculated as the ratio between the amount of water absorbed by the hydrogel during the purification and swelling period and the amount of dry polymer according to Eq. (1).

$$SD = \left[ \frac{(w_{\text{hydrogel}} - w_{\text{xerogel}})}{(w_{\text{xerogel}} - w_{\text{kaolin}})} \right] \cdot \left[ \frac{g_{\text{water}}}{g_{\text{xerogel}}} \right]; \quad (1)$$

where  $w_{\text{kaolin}}$  is the mass of kaolin and was calculated according to Eq. (2):

$$w_{\text{kaolin}} = \% \text{kaolin} \times w_{\text{xerogel}} / 100, [g]. \quad (2)$$

### 2.5. Characterization

The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Nicolet FTIR Model 500 by acquiring 32 scans with 4 cm<sup>-1</sup> resolution in 4000–400 cm<sup>-1</sup> region, on a KBr pellet. The thermogravimetric analyses (TGA) were performed on a Thermal Analysis SDT600 instrument, by heating samples of 5–10 mg from room temperature up to 1000 °C at a heating rate of 10 °C/min under a nitrogen flow.

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