PREPARATION AND CHARACTERIZATION OF GRAPHENE OXIDE SHEETS CONTROLLABLY GRAFTED WITH PMMA BRUSHES VIA SURFACE-INITIATED ATRP

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Abstract

Recently, graphene oxide (GO) has gained significant attention in many applications, such as touch displays, electronic devices or electrorheological fluids. However, neat GO is hydrophilic, which limits its efficiency in hydrophobic media, e.g. polymer matrices, oil carriers. Therefore, the utilization of GO-coated core-shell structures was proven to be advantageous. In this study, GO sheets were prepared by chemical exfoliation of graphite using modified Hummers method. The specific ATRP initiator, bromoisobutyryl bromide, was covalently immobilized onto as-prepared GO through oxygen-functional hydrophilic groups. Initiator-treated GO sheets were further grafted with poly(methyl methacrylate) (PMMA) via surface-initiated ATRP technique. The monomer conversion, molar mass and polydispersity of PMMA chains were investigated using nuclear magnetic resonance and gel permeation chromatography, respectively. The successful grafting process was confirmed by Fourier transform infrared spectroscopy. Raman spectroscopy and electric conductivity measurements revealed significant chemical reduction of GO during surface-initiated ATRP. Synthesized GO/PMMA structures exhibited considerably enhanced wettability in hydrophobic media, which was proved via contact angle measurements. Therefore, the synthesized GO/PMMA hybrids may found utilization in many aforementioned practical applications providing well-dispersed composite systems.

Keywords: Graphene, surface modification, atom transfer radical polymerization, poly(methyl methacrylate)

1. INTRODUCTION

Graphene was recently recognized as a very promising material due to its simple preparation, relatively low fabrication cost and unique physical properties (excellent thermal and electrical conductivities) [1, 2]. Unfortunately, graphene is considerably inert to its surrounding environment [3]. From its potential applicability point of view, the presence of graphene in various surroundings such as hydrogels [4], thermoplastics [5] or elastomers [6] leads to the interesting utilizations mainly in smart systems [7]. The graphene need to be homogenously dispersed in volume, in order to be effectively applied in such systems which respond to an external stimulus such as electric [8] or magnetic field [9], light [10] or pH change [11]. The main approach describing the procedure how to achieve the homogeneous dispersion of graphene in a system is reported by other authors [12], and it contains two steps. Firstly, the graphite is oxidized by Hummer's or Brody's method resulting into the graphene oxide (GO) that is characterized by very low conductivity and the presence of various oxygen-containing groups such as hydroxy, epoxy, carbonyl or carboxyl [13, 14]. Due to its considerable functionalization the post-modification of GO is possible and thus tailorable compatibility with various surroundings is possible. After successful homogenous implementation of the GO particles to the surroundings, the second step of reduction takes place using various approaches i.e. chemical (using primary and secondary amines [15] or hydrazine [16]), physical (elevated temperature [17] or gamma irradiation [4]). As-treated GO considerably recovers its delocalized pi structure and its position within the surrounding

sustains the same but the conductivity increases in several orders of magnitude, which are suitable assumptions for the potential applications.

Recently our group have found more efficient approach, in which the GO surface can be modified and reduced within a single-step reaction. The original system was based on the surface-initiated atom transfer polymerization (ATRP) of polystyrene in the presence of tertiary amine, which resulted in a controlled radical polymerization and simultaneous reduction of GO particles at the same time [18]. This study is focused on verification, whether this approach is applicable also for another polymer, specifically poly(methyl methacrylate) (PMMA). Thus, the subject of this study was to fabricate modified GO with enhanced wettability to hydrophobic dimethyl siloxane and electrical conductivity, which are important properties from the application point of view.

2. EXPERIMENTAL

2.1. Materials

Graphite (powder, < 20 μm, synthetic) was used as a precursor for GO sheets. Sulfuric acid (H_2SO_4, reagent grade, 95-98 %), sodium nitrate ($NaNO_3$, ACS reagent, ≥99%), potassium permanganate ($KMnO_4$, 97%) and hydrogen peroxide (H_2O_2, ACS reagent, 29.0-32.0 wt.% H_2O_2 basis) were employed as chemical reagents to set the proper exfoliation conditions to form GO sheets. α-bromoisobutyryl bromide (BiBB, 98%) served as an initiator linked onto GO surface. Initiator bonding was performed in the presence of proton scavenger, triethyleneamine (TEA, ≥99%). Methyl methacrylate (MMA, 99%), ethyl α-bromoisobutyrate (EBiB, 98%), $N,N,N´,N´´,N´´$-pentamethyldiethylenetriamine (PMDETA, ≥99%), copper bromide (CuBr, ≥99%) and anisole (99%) were used as a monomer, initiator, ligand, catalyst and solvent, respectively. Diethyl ether (ACS reagent, anhydrous, ≥99%) was used as a drying agent. All chemicals were purchased from Sigma Aldrich (USA) and were used without further purification (except for MMA). MMA was purified by passing through a neutral alumina column to remove MEHQ inhibitor prior its use. Tetrahydrofurane (THF, p.a.), acetone (p.a.), ethanol (absolute anhydrous, p.a.), toluene (p.a.), and hydrochloric acid (HCl, 35%, p.a.) were obtained from Penta Labs (Czech Republic). Deionized water (DW) was used during all experimental processes and washing routines.

2.2. Preparation of GO sheets

Graphene oxide (GO) was fabricated from graphite powder by a modified Hummers method [7]. The raw graphite (5 g) was vigorously stirred with H_2SO_4 (100 mL) and the mixture was cooled down to ~5°C using an ice/water bath. Subsequently, $NaNO_3$ (2.5 g) and $KMnO_4$ (15 g) were gradually added. The mixture was additionally stirred for 6 h, then, the amount of 300 mL of DW was added dropwise, while the temperature was kept below 40 °C. Finally, concentrated H_2O_2 in the amount of 40 mL was added, and the solution turned its color into brilliant brown, which indicated complete oxidization of graphite. The product was separated in a high-speed centrifuge (Sorvall LYNX 4000, Thermo Scientific, USA) operating at 10 000 rpm for 20 minutes at 25 °C. The cleaning routine was based on dispersion of the GO in 0.1 M HCl, and the re-separation in a centrifugal field. The procedure was repeated with DW several times until pH has reached a value of 7. Then, the particles were lyophilized in order to remove the residual water after the purification process. Finally, the brown powder was obtained.

2.3. Initiator bonding

The presence of reactive groups on the GO surface was preferably used to be linked with BiBB molecules. In a simple procedure, the GO (2 g), dried THF (60 mL) and TEA (12 mL) were mixed under argon atmosphere at a temperature of ~5°C ensured by an ice/water bath, while BiBB (7 mL) was drop-wise added. The product was washed with THF, acetone and water several times and then filtered with the help of PTFE filter (pore size

of 0.44 μm). The excess of water from as-treated particles was removed by filtration with diethyl ether (3x50 mL).

2.4.   Grafting of GO with PMMA chains

The GO sheets with bonded initiator (0.5 g) were transferred into a Schlenk flask equipped with a gas inlet/outlet and a septum. The system was evacuated and backfilled with argon several times. The argon-purged chemicals, namely MMA (13.90 mL, 130.5 mmol), EBiB (0.192 mL, 1.305 mmol), PMDETA (1.090 mL, 5.220 mmol), and anisole (15 mL) were gradually added. The presence of oxygen was minimized by degasing the system followed by several freeze-pump-thaw cycles. At a frozen state, the CuBr catalyst (187.2 mg, 1.305 mmol) was added as quickly as possible under gentle argon flow. The molar ratio of reactants [HEMATMS]:[EBiB]:[CuBr]:[PMDETA] was [100]:[1]:[1]:[4], while anisole served as a solvent in the amount of 50 vol.%. Finally, the flask was immersed into a silicone oil bath pre-heated to 60 °C, which initiated the polymerization process. The reaction was stopped by exposing the mixture to air and cooling down to laboratory temperature. The product was purified using DMF (3x100 mL), and finally with diethyl ether (3x50 mL). The final product was then dried in a desiccator under ambient conditions.

2.5.   Characterization

[1]H nuclear magnetic resonance (NMR) spectra were recorded at 25 °C using an instrument (400 MHz VNMRS Varian, Japan) with deuterated chloroform (CDCl$_3$) as a solvent. The molar mass and polydispersity (Đ) of PMMA chains were investigated using gel permeation chromatography (GPC) on the GPC instrument (PL-GPC220, Agilent, Japan) equipped with GPC columns (Waters 515 pump, two PPS SDV 5 μm columns (diameter of 8 mm, length of 300 mm, 500 Å + 105 Å)) and a Waters 410 differential refractive index detector tempered to 30 °C. The samples for NMR spectroscopy and GPC analysis were prepared by their dilution with CDCl$_3$ and THF, respectively, followed by the purification process, in which they were passed through a neutral alumina column. Fourier transform infrared (FTIR) spectra (64 scans, resolution of 4 cm^{-1}) were recorded on a Nicolet 6700 (Nicolet, USA) within a wavenumber range of 4000-600 cm^{-1}, while the ATR technique with a Germanium crystal were employed. The spectra were recorded at room temperature. The Raman spectra (3 scans, resolution of 2 cm^{-1}) were collected on a Nicolet DXR (Nicolet, USA) using an excitation wavelength of 532 nm. The integration time was 30 s, while the laser power on the surface was set to 1 mW. The powders were compressed to the form of pellets (diameter of 13 mm, thickness of 1 mm) on a laboratory hydraulic press (Trystom Olomouc, H-62, Czech Republic). The pellets were used for electrical conductivity measurements as well as for contact angle (CA) determination. The former investigation was performed by two-point method at laboratory temperature with the help of electrometer (Keithley 6517B, USA). The latter one was evaluated from the static sessile drop method carried out on a Surface Energy Evaluation system equipped with a CCD camera (Advex Instruments, Czech Republic). A droplet (5 μL) of silicone elastomer was carefully dripped onto surface and the CA value was recorded. The presented CA results are the average values from 10 independent measurements.

3.   RESULTS AND DISCUSSION

Regarding the possible applications of GO/PMMA structures in composites, the length of polymer brushes on the GO surface tremendously affects the properties of the composites as this feature can alter interactions with the matrices. Therefore, the attention was paid to analyses of properties of grafted PMMA on molecular level. The weight-, and number-average molecular weights, and Đ of PMMA were determined by GPC analysis (**Figure 1**) taking into account the assumption, that PMMA chains grew similarly from free and bond initiators [19]. The values of aforementioned quantities were 6070 and 8170 g·mol^{-1}, while Đ equaled 1.35 implying the uniformity of grafted chains. The polymerization was stopped after 2 h at 82 % conversion.
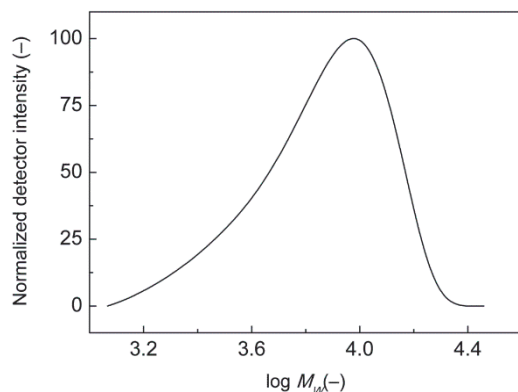
Figure 1 GPC chromatogram of PMMA chains showing the unimodal peak that confirms their low polydispersity

In order to prove the presence of PMMA brushes on GO surface in GO/PMMA composite, the FTIR spectra were examined as shown in **Figure 2**. In the spectrum of modified material (**Figure 2b**), the obvious peaks occurring around 3383 and 2924 cm^{-1} were attributed to CH stretching vibrations. A sharp peak at 1732 cm^{-1} was a sign of CO double bond stretching, while raised absorption level at 1464 cm^{-1} represented the CH_3 and CH_2 deformation vibrations. The presence of peaks at 1283 and 1147 cm^{-1}, and finally 823 cm^{-1} reflected COC single bond deformation vibration. In conclusion, the FTIR analysis revealed characteristic behavior of PMMA chains, thus the synthesis of GO/PMMA was considered to be successful.
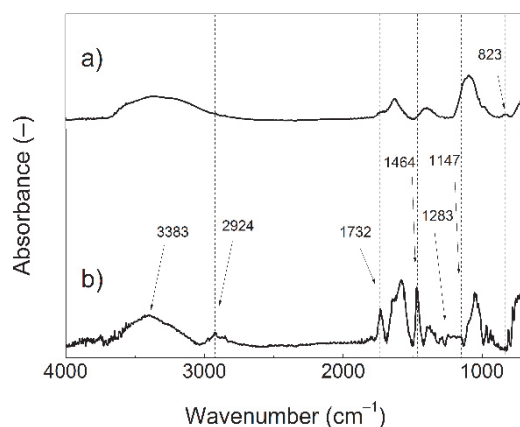

Figure 2 FTIR spectra of neat GO sheets (*a*), and their PMMA-grafted analogues (*b*) with denoted characteristic wavenumbers

The reduction of GO due to modification with polymer was examined by Raman spectroscopy. **Figure 3a** displays the typical characteristics of a carbon material with distinguished two major peaks occurring around ~1340 cm^{-1} and ~1590 cm^{-1}. The former peak is called the D-band and it is attributed to the vibrations of disordered graphene sheets, while the latter peak is called the G-band which is associated with the sp^2 vibrations of an ideal graphene sheet [20]. Comparing the spectra (**Figure 3**), shifted Raman D and G bands were attributed to a reduction of GO/PMMA structures due to reaction conditions (especially presence of PMDETA). The ratio of peak intensities, I_D/I_G, in the neat GO and GO/PMMA increased from 0.90 to 1.06 clearly showing enhanced reduction. The 2D peaks in both spectrograms indicated still disordered (decoupled) multilayer graphene even after surface-initiated ATRP. The reduction was further evaluated by the electrical conductivity measurements.
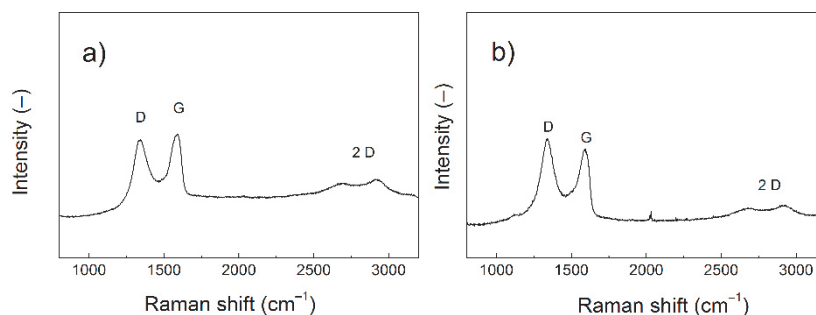
Figure 3 Raman spectra of neat GO (*a*) and GO/PMMA structures (*b*) with denoted characteristic bands

The average value of electrical conductivity was found to be $(1.00\pm0.20)\times10^{-8}$ S/cm for bulk GO, which is a similar value with that reported by Zhang et al. [7]. The conductivity of bulk GO/PMMA was calculated to be $(6.30\pm1.26)\times10^{-8}$ S/cm. The higher conductivity (by a factor of 6.30) of the latter particles was explained as a consequence of GO reduction as well as the presence of PMMA chains grafted onto GO substrate, as these grafts potentially increased the distances among the GO sheets.

Figure 4 shows the side-views of dimethyl siloxane droplets onto the pellets consisted of investigated materials. As can be seen, the average value of contact angle in the case of neat GO was around ~49.9°, and ~38.7° when GO/PMMA structures were used. The observation clearly proved the improved wettability and hence dispersibility of modified material in hydrophobic media. Therefore, it can be asserted that common drawback of neat GO was successfully eliminated, and synthesized GO/PMMA structures can be readily used in practice to fabricate well-dispersed composite systems.
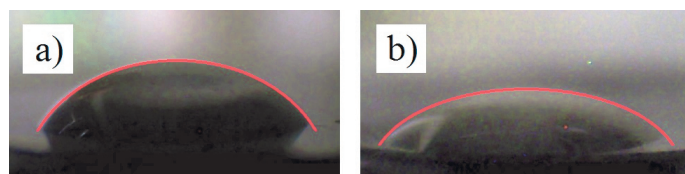

Figure 4 Sessile droplets of dimethyl siloxane onto neat GO (*a*) and GO/PMMA (*b*) pellets with denoted shape lines (red)

4.   CONCLUSION

In this study, a successful grafting process of GO sheets with PMMA brushes via surface-initiated ATRP is presented. The designed procedure allowed controllable modification of GO sheets with polymer, while a significant reduction of GO was achieved at the same time. The presence of PMMA grafts was proved using FTIR spectroscopy. The Raman spectroscopy and conductivity measurements confirmed significant chemical reduction of the investigated material. Contact angle measurements revealed considerably enhanced wettability of GO/PMMA in hydrophobic media, which implies better dispersibility in such systems. The prepared structures are promising candidates to be used in actuators, haptic devices or electrorheological fluids.

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