

## CONTROLLABLE REDUCTION OF GRAPHENE OXIDE/POLY(BUTYL ACRYLATE) HYBRIDS UNDER ATRP CONDITIONS

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### Abstract

This study is aimed on the controllable reduction of the graphene oxide (GO) sheets during surface initiated atom transfer radical polymerization (SI-ATRP). GO sheets were successfully synthesized using Hummers method and properly characterized by Fourier transform infrared spectroscopy (FTIR). SI-ATRP approach was used to simultaneously modify the GO surface by poly(butyl acrylate) (PBA) brushes and its chemical reduction in the single-step synthesis. The presence of the polymer brushes on the GO sheets was investigated by gel permeation chromatography, nuclear magnetic resonance and FTIR. Simultaneous GO reduction during polymerization was confirmed using Raman spectroscopy and finally by conductivity measurement. Compatibility of the GO and GO-PBA sheets was investigated via contact angle measurements of sessile drop between GO substrates and poly(dimethyl siloxane). From the potential applicability point of view, the modification of graphene-based hybrids by polymers is highly important especially when the compatibility as well as conductivity of GO-PBA sheets with surroundings plays a crucial role i.e. the light-stimulated sensors based on silicon or other elastomers.

**Keywords:** Graphene oxide, SI-ATRP, reduction, hybrids, polymer brushes

### 1. INTRODUCTION

Graphene was recently recognized as a very promising material, due 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] lead to the interesting utilizations mainly in smart systems [7, 8]. In order to be effectively applied at such systems whose responding on external stimulus such as, electric [9] or magnetic field [10], light [11] or pH [12] the graphene need to be homogenously dispersed in volume. Therefore, the main approach how to reach the graphene homogenously dispersed in the system also reported by other authors [13] containing two steps. Firstly, the graphite is oxidized by Hummer's or Brody's method resulting into the graphene oxide (GO) with very low conductivity and various oxygen containing groups such as hydroxy, epoxy, carbonyl or carboxyl [14, 15]. Due to the considerable functionalization, the post-modification of GO is possible and thus tailorable compatibility with various surroundings is obtained. 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 [16] or hydrazine [17]), physical (elevated temperature [18] or gamma irradiation [19]). Such treated GO considerably recovers its delocalized  $\pi$  structure and its position within the surrounding sustains the same but the conductivity was increased in several orders of magnitude and thus suitable for its potential applications. Recently our group recognized that GO particles can be reduced within the single-step reaction during the SI-ATRP of polystyrene, due to the presence of tertiary amine PMDETA concurrently acting in two processes, promoting controlled radical polymerization and simultaneous reduction

of GO particles [20]. Moreover it was also proved that such concept is also working for other monomeric systems such as poly(glycidyl methacrylate) [21] and its application as smart system in electrorheology.

This study is focused on the verification of such approach based on SI-ATRP and another monomer poly(butyl acrylate) (PBA) is still valid and how the monomer nature influences the final product from the polymerization rate as well as GO reduction point of view. The PBA polymer chains were analyzed using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Successful modification was proved by FTIR, and energy dispersive spectroscopy (EDS). Reduction of the graphene oxide particles was investigated with the help of conductivity measurement and Raman spectroscopy, and finally the compatibility of GO and GO-PBA particles with silicone oil and silicone elastomer was elucidated.

## 2. EXPERIMENTAL

### 2.1. Materials

Graphite (powder, < 20  $\mu\text{m}$ , synthetic) was used as a precursor for GO sheets. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , reagent grade, 95-98 %), sodium nitrate ( $\text{NaNO}_3$ , ACS reagent,  $\geq 99\%$ ), potassium permanganate ( $\text{KMnO}_4$ , 97%) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , ACS reagent, 29.0-32.0 wt.%  $\text{H}_2\text{O}_2$  basis) were employed as chemical reagents to set the proper exfoliation conditions to form GO sheets.  $\alpha$ -bromoisobutyl bromide (BiBB, 98%) served as an initiator linked onto GO surface. Initiator bonding was performed in the presence of proton scavenger, triethylamine (TEA,  $\geq 99\%$ ). Methyl methacrylate (MMA, 99%), ethyl  $\alpha$ -bromoisobutyrate (EBiB, 98%),  $N,N,N',N'',N'''$ -pentamethyldiethylenetriamine (PMDETA,  $\geq 99\%$ ), copper bromide ( $\text{CuBr}$ ,  $\geq 99\%$ ) and anisole (99%) were used as a monomer, initiator, ligand, catalyst and solvent, respectively. Diethyl ether (ACS reagent, anhydrous,  $\geq 99\%$ ) was used as a drying agent. All chemicals were purchased from Sigma Aldrich (USA) and were used without further purification (except for n-BA). n-BA was purified by passing through a neutral alumina column to remove MEHQ inhibitor prior to its use. Tetrahydrofuran (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. Poly(dimethyl siloxane) (PDMS) Sylgard 184 (Dow corning, USA) was used as received.

### 2.2. Preparation of GO sheets

Graphene oxide (GO) was fabricated from graphite powder by a modified Hummers method [22]. The raw graphite (5 g) was vigorously stirred with  $\text{H}_2\text{SO}_4$  (100 mL) and the mixture was cooled down to  $\sim 5^\circ\text{C}$  using an ice/water bath. Subsequently,  $\text{NaNO}_3$  (2.5 g) and  $\text{KMnO}_4$  (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 maintained under  $40^\circ\text{C}$ . Finally, concentrated  $\text{H}_2\text{O}_2$  in the amount of 40 mL was added, and the solution turned its colour 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  $25^\circ\text{C}$ . The cleaning routine was based on the dispersion of the GO in 0.1 M HCl, and their 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 amount of water after purification and 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  $\sim 5^\circ\text{C}$  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  $0.44\mu\text{m}$ ). The excess of water from treated particles was removed by filtration with diethyl ether (3x60ml).

## 2.4. Grafting of GO with PBA 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 degassing 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. During the reaction, the viscosity of the mixture was observed to gradually increase. The reaction was stopped by exposition of the mixture to air and cooling down to laboratory temperature. The product was purified by filtration using DMF (3x100mL) and finally with diethyl ether (3x 50 mL). Final product was then dried in desiccator upon ambient laboratory conditions.

## 2.5. Characterization

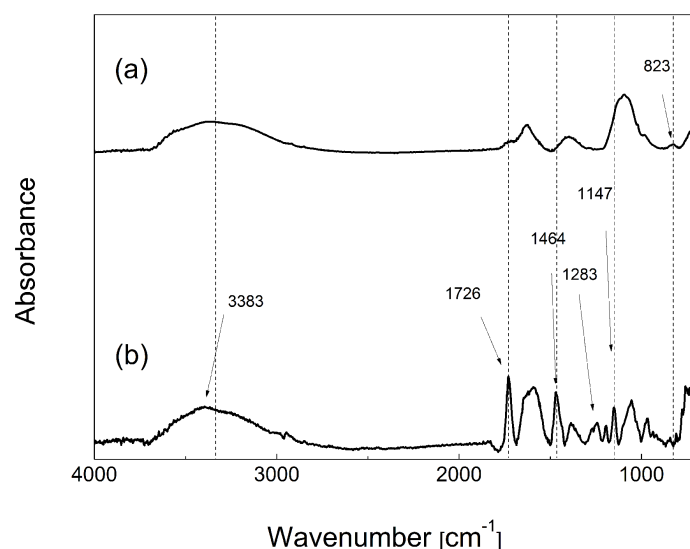
<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded at 25 °C using an instrument (400 MHz VNMRS Varian, Japan) with deuterated chloroform (CDCl<sub>3</sub>) as a solvent. The molar mass and polydispersity ( $\bar{D}$ ) of PMMA chains were investigated using gel permeation chromatography (GPC) on the GPC instrument (PL-GPC220, Agilent, Japan) equipped with GPC columns (Waters 515 pump, two PPS SDV 5  $\mu$ m 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<sub>3</sub> and THF, respectively, followed by the purification process, in which they were passed through a neutral alumina column. The energy dispersive spectrometry (EDS) was performed on a Tescan (VEGA II, Czech Republic). Fourier transform infrared (FTIR) spectra (64 scans, resolution of 4 cm<sup>-1</sup>) were recorded on a Nicolet 6700 (Nicolet, USA) within a wavenumber range of 3600-600 cm<sup>-1</sup>, while the ATR technique with a Germanium crystal was employed. The spectra were recorded at room temperature. The Raman spectra (3 scans, resolution of 2 cm<sup>-1</sup>) 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  $\mu$ L) of PDMS 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

### 3.1. SI-ATRP of PBA from GO sheets

The prepared GO sheets were grafted with PBA polymer chains using SI-ATRP approach. The resulting PBA was analyzed from the reaction mixture by GPC. It was found that polymer has relatively low molecular weight, due to the presence of the GO sheets, and PMDETA as an acting ligand of the ATRP reaction also reduces the GO sheets. The  $M_n$  of the PBA brushes was 1980 g mol<sup>-1</sup> and polydispersity index (PDI) was 1.10. The monomer conversion in this case was 21% calculated from <sup>1</sup>H NMR which well-correlates with the GPC results. The successful grafting process was confirmed by FTIR investigations. In the **Figure 1a** the presence of the hydroxyl groups at 3380 cm<sup>-1</sup>, carbonyl groups broad at 1726 cm<sup>-1</sup> and epoxy groups from 900 to 700 cm<sup>-1</sup>. The presence of the butyl acrylate polymer brushes can be clearly seen as a sharp peak at 1726 cm<sup>-1</sup> as a

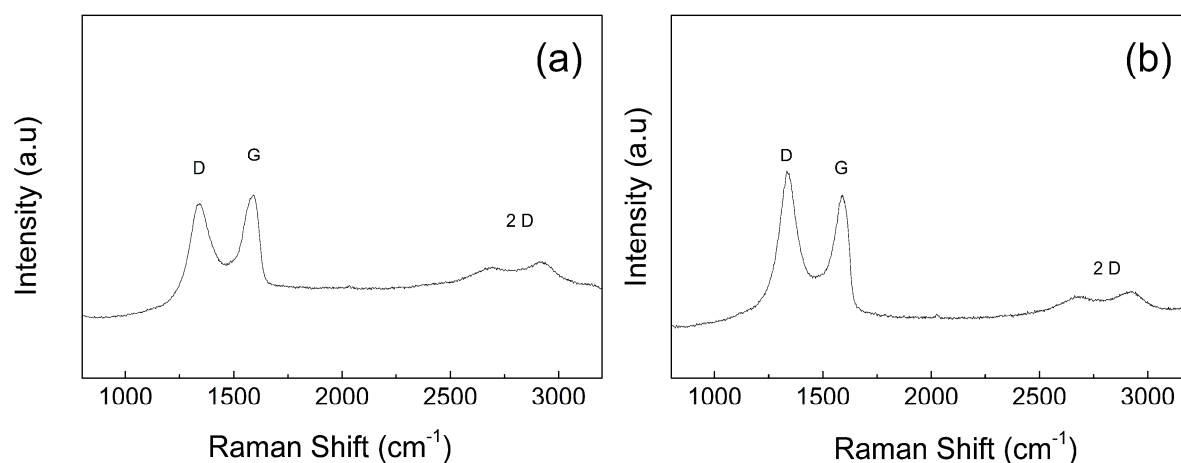
carbonyl band from acrylate. The ester absorption region was found at 1283 and 1147  $\text{cm}^{-1}$  and butyl vibrations at 1464  $\text{cm}^{-1}$ . All these findings confirmed successful implementation of the PBA brushes on the surface of the GO particles.



**Figure 1** FTIR spectra of the neat GO (a) and GO-PBA (b) particles

### 3.2. Reduction of the GO particles during SI-ATRP

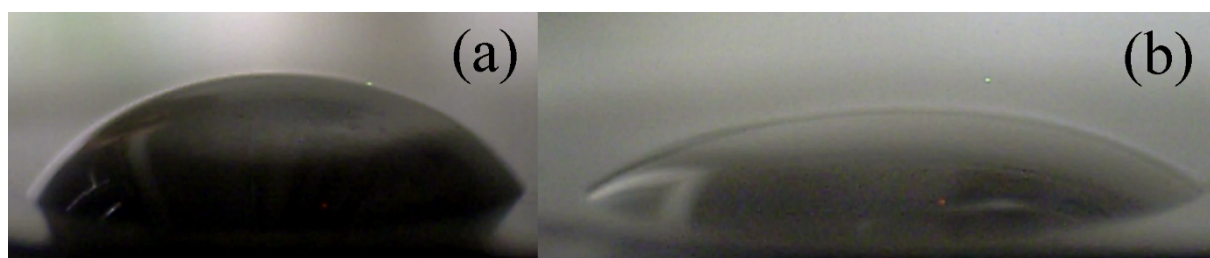
In order to confirm the reduction of the GO sheets during the SI-ATRP process, Raman spectroscopy was used as a useful tool for comparison between the broad D and G peaks corresponding to the  $\text{sp}^2$  and  $\text{sp}^3$  hybridized forms of carbon atoms in the GO sheets. In **Figure 2** can be seen comparison between neat GO sheets and GO-PBA, when the significant change between the peak intensities was obtained after SI-ATRP process. Further it can be seen that 2D structure of GO created during oxidation sustains nearly the same also after modification with PBA brushes, but the significant reduction of the GO sheets was achieved, when the ratios between  $I_D/I_G$  for neat GO and  $I_D/I_G$  for GO-PBA was changed from 0.90 to 1.10, respectively. From the conductivity point of view, the investigations provided similar results as obtained from Raman spectroscopy and confirm the reduction of the GO after modification. In this case neat GO has conductivity  $1 \times 10^{-8} \text{ S cm}^{-1}$  and GO-PBA  $4.9 \times 10^{-7} \text{ S cm}^{-1}$ . Therefore, it can be stated that within the SI-ATRP process, the reduction of the GO and simultaneous grafting of PBA polymer brushes is possible.



**Figure 2** Raman spectra of the neat GO (a) and GO-PBA (b) particles

### 3.3. Compatibility of the GO sheets and GO-PBA with PDMS

Compatibility of the GO particles with the surrounding when they will be dispersed is a crucial role for their potential applications as light sensors or actuators [23-25]. Since, elastomeric matrices are usually used as surroundings, in our case the compatibility between the neat GO and GO-PBA with PDMS was investigated. As can be seen in the **Figure 3**, the contact angle between the neat GO and PDMS is  $49.9^\circ \pm 3.2$ , while the presence of relatively long aliphatic butyl chain decreases the contact angle to  $28.7^\circ \pm 2.7$  indicating improved interactions between the surface of the GO-PBA with methyl moieties from PDMS in comparison the neat GO, where only hydroxyl, carbonyl, carboxyl and epoxy groups are present.



**Figure 3** Images from CCD camera of the PDMS droplets on the GO (a) and GO-PBA (b) particles surface

## 4. CONCLUSION

This study was aimed on the synthesis of GO-PBA hybrids using SI-ATRP technique, allowing the simultaneous modification of GO surface with PBA polymer chains and tailorable chemical reduction in several orders of magnitude. The successful modification of GO was proved using FTIR spectroscopy, while the reduction of GO was confirmed via conductivity and Raman spectroscopy investigations. In order to prove the potential applicability of such systems the compatibility with PDMS was elucidated and it was found that GO particles with PBA polymer chains provide enhanced compatibility with investigated surroundings while the conductivity was increased in one order of magnitude.

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