



## Macromolecular Nanotechnology

## Poly(glycidyl methacrylate)-grafted clay nanofiller for highly transparent and mechanically robust epoxy composites



Khouloud Jlassi<sup>a,b,c</sup>, Sarath Chandran<sup>d</sup>, Matej Mičušík<sup>e</sup>, Mémia Benna-Zayani<sup>a,b,\*</sup>, Yusuf Yagci<sup>f</sup>, Sabu Thomas<sup>d,\*</sup>, Mohamed M. Chehimi<sup>c,\*</sup>

<sup>a</sup> Laboratoire d'Application de la Chimie aux Ressources et Substances Naturelles et à l'Environnement (LACReSNE), Faculté des Sciences de Bizerte, University of Carthage, Zarzouna-Bizerte, Tunisia

<sup>b</sup> Institut Supérieur des Sciences et Technologies de l'Environnement (ISSTE), Borj Cédria, 2050 Hammam-Lif, Tunisia

<sup>c</sup> Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR CNRS 7086, 15 rue JA De Baïf, Paris, France

<sup>d</sup> International and Interuniversity Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, Kerala, India

<sup>e</sup> Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

<sup>f</sup> Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

## ARTICLE INFO

## Article history:

Received 25 June 2015

Received in revised form 3 September 2015

Accepted 5 September 2015

Available online 7 September 2015

## Keywords:

Bentonite

(3-Mercaptopropyl)trimethoxysilane

Poly(glycidyl methacrylate)

Photopolymerization

Nanocomposites

Reinforced epoxy

## ABSTRACT

Poly(glycidyl methacrylate) (PGMA)/clay nanocomposites were prepared by free radical in situ photopolymerization using intercalated chain transfer agent (3-mercaptopropyl)-trimethoxysilane (MPS) in the layers of bentonite (B) clay. The natural bentonite was treated with MPS (at 1–5% v/v) which acts as both intercalant and chain transfer agent. Glycidyl methacrylate (GMA) was photopolymerized in situ in the presence of the silanized bentonite (B-MPS) using 2,2-azobisisobutyronitrile (AIBN). The intercalation ability of MPS and exfoliated nanocomposite structure were evidenced by both X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). Surface analysis and morphologies of the resultant nanocomposites were also studied. The mass loading of PGMA reached 81 wt.% while XPS spectra, particularly the high resolution C1s region, resemble those of pure PGMA. The primary B-MPS/PGMA nanocomposite was then used in the preparation of nanocomposite coatings by mixing it with di-glycidyl ether of bisphenol A (DGEBA) epoxy matrix and 4,4-diaminodiphenyl sulfone (DDS) hardener in order to obtain ternary Epoxy/B-MPS/PGMA. The latter was cured and then was compressed into 5 mm thick sheets; it was found to be transparent with mixed intercalated/exfoliated structure. The thermal and mechanical performances of Epoxy/B-MPS/PGMA are by far superior to those of the reference epoxy–pristine bentonite nanocomposite.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polymer–clay nanocomposites have been widely investigated in recent years due to enhancement in mechanical, thermal, gas barrier, catalytic and fire retardant properties that nanoclay imparts to polymer matrices [1–5]. The improvement in

\* Corresponding authors at: Laboratoire d'Application de la Chimie aux Ressources et Substances Naturelles et à l'Environnement (LACReSNE), Faculté des Sciences de Bizerte, University of Carthage, Zarzouna-Bizerte, Tunisia (M. Benna-Zayani), International and Interuniversity Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, Kerala, India (S. Thomas), ICMPE, CNRS (UMR 7182), 2-8 rue Henri Dunant, 94320 Thiais, France (M.M. Chehimi).

E-mail addresses: [memiabenna@yahoo.fr](mailto:memiabenna@yahoo.fr) (M. Benna-Zayani), [sabuchathukulam@yahoo.co.uk](mailto:sabuchathukulam@yahoo.co.uk) (S. Thomas), [chehimi@univ-paris-diderot.fr](mailto:chehimi@univ-paris-diderot.fr) (M.M. Chehimi).

properties combined with the low cost of manufacturing of polymer–clay nanocomposites has led to their use in engineering applications for aerospace, automobiles, food packaging, and electronics among others [6]. One well known approach to maximize performances of nanocomposite materials is to obtain well dispersed single clay sheets in the polymer matrix [7,8]. In addition, it is important to strengthen molecular interactions between the clay nanofiller and polymer matrix in order to obtain robust nanocomposites [9].

Thermoplastic-based polymer–clay nanocomposites can be manufactured through three main strategies according to the starting materials and processing techniques: solution exfoliation, melt intercalation and in situ intercalative polymerization [10]. Disadvantages of the first two methods are the co-intercalation of solvents in the case of the solution reaction and slow polymer transport into the interlayer space [11]. In contrast, in situ polymerization holds great promises as demonstrated by several investigations [7]. The approach rests on the modification of clay by intercalating into its interlayer space functional compounds such as quaternary ammonium [12–14], iodonium [15], phosphonium [16], diazonium salts [17], silane coupling agents [18,19] or quaternary ammonium-bearing functional monomer [20]. It follows that intercalation of monomers triggers the growth of polymer chains in the clay galleries followed by exfoliation and the nanocomposite.

In situ polymerization can be initiated either by thermal polymerization and photopolymerization using a variety of initiating mechanisms [21–24]. Moreover, several conceptually different approaches, namely copper (I) catalyzed azide/alkyne cycloaddition (CuAAC) “click” reaction [25,26] and multiple hydrogen bonding interactions [27] were shown to be attractive processes for the clay/polymer nanocomposite preparation. Particularly, the photochemical route for clay/polymer nanocomposites offers distinct advantages over thermal methods in the sense it is a green process, does not necessarily require drastic monomer purification procedures, can be adapted to many systems, can be confined at surfaces and especially permits to provide patterned polymer coatings [28,29]. Among the photochemical routes for clay–polymer nanocomposites, the use of chain transfer agents strategy is well-documented and provides polymers by free radical polymerization [30–33]. It was demonstrated that the end groups borne by the polymer chains depend on the nature of the transfer agent [33,34]. In the present work, the chain transfer agent is intercalated within the layered silicate through silylation reaction by using commercially available mercaptosilane. The designed strategy appeared to be more simple and economical than the conventional ammonium ion based intercalation methodology.

The aim of this manuscript is to describe the in situ preparation of polymer/clay nanocomposites using (3-mercaptopropyl)-trimethoxysilane acting both as intercalation and chain transfer agent. Glycidyl methacrylate (GMA) was deliberately selected as the monomer in the subsequent polymerization process in order to provide not only intercalated and exfoliated polymer chains but also compatibility with the reinforcement material epoxy resin through the glycidyl groups [19]. Moreover, PGMA chains can readily be crosslinked by amines such as 4,4'-diaminodiphenyl sulfone (DDS) [35]. The thermal and mechanical properties of epoxy reinforced by clay–PGMA nanocomposite filler were conducted and compared with the reinforcement by unmodified clay in order to verify the role of the interface chemistry of the PGMA chains grafted to the bentonite lamellae.

## 2. Materials and methods

Di-glycidyl ether of bisphenol A (DGEBA) epoxy resin (Lapox L-12) with an epoxy equivalent between 5.25 and 5.40 eq kg<sup>-1</sup> and viscosity between 1.15 and 1.20 g cm<sup>-3</sup> along with the curing agent 4,4'-diaminodiphenyl sulfone (DDS; Lapox K-10) which is an aromatic diamine, (DDS) is a pale pink powder with a melting temperature close to 150 °C. Both DGEBA and DDS were obtained from Atul Industries (Gujarat, India). 3-Aminopropyltriethoxymercaptosilane (MPS) and the monomer glycidyl methacrylate (GMA, 99%, Aldrich) were passed through basic alumina column to remove impurities. 2,2'-Azobisisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized from ethanol before use. The organic solvents used were of analytical grade and deionized (DI) water was used for washing and solution preparations.

### 2.1. Natural purified clay

The raw bentonite was extracted from the town of Berka in the west-south of Tunisia. The clay was purified according to the standard procedure which leads to a homoionic sodium clay (B–Na). It is an inter-stratified smectite–illite, containing a 78% smectite and 20% illite with a very small amount of kaolinite. Its smectic fraction is dioctahedral and has a pronounced montmorillonite character. Its cation exchange capacity is about 102 meq/100 g of calcined clay and its total specific surface is ~736 m<sup>2</sup> g<sup>-1</sup>. The average structural formula is: (Si<sub>7.653</sub>Al<sub>0.348</sub>)<sub>IV</sub>(Al<sub>2.775</sub> Fe<sub>0.614</sub> Mg<sub>0.565</sub> Ti<sub>0.033</sub> Mn<sub>0.001</sub>)<sub>VI</sub> O<sub>20</sub> (OH)<sub>4</sub>Na<sub>0.623</sub>Ca<sub>0.017</sub>K<sub>0.259</sub>.

### 2.2. Preparation of the bentonite intercalated chain transfer agent (B–MPS)

The intercalated chain transfer agent (B–MPS) was prepared through silanization of Na–B and the clay-modifying agent in an aqueous solution. Sodium bentonite (1 g) was dispersed in 100 ml of deionized water using a mechanical stirrer for 1 h. Then, different amounts of mercaptosilane were added drop wise in the previous mixture (1%, 3% and 5% v/v), and the dispersion was left under continuous stirring for 5 h at room temperature in inert atmosphere. The dispersion was diluted by an equal amount of DI water and centrifuged at 5000 rpm for 20 min. The collected solids were washed with 200 mL DI water,

Download English Version:

<https://daneshyari.com/en/article/1394711>

Download Persian Version:

<https://daneshyari.com/article/1394711>

[Daneshyari.com](https://daneshyari.com)