



Polystyrene–graphene oxide (GO) nanocomposite synthesized by interfacial interactions between RAFT modified GO and core–shell polymeric nanoparticles



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ABSTRACT

Here we report simple and robust one-pot method for the preparation of polystyrene (PS)/graphene oxide (GO) nanocomposite using reversible addition fragmentation chain transfer (RAFT) modified GO in surfactant free emulsion polymerization (SFEP). The results suggested that ionic comonomer, styrene sulfonate sodium salt (SS-Na), concentration plays vital role in forming PS/GO nanocomposite. X-ray and electron diffraction studies suggest that there is no recombination of GO sheets when moderate SS-Na concentration is used, resulting complete exfoliation of GO sheets in the PS/GO nanocomposite. The formation of core–shell particles in which PS is the core and polystyrene sulfonate sodium salt (PSS-Na) is the shell, and the specific interactions between functional groups of GO and PSS-Na are attributed as the driving forces for the PS/GO nanocomposite formation.

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1. Introduction

Graphene, two-dimensional carbon nanostructure [1,2], has attracted huge attention recently since it holds great potential applications in many technological fields [3–8]. However, lack of efficient synthetic method for the preparation of processable graphene sheets in large quantities has been the bottleneck for exploiting most useful applications. Chemical oxidation is considered to be one of the suitable methods in preparing large scale of exfoliated graphene oxide sheets which on reduction lead to graphene synthesis [9]. In this method, graphene oxide (GO) obtained by oxidation of graphite followed by exfoliation of graphite oxide layers using ultrasonic wave and on further reduction by hydrazine gives graphene. GO has several functional groups such as hydroxyl, carbonyl, epoxy also carboxylic groups mainly at the edges of carbon sheets, which enables the modification, and formation of nanocomposites of graphene with varieties of other materials including functional polymers.

The incorporation of small amount of graphene into polymers [10–14] can achieve substantial enhancement in properties like reinforcement, damage tolerance, electrical and thermal conductivity, corrosion protection, abrasion resistance, flame retardancy,

etc. It is well known fact that graphene nanocomposites properties strongly depend on effective dispersion of graphene in the polymer matrix and good interfacial adhesion between polymer and graphene.

Researchers in the field of composites have grabbed the opportunity to develop multi-functional polymer nanocomposites (PNCs) filled with graphene oxide. Functionalized graphene (FG) has its natural advantages to be ideal nanofiller for PNCs since the FG still possesses most physical properties of graphene although it has a partly damaged carbon structure; and the functionalities on the surface of graphene can enhance the dispersion of graphene in polymeric matrices and the interfacial interaction between graphene and polymeric matrices. Recently, GO coated with PS was prepared using different methods via pickering emulsion polymerization [15], miniemulsion polymerization [16] and several controlled radical polymerization (ATRP [17], RAFT [18]), electrostatic interactions and π – π accumulations [19], etc.

Controlled/living radical polymerization (CLRP) such as RAFT polymerization [20], ATRP [21] with grafting-from and grafting-to methods leading to the route for post modification and improvement of final GO hybrid structures, shows great scope for materials applications. Among several CLRP, RAFT polymerization is often used method for designing different architectures due to its several advantages such as use of wide range of monomers as well as it works in simple reaction conditions [22–26].

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Combination of RAFT process and GO practically may lead to exfoliated GO tailor-made polymer nanocomposites with core-shell morphology. The hydroxyl groups of GO on esterification with carboxylic group of RAFT agent lead to formation of RAFT modified-graphene oxide (RGO) [16].

As per our knowledge, synthesis of GO modified with core-shell polymer nanoparticles via one pot process along with improved dispersibility in aqueous media has not been reported in literature. Here we report, the successful synthesis of core-shell polystyrene-polystyrene sulfonate (PS-PSS-Na) particles with GO sheets forming “smart-composite” using surfactant free emulsion polymerization. The approach developed presents a smart route to produce novel GO-based polymeric nanostructures with potential as important building blocks in nanocomposite materials.

2. Experimental section

2.1. Materials

Graphite powder, 1,3-dicyclohexyl carbodiimide (DCC), 4-dimethyl amino pyridine (DMAP), styrene sulfonate sodium salt (SS-Na) were purchased from Sigma-Aldrich. Potassium persulfate (KPS), hydrogen chloride (HCl 35%), potassium permanganate and phosphoric acid were purchased from Merck India. Dimethyl formamide (DMF), dichloromethane (DCM) were purchased from Fluka. Styrene was purchased from Sisco Chem., India and distilled under vacuum. Sulfuric acid (99%) and hydrogen peroxide (30%) were purchased from Fisher Scientific. For all the polymerization reactions HPLC grade water (Fisher Scientific) was used. Synthesis of RAFT Agent [3-Benzylsulfanyl-lthiocarbonylsulfanyl) propionic acid] was carried out according to previously reported literature [27].

2.2. Preparation of highly oxidized graphene oxide (GO)

Natural graphite powder was oxidized to graphene oxide (GO) by using a simplified Hummer's method. The procedure is as fol-

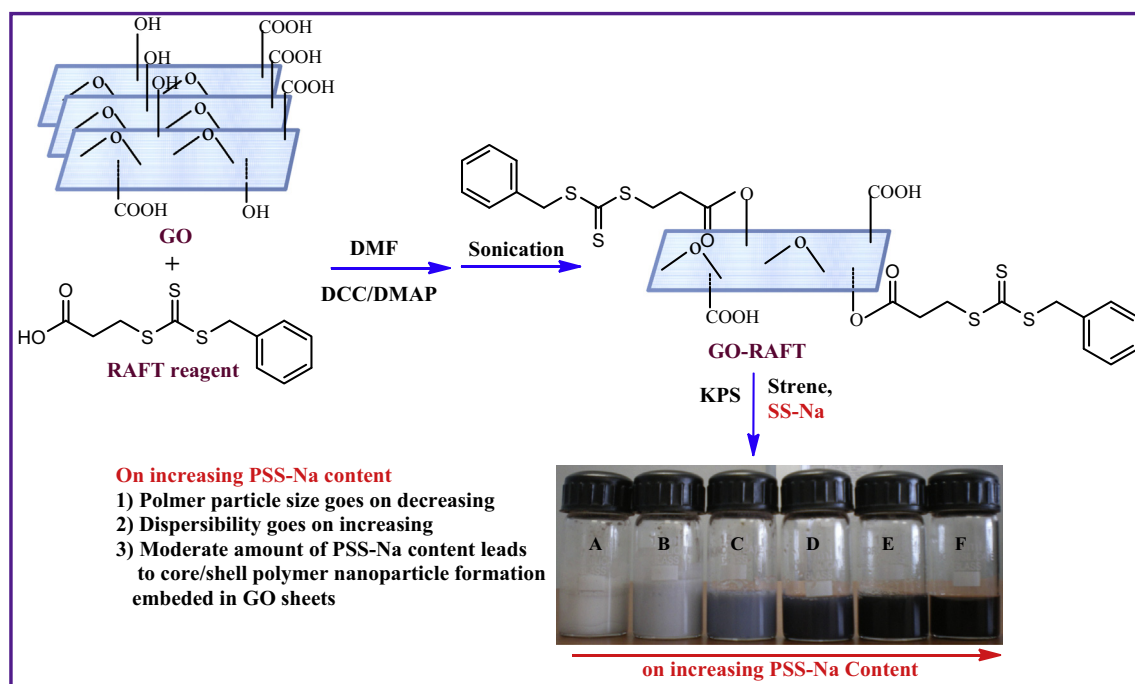
lows: The graphite powder (1 g) was mixed with concentrated $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4$ (320:80 ml) and potassium permanganate (3 g) using magnetic stirrer. All materials were added very slowly and the mixture was stirred for next 3 days. The mixture color changed from dark green to dark brown. Then to stop reaction, 30% H_2O_2 was added into the solution until the color of the mixture changed into brilliant yellow indicating fully oxidized graphite. Then the mixture was washed three times with dil. HCl and millipore water until pH in the range of 4–5 was achieved. The washing was carried out by centrifugation followed by decantation. Finally the highly oxidized graphene oxide product was dried under vacuum.

2.3. Synthesis of GO-RAFT agent

GO (125 mg) was stirred in DMF (25 ml) for 15 min, after which it was sonicated for a further 15 min by using ultra sonicator. The sonication was done to allow effective dispersion of the GO sheets in the solvent DMF. RAFT agent (125 mg) was then added and the resultant mixture stirred for 5 min at room temperature. After that DCC (125 mg) and DMAP (25 mg) were added to the solution and the mixture was stirred at room temperature for 24 h (Scheme 1). The solvent was removed under vacuum and the solid was washed with DCM until the washings are free of the RAFT agent. The coupling of GO and RAFT was monitored by UV-Vis spectroscopy. The washings after the reaction were done to remove the unattached RAFT agent. The resultant product was then dried under vacuum to yield GO-RAFT.

2.4. In-situ emulsion polymerization for nanocomposites preparation using GO-RAFT

In 25 ml round bottom flask, 10 ml of water was taken. After 15 min of N_2 purging, GO-RAFT was added into the water and dispersed using sonication for 5 min. Initiator KPS (10 mg) was added to it. Then ionic monomer styrene sulfonate sodium salt (SS-Na) was added to the reaction mixture, followed by hydrophobic monomer [styrene (1.1 ml)]. This mixture was refluxed at 70°C at 500 rpm stirring speed for 20 h (Scheme 1). Finally we collected



Scheme 1. Schematic representation of PS/GO nanocomposite synthesis.

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