Progress in Organic Coatings 99 (2016) 23–31

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Polystyrene/graphene oxide nanocomposites synthesized via Pickering polymerization

Yue Liu, Yuhong Zhang, Lanlan Duan, Weili Zhang, Mingji Su, Zhengguang Sun**, Peixin He*

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Ministry of Education, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, People's Republic of China

A R T I C L E I N F O

Article history:
Received 5 January 2016
Received in revised form 22 March 2016
Accepted 25 April 2016
Available online 21 May 2016

Keywords:
Polystyrene
Graphene oxide
Pickering emulsion polymerization
Nanocomposite

A B S T R A C T

The synthesis of graphene oxide (GO)—based nanocomposite materials, as environment-friendly nanostructures suitable for novel applications, has received significant attention in recent years. In this paper, a series of GO have been successfully fabricated utilizing the modified Hummers' method. GO was characterized by Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy (RS), X-ray diffraction analysis (XRD), Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) respectively. The characterization results showed that GO nanosheets have hydrophilic oxygen-containing functional groups and were well exfoliated. The graphene oxide/polystyrene (PSt) nanocomposite emulsion was synthesized via Pickering emulsion polymerization in the presence of GO nanosheets as a sole emulsifier. TEM, SEM and XRD results all suggested the successful preparation of GO-stabilized PSt colloidal particles. The Pickering emulsion products showed that the average diameter of nanocomposite particles can be well controlled from 240 to 320 nm by variation of the GO content. The GO layer was wrapped on the surface of PSt microspheres. PSt/GO nanocomposites have higher crystallinity and better thermal stability than pure PSt. Graphene oxide was not only being used as an effective solid stabilizer for Pickering emulsion, but also dispersed homogeneously into the production of polystyrene as highly effective nanofiller.

1. Introduction

Since the surprising discovery in 2004 that "free-standing" two-dimensional graphene can exist, there has been immense excitement in both material science and engineering owing to its unusual and exceptional properties [1]. To date, single-layer graphene is the strongest material ever measured, and this is accompanied by a range of other extraordinary physical properties such as high thermal conductivity, high electrical conductivity, low gas permeability and high surface area [2]. One of the most promising methods for large scale production of graphene is by chemical oxidation exfoliation of graphite leading to graphene oxide (GO) [3–6]. As a chemically exfoliated graphene derivative, GO is easy to be modified and functionalized [7,8]. Another unique and interesting property of GO is its amphiphilic nature with an edge-to-center distribution of hydrophilic and hydrophobic domains [9,10].

GO and GO-based materials have attracted tremendous attention due to their widely potential applications, such as adsorption and desorption [11], the separation of pollutants [12], catalytic supports for chemical reactions [13], as well as optical [14], electronic [15,16], dielectric [17] and coating [18] applications. Chu et al. [17] prepared a novel sandwich composite material based on few-layer graphene nanosheets (FLGs) composed of functionalized porous graphene, pristine graphene and functionalized porous graphene. Sandwich FLGs/poly (vinylidene fluoride) (PVDF) composites were fabricated and the composites showed excellent dielectric properties among carbon-based fillers/PVDF composites.

An emulsion stabilized by solid particles instead of organic surfactants is called Pickering emulsion [19]. Pickering emulsions are stabilized by the adsorption of solid particles at the interface between two immiscible liquids. The emulsion droplets of polymerizable monomers have also been stabilized by solid particles which act as robust barrier to prevent the phase separation of emulsions to fabricate colloid structure. As a versatile approach for the design and production of various nanostructured materials, Pickering emulsion polymerization has been proven as a fascinating method to fabricate novel polymer/inorganic nanocomposites.

* Corresponding author.
** Corresponding author.
E-mail addresses: 150866430@qq.com (Z. Sun), peixinhe@aliyun.com (P. He).

http://dx.doi.org/10.1016/j.porgcoat.2016.04.034

Until now, most of the reports in the literature were concerned with the design of Pickering emulsions with various types of inorganic particles such as clay [20,21], ZnO [22], TiO_2 [23], SiO_2 [24,25] and Fe_3O_4 [26]. These solid particles were employed as stabilizer to prepare polymer/inorganic nanocomposite microspheres based on Pickering emulsions. Pickering emulsions are stabilized by solid particles rather than low molecular weight surfactants or organic surfactants [27]. The various reports showed that the Pickering emulsion approach can be effectively used for the preparation of nanocomposite latexes with control of particle size, size distribution or interesting morphology. We also reported the fabrication of polymer/silica nanocomposite microspheres using hydrophilic silica as stabilizer. During the preparation, the cationic monomer, 2-(methacryloyl) ethyltrimethylammonium chloride, was used as auxiliary monomer to promote the formation of raspberry-like nanocomposite microspheres [28].

For Pickering emulsions, the hydrophobicity/hydrophilicity of solid particles plays an important role in determining the type of emulsions formed. Graphene oxide not only remains a special surface property and layered structure, but also introduces a lot of oxygen containing functional groups, such as carboxyl, hydroxyl, epoxy and carbonyl group on the surface and edge [29]. Thus, GO can adhere to interfaces and lower interfacial energy, acting as surfactant. The use of GO as a colloidal stabilizer represented a unique work towards the creation of hybrid materials [30], specifically in preparing polymer composites via dispersed phase polymerization such as miniemulsion polymerization [31,32]. Good dispersion was crucial for achieving the desired enhancement in the final physical and chemical properties of the composites [33].

Some reports have confirmed that GO are capable to stabilize the oil droplets to produce O/W emulsion. Kim et al. determined that GO is amphiphilic, which allows it to stabilize oil droplets in water [34], He et al. [35] investigated the effects of the types of oil, the sonication time, the GO concentration, the oil/water ratio, and the pH value on the stability, type, and morphology of these emulsions. The formation of polymer microspheres is proven to be correlative with the interaction between the growing polymer chains and GO inorganic particles. It has already been demonstrated that GO sheets can stabilize the emulsion or miniemulsion polymerization without the use of additional surfactant [36,37]. Gudarzi et al. [36] fabricated high performance poly (methyl methacrylate) (PMMA)–GO nanocomposites. A novel method based on Pickering emulsion polymerization has been introduced that assures fine dispersion and enhances loading. The major idea is to use a high affinity of graphene oxide (GO) for assembly at the liquid–liquid interface for Pickering emulsion polymerization. This new method paves the way for an environmentally benign process for the production of high quality polymer graphene nanocomposites as it is water-based (no organic solvent is employed) and soap free. Thicket et al. [37] demonstrated a successful synthesis of hybrid hollow capsules via Pickering miniemulsion polymerization, consisting of a cross-linked polymer shell coated with GO nanosheets. The inherent surface activity of the GO nanosheets stabilized the initial emulsion, enabling polymerization within dispersed oil droplets and the formation of a polymer shell via in situ phase separation. The creation of GO-based composite materials was a highly explored field, driven by an enhancement in specific properties that tensile strength, stiffness, thermal and electrical conductivity, due to the effective incorporation of GO sheets into the matrix of the material [38,39].

We tried to stabilize the styrene droplets by GO via the treatment such as homogenization, stirring or ultrasonic treatment using an ultrasonic processor. In this article, we report the synthesis and characterization of a range of PSt/GO nanocomposite emulsion by Pickering emulsion which is water-based, soap-free, and having no organic solvent remaining in the presence of GO. The study shows that GO has better dispersion and amphipathy than graphite and can be used as Pickering surfactant. The nanocomposites have a good stability and the thermal property is improved if compared with conventional homopolymer of polystyrene. The mechanism of Pickering emulsion polymerization stabilized by GO is then proposed, which provides an effective method to fabrication of polymer/inorganic composites.

Table 1
Formulations of PSt/GO Pickering emulsion polymerizations at 70 °C.

Run	St, g	GO, mg	AIBN, g	H_2O, mL
1	5	7.5	0.1	100
2	5	10	0.1	100
3	5	12.5	0.1	100
4	5	15	0.1	100
5	5	20	0.1	100
6	5	25	0.1	100

2. Experimental procedure

2.1. Materials

Natural flake graphite was purchased from Aladdin. Sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), dodecyl sodium sulfate (SDS) and styrene(St, purity ≥ 99%) were supplied from Chinese Medicine Group Chemical Reagent Co. Ltd. 2, 2-Azobis (isobutyronitrile) (AIBN) was purchased from Shanghai Shisihewei Chemical Co., Ltd. China, and purified by recrystallization. All of the water used in this work was Nanopure water (18.2 MΩ).

2.2. Preparation of graphene oxide

GO suspension was synthetized from natural graphite powder according to the modified Hummers' method and ultrasonication [40,41]. 2.5 g natural graphite powder, 1.25 g $NaNO_3$ powder and 54 mL H_2SO_4 (98%) were mixed in the beaker under stirring in an ice-bath. Then 7.5 g $KMnO_4$ was slowly added into the beaker with vigorous stirring to avoid the temperature rising above 20 °C. The mixture system was heated to 35 °C and maintained for 30 min before adding H_2O (170 mL). Once the temperature of 98 °C was reached, it was maintained for 15 min. Subsequently, 425 mL water was added slowly, and H_2O_2 until was added until color becomes bright yellow. Finally, the resulting product was collected by centrifugation and washed with deionized water, until the pH value of the upper layer suspension was about 3.3. The GO solutions were kept as stabilizer for the Pickering emulsion polymerization in the next preparation process.

2.3. Preparation of PSt/GO composites

The PSt/GO composite emulsions were prepared using varying amount of GO aqueous dispersion as a stabilizer in the emulsion polymerization. Polymerization of the emulsion was carried out according to the feed ratios shown in Table 1. The polymerization procedure is described as follows: the oil phase (styrene and 2.0 wt% AIBN) and GO water solution (5 mg/mL) were added into a 250 mL three-neck round bottom with the mechanical agitation for 30 min, Pickering emulsion was formed after sonicated with 600 W equipment for 6 min. During sonication, the flask was immersed in an ice bath to avoid overheating. Afterwards, the Pickering emulsion equipped with a nitrogen inlet and a reflux condenser with an outlet to a bubble counter at 70 °C for 8 h under stirring. Finally, the mixture was cooled to room temperature in order to obtain PSt/GO nanocomposites emulsion. The overall synthetic procedure is shown in Fig. 1. As for PSt emulsion polymerization, it was car-