Applied Surface Science 393 (2017) 1–10

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full length article

Nitrile functionalized halloysite nanotubes/poly(arylene ether nitrile) nanocomposites: Interface control, characterization, and improved properties

Xinyi Wan [a], Yingqing Zhan [a,b,*], Guangyong Zeng [a], Yi He [a,b,c,*]

[a] School of Chemistry and Chemical Engineering, Southwest Petroleum University, 8 Xindu Avenue, Chengdu, Sichuan, 610500, China
[b] Oil & Gas Field Applied Chemistry Key Laboratory of Sichuan Province, Southwest Petroleum University, Chengdu, Sichuan, China, 610500
[c] State Key Lab of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, 8Xindu Avenue, Chengdu, Sichuan, 610500, China

ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form
27 September 2016
Accepted 28 September 2016
Available online 29 September 2016

Keywords:
Halloysite nanotubes
Poly(arylene ether nitrile)
Functionalization
Tensile properties
Dielectric permittivity
Thermal stability

ABSTRACT

To develop high-performance halloysite nanotube (HNT)-based nanocomposites, the two key issues need to be considered: precise interface control and the dispersal of HNTs. This study presents an efficient way to functionalize halloysite nanotubes with 3-aminophenoxy-phthalonitrile, followed by compounding with poly(arylene ether nitrile) (PEN), to prepare functional nanocomposite films. The surface functionalization of HNTs was characterized and confirmed by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Compared with neat PEN, the tensile strength and modulus of the resulting PEN nanocomposites with 3 wt% functionalized HNTs were found to increase by 25.7% and 20.7%, respectively. The good dispersion and high capacitance of the dielectric layer resulted in PEN/HNTs nancomposites with enhanced dielectric permittivity and relatively low dielectric loss. Moreover, the addition of functional HNTs greatly improved the thermal stability of PEN, which could be further enhanced through the chemical cross-linking reaction between the functional HNTs and the PEN matrix. This work provides a new path toward obtaining advanced polymer-based nanocomposites with functional properties.

1. Introduction

Polymer-based nanocomposites have received considerable attention and research efforts from both academia and industries, with the aim of enhancing their mechanical and barrier properties and/or introducing new functionalities, such as magnetic and electrical properties [1–3]. For this purpose, various nanofillers, including zero-dimensional nanoparticles [4–8], one-dimensional nanotubes [9–11], and two-dimensional nanosheets [12–15], have been widely adopted because of their excellent mechanical strength, thermal stability, and electrical properties, among others. Of these nanofillers, layered silicates and carbon-based nanofillers are the most popular. However, before layered silicates are incorporated into the polymer matrix, they need to be exfoliated, which is a costly and time-consuming process. The incorporation of low contents of carbon nanotubes and graphene into the polymer can lead to a significant improvement of various properties; however, the large-scale production of these materials remains a huge challenge because of the high cost involved.

Recently, halloysite nanotubes (HNTs) as a new kind of silicate have drawn considerable attention as fillers for polymers [16–18]. Typically, halloysite nanotubes with the chemical formula $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$ present a two-layered aluminosilicate structure with lumen and external diameters of 10–15 nm and 50–80 nm, respectively. Besides, halloysite nanotubes have a length of about 1000 nm, which results in a high aspect ratio. Because of their unique chemical and physical structure, halloysite nanotubes have notable advantages compared with carbon nanotubes, graphene, and MMT. On the one hand, halloysite nanotubes are chemically non-toxic to humans and the environment, making them good candidates for applications in which bio-compatibility is a high priority [19]. On the other hand, because there is less π-π interaction between the tubulars, as well as less functional groups on the outer surface, halloysite nanotubes can more easily be dispersed in the polymer matrix compared with carbon nanotubes and graphene. In addition, HNTs have abundant natural sources; thus,

* Corresponding authors at: School of Chemistry and Chemical Engineering, Southwest Petroleum University, 8 Xindu Avenue, Chengdu, Sichuan, 610500, China
E-mail addresses: 201599010032@swpu.edu.cn (Y. Zhan), heyi007@163.com (Y. He).

http://dx.doi.org/10.1016/j.apsusc.2016.09.148
0169-4332/

they are lower in price than CNTs [20]. These features make HNTs promising alternatives for polymer-based composites.

In recent research, many general and engineering polar polymers, including epoxy [21], polyamides [22], polyethyleneimine [23], polyvinyl alcohol [24] and polyacrylates [25], have been used as polymer resins to explore functional HNTs/polymer nanocomposites. Furthermore, halloysite nanotubes have been used as nanofillers to reinforce medium- and low-polarity polymers [26,27]. Although some achievements have been made in the field of halloysite nanotubes/polymer composites, there are still some drawbacks that need to be addressed, such as the shear-induced breakage under the sonication process and the poor interfacial interaction between the halloysite nanotubes and the polymer matrix due to the absence of reactive groups on the surface of HNTs [28,29]. These issues greatly influence the reinforcing efficiency of a typical polymer, leading to inadequate mechanical properties of the nanocomposites. Therefore, the functionalization of halloysite nanotubes is very important. Chemically modified HNTs have been reported to be more useful than pristine ones due to their enhanced dispersion and interfacial adhesion with the polymer matrix [30–33]. Nonetheless, the present chemical modifications of HNTs are mainly related to medium and low-polarity polymer systems. Considering the above discussion, it is important to develop the appropriate chemical modification of HNTs to achieve polymer systems with strong polarity and to explore the application of HNTs in special engineering polymer nanocomposites.

Among the many special engineering polymers, poly(arylene ether nitrile) (PEN), as a new kind of semi-crystalline special engineering polymer, has emerged as a novel advanced polymer material that can be potentially used in the military, automotive, and electronics industries, among others [34–37]. Because of its outstanding physical and chemical properties, such as excellent mechanical strength, high thermal stability, good molding, and workability, poly(arylene ether nitrile) (PEN) has been selected as an ideal polymer matrix for exploring functional polymer composites. During the last several years, several nanoscale-fillers, including carbon nanotubes, graphene nanosheets, barium titanate, and magnetic nano-particles, have been incorporated into the PEN matrix to introduce electrical, magnetic, and dielectric properties [38–41]. However, although functional PEN nanocomposites can be obtained by incorporating the above-mentioned nanofillers, several issues still need to be addressed before these nanocomposites can be widely applied. Hence, many researchers are focused on finding an alternative filler to reinforce PEN with the desired properties. The incorporation of halloysite nanotubes, which are chemically nontoxic, easily dispersed, and lower priced, into the poly(arylene ether nitrile) matrix is expected to overcome the above issues toward achieving high-performance functional polymer composites.

In the present study, a novel type of halloysite nanotubes/poly(arylene ether nitrile) nanocomposites with improved dielectric permittivity, thermal stability, and tensile strength was fabricated through a simple solution-casting method. For this purpose, the dispersion of halloysite nanotubes and the interfacial interaction with the PEN matrix were the two key issues that had to be considered. Unlike carbon nanotubes and graphene oxides, which have abundant functional groups, such as hydroxyl and carboxyl groups, the presence of lesser hydroxyl groups on the outside of HNTs makes it hard to achieve surface modification through chemical reaction. Besides, poly(arylene ether nitrile) is a typical strong-polarity polymer with nitrile groups on the molecular chains. Considering the interfacial compatibility, the modification of halloysite nanotubes with similar polarity is technically required. Recently, our previous research showed that the nitrile groups on the aromatic ring could serve as a potential site for polymer cross-linking and promote the adhesion of the polymer to many substrates through polar interactions [42]. In view of this, HNTs were first reacted with isophorone diisocyanate (IPDI), which has double isocyanate groups, followed by grafting of 3-aminophenoxy-phthalonitrile to obtain nitrile functionalized HNTs. The grafting of nitrile groups onto the surface of HNTs was expected to achieve interfacial compatibility with PEN through polar interactions. Therefore, functional HNTs/poly(arylene ether nitrile) nanocomposite films were prepared through a simple solution-casting method. Because of the good dispersion and strong interfacial adhesion between the halloysite nanotubes and PEN, significant improvements in dielectric permittivity, thermal stability, and tensile strength were achieved. The properties of as-prepared PEN/HNT nanocomposites can be further enhanced by the chemical cross-linking between the HNTs and the PEN matrix, which provides a new path toward obtaining halloysite nanotube–based functional polymer nanocomposites. The enhanced dielectric constant of the PEN nanocomposites, as well as their high thermal stability and mechanical strength, makes them potentially useful in capacitor fields, which require high-performance dielectric materials.

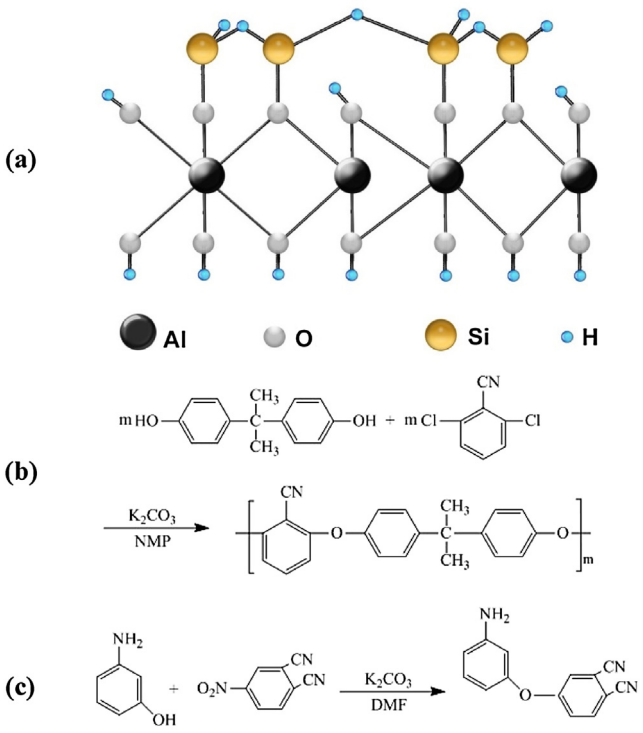

Fig. 1. (a) Schematic illustration of crystalline structure of HNTs, (b) and (c) synthesis schedule of poly(arylene ether nitrile) and 3-aminophenoxy-phthalonitrile.

2. Experimental

2.1. Materials

Halloysite nanotubes ($Al_2Si_2O_5(OH)_4{\cdot}2H_2O$, HNTs, diameter: 30–70 nm, length:1–3 μm) were purchased from Sigma-Aldrich. The crystalline structure of HNTs was shown in Fig. 1a. Isophorone diisocyanate (IPDI) were purchased from Aladdin, China. Other materials such as N,N- dimethylformamide (DMF, purity ≥ 99.5%) and *N,N*-dimethylacetamide (DMAC, purity ≥ 99.5%) were supplied by Kelong Chemical Reagent Factory (Chengdu, China). Poly(arylene ether nitrile) (PEN) was synthesized from resorcin and 2, 6-dichlorobenzonitrile, as shown in Fig. 1b. The