Characterization of Non-Covalently Functionalized Halloysite

Danae Lopes Francisco, Lucilene Betega de Paiva, Wagner Aldeia, Ademar B. Lugão and Esperidiana A. B. Moura

Abstract The inorganic nanotube halloysite (HNT) is a promising type of natural occurring filler for polymers. Its characteristics, such as high aspect ratio (10–50), small size, and high strength (elastic modulus—140 GPa) suggest that HNTs have a potential use in high-performance polymer nanocomposites. Compared to other nanoclays and nanosilica the relatively low content of hydroxyl groups on their surfaces makes HNTs relatively hydrophobic, although, sometimes, this is not sufficient for guaranty a good interfacial adhesion in composite systems. Further hydrophobic treatment is required to improve HNTs compatibility with polymer matrixes, maximizing interfacial interactions. In the present study, different percentages of EPB (2,2-(1,2-ethene diyldi-4,1-phenylene) bisbenzoxazole) was used to perform a non-covalent functionalization of halloysite, based on electron transfer interactions. The functionalization is characterized by specific surface area (BET), thermogravimetric analysis (TG) and water/toluene extraction experiment.

Keywords Halloysite · EPB · BET · TG

Introduction

Extensive research about halloysite (HNT) began in the 1940s and has regained attention in recent years. HNT is a natural multiple-walled inorganic nanotube (1D), with a geometry similar to that of carbon nanotubes (CNTs). Its chemical formula is

D. L. Francisco (✉) · L. B. de Paiva · W. Aldeia
IPT, Group for Bionanomanufacturing, Laboratory of Chemical Process and Particle Technology, Institute for Technological Research of State of São Paulo, São Paulo, Brazil
e-mail: danae_lopes@hotmail.com

D. L. Francisco · A. B. Lugão · E. A. B. Moura
Center for Chemical and Environmental Technology (CQMA), Nuclear and Energy Research Institute, São Paulo, SP, Brazil

B. Li et al. (eds.), *Characterization of Minerals, Metals, and Materials 2018*, The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-319-72484-3_34

similar to that of kaolinite, represented by $Al_2Si_2O_5$ $(OH)_4{\cdot}nH_2O$, where n can vary from 0 to 2, representing dehydrated and hydrated halloysite, respectively [1–3].

The halloysite nanotubes (HNTs) vary from size depending on the crystallization conditions and on their geological origin. Some of their main characteristics, such as tubular microstructure, reduced size, high aspect ratio (10–50), high mechanical strength (elastic modulus—140 GPa) have raised interest for its application in polymers, resulting in high-performance polymer nanocomposites [4–10].

Most of the aluminols (Al-OH) groups are located in the inner part of the halloysite, while on the outer surface the siloxane group (Si–O–Si) is present with a few silanols/aluminols on the edges of the sheets. The relatively small amount of hydroxyl groups (O–H) on halloysite surface makes it relatively hydrophobic when compared to other nanoclays and nanosilica. Sometimes, the halloysite natural hydrophobicity is not sufficient for interfacial adhesion in the composites, so it is necessary to proceed with HNTs hydrophobic treatment, prior to its incorporation into polymers, maximizing the interfacial interactions [1, 2].

Halloysite functionalization can be divided into two main groups: covalent functionalization and non-covalent functionalization [1]. In the present study, a non-covalent functionalization based on electron transfer interactions using EPB (2,2-(1,2-ethene diyldi-4,1-phenylene) bisbenzoxazole) as functionalizer is evaluated.

Experimental

Materials

Halloysite nanotubes; CAS number 1332-58-7, chemical formula $Al_2Si_2O_5(OH)_4{\cdot}2\,H_2O$, molecular weight of 294.19 g/mol, true specific gravity of 2.53 g/ml, diameter between 30 and 70 nm, and length between 1 and 3 μm, purchased from Sigma Aldrich.

The non-covalent functionalizer 2,2′-(1,2-ethene diyldi-4,1-phenylene) bisbenzoxazole (EPB); CAS number 1533-45-5, empirical formula $C_{28}H_{18}N_2O_2$, molecular weight of 414.45 g/mol and melting point higher than 300 °C, purchased from Sigma Aldrich.

Functionalization of HNTs

Different percentages of EPB were used to functionalize halloysite, as shown in Table 1, by blending both mechanically. The HNTs were previously dehumidified at a temperature of 80 °C for 24 h.

Table 1 Composition of studied samples

Samples	Halloysite (wt%)	EPB (wt%)
100H	100	0
99,75HE	99.75	0.25
95HE	95	5
90HE	90	10

Characterization

Water/Toluene Extraction Experiment

The extraction experiment was used to verify the hydrophobicity of pristine halloysite and of functionalized halloysite. In separated glass tubes were added about 0.2 g of each composition of the studied samples. First it was added 10 mL of toluene followed by bath sonication for 10 min, further 10 mL of deionized water was added and followed for more 10 min of bath sonication. Observation on retention of the samples was made after rest.

Thermogravimetric Analysis (TG)

Thermogravimetric analysis was carried out on a Mettler Toledo TGA/DSC1 from 25 to 1000 °C, at a heating rate of 10 °C/min, under N_2 flow. Two TG assays were performed for each sample, with a mass about 15 mg.

BET Method

The specific surface area of the samples was determined by Brunauer, Emmett and Taller (BET) isotherms with a Micromeritics Gemini V. The samples were previously dehumidified under vacuum at a temperature of 60 °C.

Results and Discussion

Water/Toluene Extraction Experiment

The hydrophilicity tests using toluene and water (Fig. 1) shows that HNTs do not undergo swelling in water and have a more hydrophilic character since it stays in the water phase. The functionalized HNTs increased their affinity with toluene and presented a shift to the toluene phase, indicating that there is an interaction between EPB and HNTs.

Thermogravimetric Analysis (TG)

Table 2 shows the results of the thermogravimetric analysis. The mass loss in the range of temperature between 25 and 100 °C is related to the release of physically adsorbed water. The pristine HNT (100H) shows the highest mass loss. Samples functionalized with EPB showed a lower mass loss in this region, indicating that functionalization is responsible for changing HNT characteristic, lowering its affinity for free water adsorption. In the second range of temperature (100–250 °C) occurs HNT interlamellar water loss. Functionalized HNTs also present a lower mass loss than pristine nanotubes in this region, which may be attributed to the presence of the functionalizer in its structure. In the range of temperature between 250 and 650 °C, functionalized samples present a greater mass loss than the pristine halloysite, indicating the degradation of the functionalizer EPB. Similar tendencies were observed by Pontón et al. [11] for functionalized titanate nanotubes.

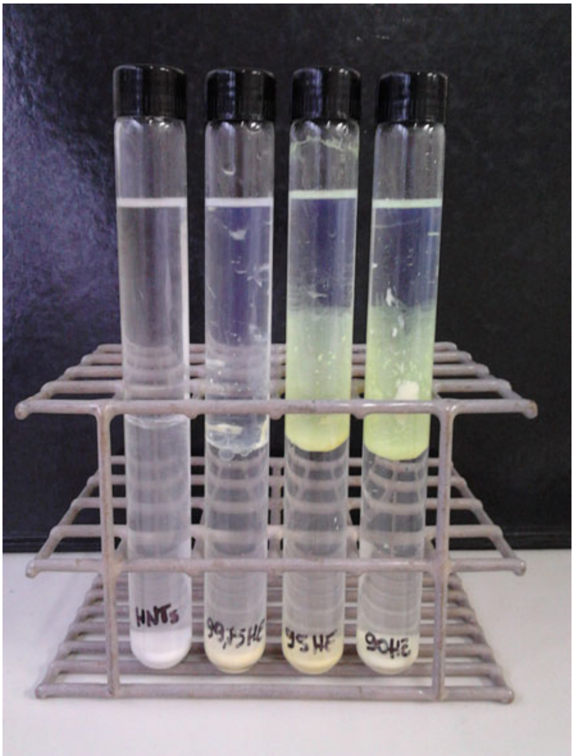

Fig. 1 Water/toluene hydrophilicity test of samples 100H (HNTs), 99,75HE, 95HE and 90HE

Table 2 Results of thermogravimetric analysis of pristine HNT and of functionalized HNTs with different percentages of EPB (99,75HE, 95HE, 90HE)

Sample	25–100 (°C) wt (%)	100–250 (°C) wt (%)	250–650 (°C) wt (%)
100H	2.09 ± 0.34	3.62 ± 0.55	16.27 ± 0.50
99,75HE	1.96 ± 0.01	3.08 ± 0.01	16.44 ± 0.36
95HE	1.52 ± 0.49	2.42 ± 0.60	19.61 ± 0.13
90HE	1.76 ± 0.76	2.84 ± 1.21	24.08 ± 0.55

Brunauer-Emmett-Teller (BET) Surface Area Analysis

The results obtained by BET method (Fig. 2; Table 3) shows that the surface area tends to decrease with the increase of EPB percentage in HNT, other authors also observed the same effect for functionalized halloysite [12, 13].

Table 3 shows that the C constant tends to decrease for samples with a higher amount of EPB showing that there is an effective interaction between halloysite surface and EPB. The higher change is observed for the sample 90HE, prepared

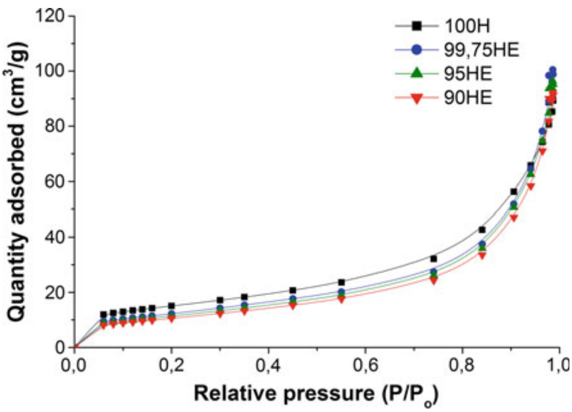

Fig. 2 BET curves of pristine HNT (100H) and of functionalized HNTs with different percentages of EPB (99,75HE, 95HE, 90HE)

Table 3 BET surface area and C constant for pristine HNT (100H) and functionalized HNT with different percentages of EPB (99,75HE, 95HE and 90HE)

Sample	BET surface area (m^2/g)	BET C value
100H	53.72	154.94
99,75 HE	44.03	107.09
95HE	41.04	101.37
90HE	38.18	95.37

with the higher amount of EBP (10 wt%). The C constant is related to the interaction of the adsorbed nitrogen molecules and the halloysite surface. The higher the C value, the higher the interaction energy between the nitrogen and Al-OH and Si–OH groups in HNT surface [12].

Conclusion

The electron-deficiency of HNT due to its metal atoms, such as aluminum, and ferrous, allows HNTs to accept foreign electron on their empty orbital, so when HNTs are blended with electron-rich species, electron transferring to HNTs can occur. In the present study the organic EPB, with a conjugated structure, is the electron-rich species and increasing the amount of this functionalizer in HNT the interaction between them became more evident and an effective electron transferring may be occurred. The hydrophilic character of HNT change to a more hydrophobic one, shifting the functionalized HNTs to toluene phase, as observed in the water/toluene extraction experiment. The mass loss related to the release of physically adsorbed water became smaller with the functionalization, indicating a lowering affinity for water in functionalized HNTs. The BET surface area was reduced with the functionalization.

References

1. Liu M, Jia Z, Jia D, Zhou C (2014) Recent advance in research on halloysite nanotubes-polymer nanocomposite. Prog Polym Sci 39:1498–1525
2. Du M, Guo B, Jia D (2010) Newly emerging applications of halloysite nanotubes: a review. Polym Int 59:574–582
3. Yi Z, Aidong T, Huaming Y, Ouyang J (2016) Applications and interfaces of halloysite nanocomposites. Appl Clay Sci 119:8–17
4. Hedicke-Höchstotter K, Lim GT, Altstädt V (2009) Novel polyamide nanocomposites based on silicate nanotubes of the mineral halloysite. Compos Sci Technol 69:330–334
5. Erdogan AR, Kaygusuz I, Kaynak C (2014) Influences of aminosilanization of halloysite nanotubes on the mechanical properties of polyamide-6 nanocomposites. Polym Compos 35:1350–1361
6. Guo B, Zou Q, Lei Y, Du M, Liu M, Jia D (2009) Crystallization behavior of polyamide 6/halloysite nanotubes nanocomposites. Thermochim Acta 484:48–56
7. Guo B, Zou Q, Lei Y, Jia D (2009) Structure and performance of polyamide 6/halloysite nanotubes nanocomposite. Polym J 41:835–842
8. Handge UA, Höchstötter KH, Altstädt V (2010) Composites of polyamide 6 and silicate nanotubes of the mineral halloysite: Influence of molecular weight on thermal, mechanical and rheological properties. Polymer 51:2690–2699
9. Prashantha K, Lacrampe M-F, Krawczak P (2013) Highly dispersed polyamide-11/halloysite nanocomposites: thermal, rheological, optical, dielectric, and mechanical properties. J Appl Polym Sci 130:313–321

10. Lecouvet B, Gutierrez J, Sclavons M, Bailly C (2011) Structure-property relationship in polyamide 12/halloysite nanotube composites. Polym Degrad Stab 96:226–235
11. Pontón PI, d'Almeida JRM, Marinkovic BA, Savíc SM, Mancic L, Rey NA, Morgado E Jr, Rizzo FC (2014) The effects of the chemical composition of titanate nanotubes and solvent type on 3-aminopropyltriethoxysilane grafting efficiency. Appl Surf Sci 301:315–322
12. Peixoto AF, Fernandes AC, Pereira C, Pires J, Freire C (2016) Physicochemical characterization of organosilylated halloysite clay nanotubes. Microporous Mesoporous Mater 219:145–154
13. Liu M, Guo B, Mingliang DDJ (2008) The Role of Interactions between Halloysite Nanotubesand 2,2′-(1,2-Ethenediyldi-4,1-phenylene) Bisbenzoxazole in Halloysite Reinforced Polypropylene Composites. Polym J 40:1087–1093