ARTICLE IN PRESS

Tunable electrorheological performance of silicone oil suspensions based on controllably reduced graphene oxide by surface initiated atom transfer radical polymerization of poly(glycidyl methacrylate)

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A B S T R A C T

This article is focused on the controllable reduction of the graphene oxide (GO) particles as a simultaneous process during surface initiated atom transfer radical polymerization (SI-ATRP) providing hybrid particles with tailored conductivity and substantial polymer shell on the particles tunable by SI-ATRP conditions. The main advantage of such approach is that both the compatibility improvement, due to the polymer layer, and conductivity tuning, due to partial GO reduction, were simply achieved in single-step reaction providing electrorheological (ER) system with enhanced performance in comparison to either neat GO or similar non-covalently bonded GO-polymer hybrids. The presence of the poly (glycidyl methacrylate) (PGMA) on the surface of GO was investigated using FTIR spectrometry, transmission electron microscopy and thermogravimetric analysis and their chain length (M_w) and polydispersity index (PDI) were determined by ^{1}H NMR and GPC, respectively. Two different GO-PGMA particle systems varied in M_w and PDI and also in electrical conductivities were prepared and their electro-responsive capabilities were investigated. The reduction of GO particles was confirmed by Raman shift as well as conductivity measurements. Electrorheological (ER) performance was investigated at various electric field strengths and repeatability of the phenomenon was confirmed by 10 on/off field cycles. Finally, with the help of dielectric measurements of GO-PGMA based ER suspensions, fitted by Havriliak–Negami model, the relaxation processes were properly investigated and the results were correlated with those obtained from electrorheological measurements.

Introduction

Graphene is two dimensional carbonaceous material with its atomic structure resembling a chicken wire [1]. Mainly due to its unique electric [1] and chemical [2] properties this layered material is of a great importance in many application fields covering a versatile area from various nanoelectronic [3] and electronic [4] components, drug delivery systems [5], biosensors [6] to energy storage devices and supercapacitors [7]. Another, very important applications are connected to pseudocapacitors [8], electro-oxidation [9], detection of organic species [10], or for removal of various environmentally harmful substances [11]

Graphene has also already been used as a dispersed phase in electrorheology [12].

The electrorheological (ER) fluids are generally heterogeneous systems composed of electrically polarizable particles dispersed in a non-conducting medium. ER fluids behave as Newtonian or slightly pseudoplastic fluids in the absence of the external electric field; however, after an application of an external electric field, they undergo a remarkable transition of their rheological properties from a liquid-like to a solid-like structure represented by a change of their behavior from Newtonian to Bingham liquids exhibiting a yield stress. This transition is caused by a creation of the internal chain-like structures from the electrically polarizable particles spanning the electrodes. These particles join themselves into structures along the direction of an external electric field due to strong dipole–dipole particle interactions increasing the overall viscosity of the ER fluids [13]. This behavior is then called ER effect. It has been reported that for ER fluids the ideal conductivity of the

particles can be found between 10^{-8}–10^{-5} S m^{-1} [14]. Conducting polymers [15] and their oligomers [16] have become a matter of an intensive research as a dispersed phase for electrorheology thanks to their tunable conductivity. Yin et al. [17] transformed composite particles composed of polyaniline shell and graphene oxide (GO) core into amorphous carbon/graphene composite particles whose ER fluids exhibited increased ER performance. However, in the case of the pure graphene-based ER fluids, graphene itself is too conducting for electrorheological (ER) fluids causing a short circuit during electrorheology measurements and has thus to be modified in order to shift its conductivity into above mentioned region. One of the possible approach is to oxidize graphene into GO. GO has been widely used as a dispersed phase in electrorheology either as individual material [18] or as composite particles 19] with various particles including clays [20], polymers [17,21], silica [20,22], etc. For instance, Zhang et al. has introduced core/shell composite materials where PGMA was used as a core and GO as a shell material [23]. With its electrical conductivity lower about several orders of magnitude when compared with graphene, GO-based ER fluids exhibited poor ER performances.

Due to layered composition of graphene, it is purely soluble in liquids due to high van der Waals forces. It tends to re-aggregate when is dispersed or exfoliated in a liquid medium [24]. Its oxidation into GO introduces various functional hydroxyl, carbonyl, carboxyl or epoxy groups [2,5] on the basal plane and carboxylic groups on to the edges stabilize the two dimensional system from re-aggregation [2]. The functional groups are further of high interest due to possible covalent attachment of other substances and molecules via these conjunctions [2].

Recently, Cvek et al. [25] introduced coating process of carbonyl iron (CI) particles with poly(glycidyl methacrylate) via atom transfer radical polymerization (ATRP) to stabilize the magnetic carbonyl iron particles and suppress their agglomeration and settling in a liquid medium. This approach was further used by Mrlik et al. [26] analogously with the GO particles. The layer of PGMA on the surface of CI particles stabilized them against oxidation and the particles provided better dispersion in a liquid medium, with suppressed tendency to re-aggregate, positively contributing to increased interfacial polarization [27], which can consequently enhance ER effect.

This study presents preparation of GO/PGMA hybrids prepared through surface initiated ATRP (SI-ATRP). Two concentrations of tertiary amine, such as N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) were used for controlled reduction of GO. The amount of PMDETA enabled also control over polymerization degree of the PGMA in one step. The controlled reduction of GO provided possible tailoring the electric conductivity promoting the ER performance of prepared ER fluids compared to typical GO-based ER fluids presented elsewhere [28]. The GO/PGMA hybrid particles were further properly analyzed and used as a dispersed phase in silicone-oil ER fluids. ER performance of the ER fluids were investigated by means of steady shear rheometry as well as their viscoelastic performance. Moreover, the dielectric properties proved the enhanced interfacial polarization using Havriliak–Negami model parameters. Finally, the repeatability of the ER phenomenon was elucidated at various electric field strengths and more than 10 on/off cycles were performed to confirm the durability of such GO-PGMA system.

Experimental section

Materials

Glycidyl methacrylate 98%, 2-bromopropionyl bromide 97%, methyl 2-bromopropionate 98%, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) 98%, copper chloride (CuCl) 97%, dimethyl formamide (DMF) (all from Sigma–Aldrich, USA) were used as received. Triethylamine (Et$_3$N) 98% from Fluka, Switzerland and tetrahydrofurane (THF) provided by POCH, Poland were dried over sodium before use. The expanded graphite (EG) powder, ECOPHIT G; GFG 50 with size of 40–55 μm (SGL Groups Carbon, Germany) was used. All other reagents and solvents were purchased from Aldrich and used as received without further purification.

Preparation of GO by oxidation of EG

The EG was oxidized by modified Brodie method [29] to obtain functional groups (hydroxyl, carboxyl and epoxy) on the surface. The amount of overall oxygen on the graphene oxide (GO) surface was investigated with XPS and was approximately 33 wt.% [30].

Immobilization of ATRP initiator on GO surface (GO-I)

The 6 g of GO was put into 1000 mL three-neck round-bottom flask. The flask was evacuated and back filled with argon three times. The freshly distilled dry THF was added into the flask and the mixture was sonicated shortly (4 min). Et$_3$N (21.7 mL, 27 mmol), was added into the reaction flask followed by drop-wise addition of 2-bromopropionyl bromide (16.5 mL, 27 mmol). The mixture was stirred at room temperature overnight, and then it was refluxed at 80 °C for one hour. The product was purified by filtration over PTFE 0.2 μm membrane. The reaction mixture was filtered and washed with 100 mL acetone. Then it was dispersed in 200 mL DMF, shortly sonicated (30 s), filtered, and washed with acetone. This procedure was repeated three times (until the filtrate was clear). Finally the product was washed with diethyl ether and dried in oven at 60 °C for 12 h under vacuum.

Synthesis of poly(glycidyl methacrylate)-grafted GO (GO-PGMA)

Polymerization was performed twice under similar conditions. In case of first polymerization, 400 mg of GO-Br (1.1×10^{-4} mol of Br, as determined from XPS[30]) was put into the 50 mL Schlenk Flask. The flask was evacuated and back filled with argon three times. The anisole (8 mL) was purged with argon and added into Schlenk flask. The PMDETA in the four molar excess (0.48 mL, 2.24×10^{-3} mol) and sacrificial initiator methyl 2-bromopropionate (0.093 mL, 0.56×10^{-3} mol) was added and the reaction mixture was shortly sonicated in ultrasonic bath (1 min). The glycidyl methacrylate (7.7 mL, 0.056 mol) was purged with argon and added into Schlenk flask. The four freeze pump thaw cycles were performed. The CuCl (0.055 g, 0.56×10^{-3} mol) was put into frozen reaction mixture under argon flow. The reaction was carried out at 50 °C and stopped after 2 h by opening flask and dissolving the mixture in 5 mL of anisole. In the second polymerization, the amount of the chemicals were chosen according to our previous paper [30], when the ratio between GO and PMDETA is crucial parameter influencing the conductivity of the GO particles. The reaction mixtures are summarized in Table 1. The monomer conversion calculated according to the ^{1}H NMR spectra, molar mass and polydispersity index determined by gel permeation chromatography are summarized in Table 1.

General characterization

The molar mass and polydispersity index of the PS chains grown from the sacrificial initiator were determined by GPC, PL-GPC220 (Agilent, Japan) with THF as an solvent at flow rate of 1.0 mL/min. Polystyrene was used as a standard and anisole as an internal standard. Monomer conversions were determined by ^{1}H NMR on a 400 MHz VNMRS Varian NMR spectrometer equipped with 5 mm 1H-19F/15N-31P PFG AutoX DB NB probe at 25 °C in deuterated