

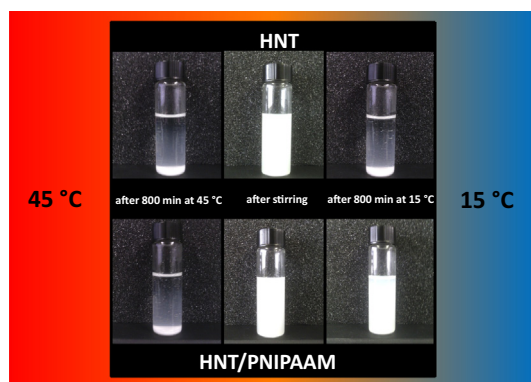
Steric stabilization of modified nanoclays triggered by temperature



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GRAPHICAL ABSTRACT



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ABSTRACT

Halloysite clay nanotubes were modified through the adsorption of poly(N-isopropylacrylamide)-amine terminated (PNIPA-NH₂) onto the external surface by exploiting electrostatic interactions at pH = 6. In spite the amount of attached polymer is rather low (1 wt%), the properties of the nanotubes are deeply modified. The apparent specific volume and isentropic compressibilities of the hybrid nanomaterial dispersed in water evidenced the transferring of the thermosensitive property from the polymer to halloysite. The hydrodynamic radius as well as the ζ-potential of the nanohybrid are consistent with the attachment of a positively charged polymer onto the negative surface of the nanotube. The colloidal stability was strongly enhanced in the temperature domain below the lower critical solution temperature. This methodology endowed to obtain hollow nanotubes with a stimuli-responsive corona.

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1. Introduction

The modification of nanoparticles by introducing a polymeric shell is a common strategy to control and trim desired properties of nanomaterials. Within these families, a relevance is given to inorganic-polymer nanoparticles with a core-shell structure that are simply produced by green, biocompatible and cheap procedures. Naturally available and sustainable nanoclays like Halloysite

(HNT) with hollow tubular shape and controlled release properties represent promising raw materials for several applications. For example, halloysite could be used as support for catalysts or as catalyst [1] itself, with potential functionalities resembling those of pristine and functionalized carbon nanotubes [2–4]. This clay was proposed as sustainable smart material only a few years ago. HNT is abundant, durable and biocompatible and, furthermore, it is cheap compared to synthetic nanomaterials with similar morphology. HNT is generated by rolling-up a kaolin sheet with a natural hydrothermal process; its size ranges between 0.5 and 1 μm in length and between 15 and 100 nm in the inner diameter

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[5]. This structure properly modified makes this material versatile as nanocontainer of species different in nature [6–12] or as nano-filler [13–16], in membranes [17,18] and rubber [19,20].

A formidable tool is provided by the different chemistry of the inner and the outer surfaces of this clay. Being that the external surface is composed of Si–O–Si groups and the internal surface of Al–OH groups, the aqueous acid–base equilibria confer negative and positive charges to the outer and inner surfaces, respectively, in a wide pH range [5]. Consequently, the selective adsorption of ionic species was revealed to be strategic in tuning the hydrophilic/hydrophobic character of nanoparticles [10–12]. The adsorption of polymers onto HNTs may dramatically change the structure as well as the physico-chemical properties in case that the polymer responds to external stimuli like temperature, pH, ionic strength and so on. It is well known the versatility of the thermo-sensitive poly(N-isopropylacrylamide) (PNIPA) and its consequent applications. This kind of polymer presents a lower critical solution temperature (LCST) the value of which depends on the solvent nature, polymer concentration, molecular weight, nature of the terminated groups, etc. [21]. PNIPA hydrogel induces a skeleton muscle inflammation over 2 months [22]. Graphene oxide covalently linked to PNIPA improved dispersibility and cell viability in water as well as in the cell medium [23]. PNIPA shell was grafted onto the surface of nanoparticles forming nanocomposites [24]. Recently, clay laponite was employed as physical cross linker for the preparation of dual sensitive double network [25]. PNIPA in beads with alginate [26] and covalently linked to HNT [27] were prepared in the domain below and above the LCST to study their response as drug carriers. PNIPA–HNT hydrogel nanocomposites were reported as suitable catalyst support [28]. We thought it would be interesting to modify HNT with ammine-terminated poly(N-isopropylamide) (PNIPA-NH₂) positively charged pursuing a simple, green and cheap methodology. Such a versatility provides tools to finely control the temperature respond of the hybrid nanomaterials for possible applications in tissue engineering, controlled drug delivery and so on.

2. Experimental section

2.1. Materials

Poly(N-isopropylacrylamide)-amine terminated (PNIPA-NH₂) (average molecular weight = 5500 g mol⁻¹) is from Sigma. Halloysite, Sigma product, (HNTs, Al₂Si₂O₅(OH)₄·2H₂O) has a specific surface area of 65 m² g⁻¹ and a specific gravity of 2.53 g cm⁻³.

2.2. Preparation of PNIPA-NH₂/HNT

Aqueous polymer solution was prepared by dissolving 2 g of PNIPA-NH₂ in 100 cm³ of water. Then, 5 g of HNT were added and the obtained dispersion was magnetically stirred for 48 h. The pH value of the dispersion was 6.0. Afterward, it was kept in a vacuum oven at 100 mbar and at 25 °C overnight. The dispersion was centrifuged to recover the functionalized material that was washed with water several times until the density of the supernatant reached the water value. Then, to perform the experiments, the obtained solid material was dispersed into water.

This well consolidated procedure [10–12] exploiting the ionic exchange allowed us to obtain nanohybrids chemically stable as after several water washing steps no polymer was released.

2.3. Methods

Dynamic light scattering (DLS) experiments were carried out by means of a Zetasizer NANO-ZS (Malvern Instruments). The

field-time autocorrelation functions were well described by a single decay, which provides the decay rate (Γ) of the diffusive mode. For the translational motion, the collective diffusion coefficient at a given concentration is $D_t = \Gamma/q^2$ where q is the scattering vector given by $4\pi n\lambda^{-1}\sin(\theta/2)$ being n the water refractive index, λ the wavelength (632.8 nm) and θ the scattering angle (173°).

The functionalized nanotubes were imaged by using a microscope ESEM FEI QUANTA 200F. Before each experiment, the sample was coated with gold in argon by means of an Edwards Sputter Coater S150A to avoid charging under electron beam.

The thermogravimetric analyses were done on the solid (obtained by evaporating the aqueous dispersion at 80 °C) by using a Q5000 IR apparatus (TA Instruments) under nitrogen flow at the heating rate of 10 °C min⁻¹. Temperature spanned from ambient to 900 °C. Calibration was performed as reported elsewhere [29].

The density ($\pm 1 \times 10^{-6}$ g cm⁻³) and speed of sound (± 0.1 m s⁻¹) were determined as functions of temperature by using a density and a sound velocity meter (DSA 5000 M, Anton Paar). The isentropic compressibility coefficients of the dispersions (β) were obtained as $100/(u^2 \times d)$ being u the ultrasonic velocity in the dispersion.

The apparent specific volume (v_{sp}) and isentropic compressibility (k_{sp}) of pristine HNT, PNIPA-NH₂ and hybrid HNT in water were calculated as

$$v_{sp} = 1/d - 10^2(d - d_0)/(C_s \times d \times d_0) \quad (1)$$

$$k_{sp} = v_{sp}\beta + 10^2(\beta - \beta_0)/(C_s \times d_0) \quad (2)$$

where d are the densities of the solutions or dispersions while d_0 are the solvent densities; C_s is the concentration of solid material into the dispersion in g/100 g of solvent. β_0 is the isentropic compressibility coefficients of water and the other symbols have the same meaning as above.

This apparatus was also used to measure the density of supernatant in the PNIPA-NH₂/HNT preparation.

The transmittance as a function of time of the aqueous dispersions of HNT and HNT/PNIPA-NH₂ (1 wt%) was measured at 25.0 ± 0.1 °C using an Analytic Jena Specord S 600 BU UV–vis spectrophotometer. The experiments were performed at a wavelength of 600 nm, at which no absorbance bands were detected.

3. Results and discussion

3.1. Preparation of PNIPA-NH₂/HNT hybrids

The nanoparticles modification with thermo-sensitive polymer is usually done via *grafting* to ensure the polymer attachment and, consequently, to guarantee the stability of the hybrids; that is a rather important feature to the light of their applications within different fields [31]. Alternatively, modification of nanoparticles can be done by exploiting weak interactions (electrostatic, ion–dipole, dipole–dipole forces) that is valuable because it is a less consuming time procedure and it has a low environmental impact. With this in mind, we modified HNTs with poly(N-isopropylacrylamide)-amine terminated (PNIPA-NH₂) taking advantage of the electrostatic interactions between the polymer terminal group, positively charged under the experimental conditions, and the negative HNT surface. The pursued methodology was successful being that the tubular shape of halloysite and the characteristic lengths in the hybrid nanomaterial were preserved as the SEM micrographs show (Fig. 1). It is well known [10,11,30] that the HNT loaded amounts of substances can be accurately determined by TGA. To this aim, thermogravimetric data were collected and shown in Fig. 2, where, for a comparison purpose, data for pristine HNT are reported. Fig. 2 illustrates that the thermograms differ in the high temperature region. The amount of PNIPA-NH₂ of 1.0 wt%

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