



Graphene oxide reduction during surface-initiated atom transfer radical polymerization of glycidyl methacrylate: Controlling electro-responsive properties



Miroslav Mrlík^{a,*}, Markéta Ilčíková^b, Tomáš Plachý^a, Vladimír Pavlínek^a, Zdenko Špitalský^b, Jaroslav Mosnáček^b

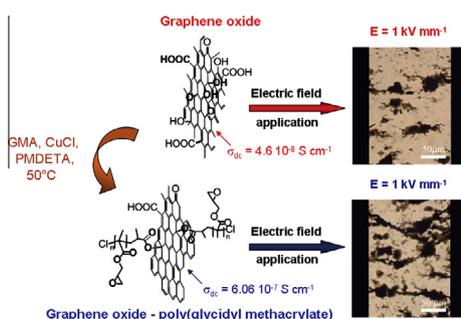
^a Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Trida T. Bati 5678, 760 01 Zlin, Czech Republic

^b Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

HIGHLIGHTS

- Unique SI-ATRP modification of graphene oxide particles with poly (glycidyl methacrylate) chains.
- Finely tuned electrical conductivity due to the surface reduction in the single step reaction.
- Hybrid 2D particles with tunable surface properties due to presence of reactive glycidyl group.
- Enhanced and tunable electro-responsive performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Unique grafting of the poly(glycidyl methacrylate) from the surface of graphene oxide (GO) with the controllable reduction of GO particles was performed in a single-step reaction using atom transfer radical polymerization technique. The control of the GO surface reduction and modification can be achieved by appropriate selection of the ratio between tertiary amine and GO particle contents. Finely tuned electrical conductivity of the GO-PGMA particles enables simple tailoring of electro-responsive properties of their silicone oil suspensions.

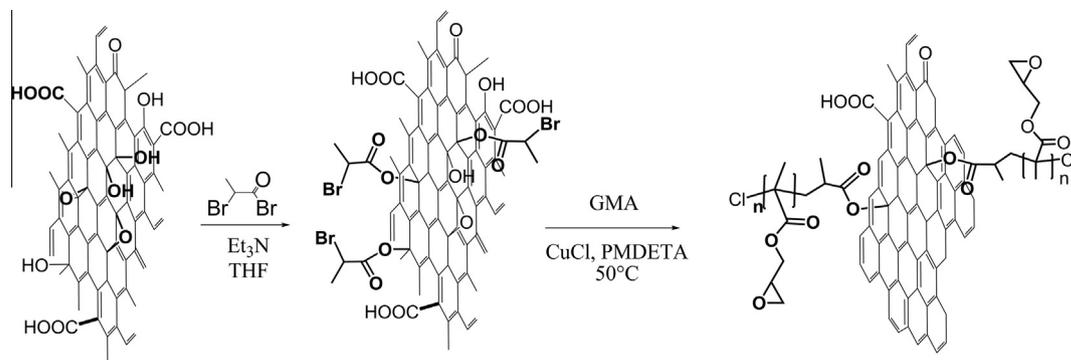
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Graphene is one of the carbon-based materials of great scientific interest due to its fascinating properties that could be useful for a variety of possible applications. Due to excellent charged carrier mobility [5], promising electrical [6] and mechanical [7] properties and also high transparency [8] graphene can be used for electronic components, energy storage, sensors or drug delivery

[1–4]. To ensure compatibility with its surroundings, functionalization of the graphene surface is necessary. Functionalized groups can be introduced by various methods [9–11]. One of the most common procedures is oxidation of graphene surface by various chemical methods [12,13]. The resulting layered graphene oxide (GO) material has various oxygen-containing groups present on the surface significantly suppressing electrical conductivity [13]. However, subsequent reduction of GO surface groups can cause an enhancement of the conductivity [14].

* Corresponding author.

E-mail address: mrlik@cps.utb.cz (M. Mrlík).



Scheme 1. Synthesis of partially reduced graphene oxide covalently modified with poly(glycidyl methacrylate) chains.

GO has been frequently applied as a dispersed phase in electrorheological (ER) suspensions [15]. Generally, the ER suspensions are two-phase colloidal systems consisting of polarizable particles dispersed in a liquid insulating medium usually silicone oil. They belong to the class of smart materials that enable control of the rheological properties such as viscosity through an application of an external electric field [16]. The viscosity changes are observable due to the formation of the internal chain-like structures of the dispersed particles that are aligned in the field lines of the applied external electric field [17]. The changes are rapid (in a timescale of order of ms) and suspensions can revert into the initial state immediately following the turning of the external field.

The most frequently used ER materials are semi-conducting polymers or oligomers [18,19] and also their carbonaceous analogues have also been recognized as suitable ER materials [20,21]. Due to its unique 2D shape also graphene has also been recently employed as a novel ER material [22,23]. However, both graphene and GO, were soon found to be unsuitable. In the case of graphene, this was due to a conductivity, that is too high, usually above $10^{-6} \text{ S cm}^{-1}$. Such high conductivity can cause short circuiting, when graphene particles are used as the dispersed phase [21]. By contrast, GO is unsuitable due to a conductivity, that is too low on the order of $10^{-9} \text{ S cm}^{-1}$ and leads to the poor ER performance of the GO silicone oil suspensions [22]. Thus, use of such graphene-based materials in electro-responsive applications is highly challenging because both the compatibility with carrier liquid and electrical conductivity have to be tailored. To improve the ER performance, various core-shell graphene-based composite particles were fabricated where graphene was used as either core [24] or shell material [25], or in hybrid composite particles [26]. Furthermore, several studies employed controlled radical polymerization enabling tuning of the material properties by the polymer layer thickness [27]. Very recently we found that electrical conductivity of GO can be finely tuned by adjusting the ratios of tertiary amine to GO and of tertiary amine ligand to copper catalyst during atom transfer radical polymerization (ATRP) [28].

Poly(glycidyl methacrylate) (PGMA) is a well known polymer with a variety of promising properties such as drug delivery or biomolecule binding, arising from the presence of reactive epoxy functional groups [29]. Moreover, the epoxy functional groups were effectively used for modification of water purification membranes [30]. Therefore, the modification of the GO surface with PGMA shows tremendous potential for applications in various research fields and in industry.

A combination of GO and PGMA was already applied as a promising core-shell material for ER suspensions, where the GO was used as the shell material [31]. However, due to the impossibility of the conductivity tuning, this system provided only moderate ER performance, even when 15 wt.% of the core-shell particles were used.

In this study we applied the possible tuning of the GO electrical conductivity during ATRP for preparation of new GO/polymer hybrids applicable as a dispersed phase in ER suspensions. Thus surface-initiated ATRP (SI-ATRP) technique was used for the grafting of the GO surface with PGMA chains. This approach allowed easy one-step tailoring of both the compatibility with carrier liquid and electrical conductivity of modified GO. PGMA was chosen for the modification on the basis of recently reported positive effect of PGMA on the stability of carbonyl iron-based MR suspensions [32]. The controllable ER performance was investigated with the help of rheometry in the absence and in the presence of the external electric field and by using optical microscopy observation of the developed internal chain-like structures. Adjustable properties of this type of graphene-based particles were clearly demonstrated and the tailoring of the ER performance was therefore verified.

The synthesis of the PGMA-grafted GO (GO-PGMA) is shown in the Scheme 1. The GO was first covalently modified by ATRP initiator (GO-I) and SI-ATRP of GMA was then performed under two different sets of conditions (see Table S1) to prepare GO grafted with PGMA with different polymerization degrees and various dispersibilities in suspensions (GO-4330 and GO-8500). At the same time, two various tertiary amine to GO ratios were used to obtain different degrees of GO reduction and thus slightly different electrical conductivities of the synthesized GO-PGMAs.

Transmission electron microscopy (TEM) images of the GO and GO-grafted PGMA showed the 2D layered structure (Fig. 1). The darker areas in the Fig. 1a corresponds to the few layers of GO lying in tandem while the lighter areas correspond to the nearly single GO layer. After grafting of PGMA from the GO surface, the polymer chains present in the GO-PGMA particles appeared as a continuous dark area forming a flossy-like structure (Fig. 1b). The modification of GO surface by ATRP initiator as well as by PGMA chains was confirmed also by ATR Fourier transform infrared (FTIR) spectroscopy (see Fig. S1). In addition to peaks with increased intensity attributed to PGMA, a significant decrease of intensity was observed for the peak at 3383 cm^{-1} following SI-ATRP of GMA (see Fig. S1). This corresponds well with the decreasing content of hydroxyl groups on the GO surface due to the partial reduction of GO during ATRP.

Thermogravimetric analysis (TGA) measurements were performed in order to further examine the changes during the GO surface modification. As can be clearly seen in Fig. 2, approximately 7 and 10 wt.% of the PGMA was covalently bonded to GO for GO-4330 and GO-8500, respectively. Furthermore, reduction of the GO within the SI-ATRP can be clearly visible and oxygen containing groups ($-\text{OH}$ and $-\text{COOH}$) are released in the $190\text{--}260 \text{ }^\circ\text{C}$ temperature range. The highest drop (solid line) at approximately $300 \text{ }^\circ\text{C}$ was observed for the neat GO particles indicating the highest content of the oxygen containing groups (36 wt.%). Furthermore, in case of GO-I (dashed line) the drop shifted to the lower

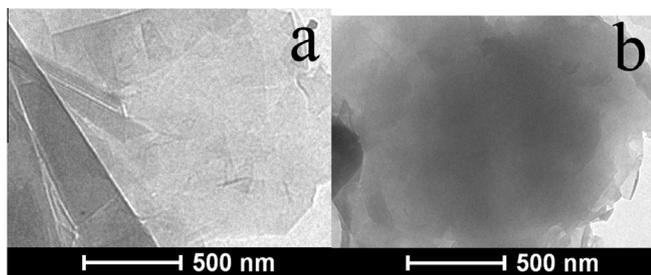


Fig. 1. TEM images of GO (a) and GO-PGMA (b) particles.

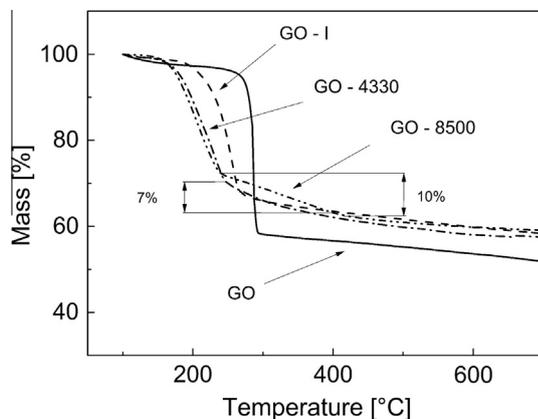


Fig. 2. TGA curves of the various GO-based samples.

temperatures starting at 140 °C, and the organic content was estimated to be 32 wt.%.

However, due to the presence of the tertiary amine (PMDTA) in the polymerization system, a significant reduction was visible for materials synthesized using ATRP of GMA in the case of shorter chains (GO-4330) with even greater reduction in the case of longer chains (GO-8500), showing that only 28 wt.% and 26 wt.% of oxygen containing groups were present after reduction, respectively.

Reduction of GO particles during the ATRP polymerization should cause an increase in their conductivity. The data in Table 1 clearly shows that conductivity increased after application of SI-ATRP to the GO surface. A higher increase in conductivity was obtained in the case of GO grafted with longer PGMA chains due to the higher tertiary amine to GO ratio used during the polymerization and thus providing a higher degree of GO surface reduction. Table 1 also shows that GO particles density decrease with increasing PGMA chain length; this is due to the increasing ratio between polymer and GO in the sample.

The finely tuned GO reduction obtained during the grafting of PGMA from the GO surface was further investigated for the applicability of the GO-PGMA in ER suspensions. The neat and GO-PGMA particles were mixed into the silicone oil (Lukosiol, M200, $\eta_c = 194$ mPa s). Correlation of the flow curves, at low and high external electric field strengths, with the corresponding optical microscopy images, was performed at the same voltage output and particles concentration. Fig. 3a shows the behaviour of suspensions containing neat GO and GO-8500 particles. At low external electric fields the particles and agglomerates of GO or GO-PGMA, did not exhibit properly developed internal structures. However, after the application of high external field strengths, the particles and agglomerates became polarized and formed the internal chain-like structures, with the chain direction perpendicular to the electrodes. This resulted in the change of the rheological properties, including the significant increase in the dynamic yield

Table 1

The conductivity, σ , and density, ρ , of bare GO, GO-I and GO-PGMA particles, where labelling indicate the molecular weight of PGMA chains.

Sample code	GO	GO-I	GO-4330	GO-8500
σ [S cm^{-1}]	$4.60 \cdot 10^{-8}$	$1.1 \cdot 10^{-8}$	$1.21 \cdot 10^{-7}$	$6.06 \cdot 10^{-7}$
ρ [g cm^{-3}]	2.54	2.51	2.23	2.14

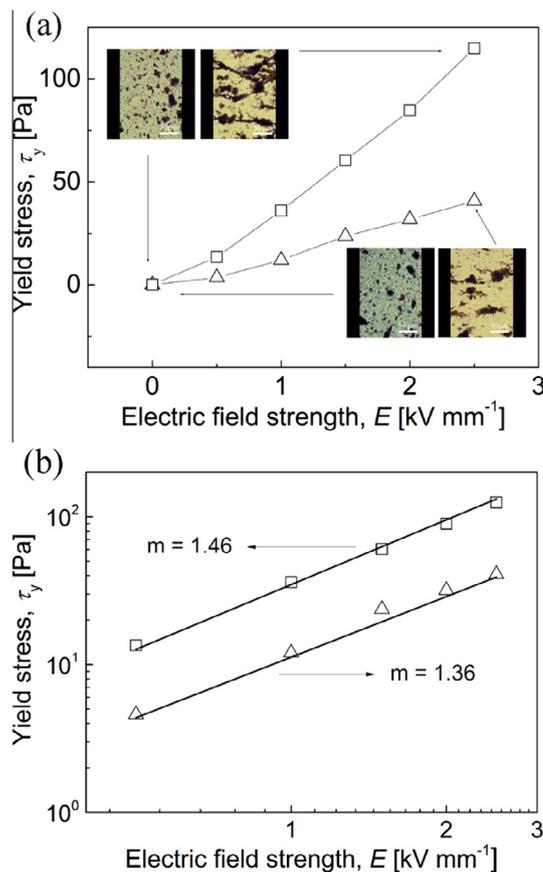


Fig. 3. Yield stress, τ_y , vs. electric field strength, E , for 10 wt.% of (Δ) GO and (\square) GO-8500 particles in silicone oil suspensions. (a) Comparison of the experimental data with online investigation upon similar electric field strengths, where insets are micrographs of suspensions with scale bar of 50 μm and (b) investigation of the mechanism, where the solid line represents power-law model fit.

stress, that is used as a measure of the rigidity of the internal structures significantly increased. Moreover, the development of the internal structures is more distinct for the GO-8500 (Fig. 3a insets) due to the suitable conductivity after the controlled reduction. Therefore, higher yield stresses were obtained for the suspensions that included the modified particles.

To investigate the mechanism of the internal chain-like structures formation, similar to the previous studies, the power-law model in the form of $\tau_y \propto E^m$ was applied for fitting of the experimental data (Fig. 3b) [15,24]. The exponent m nearly reaches values close to 1.5 for both ER suspensions, specifically 1.36 and 1.46 for GO and GO-8500, respectively, indicate that in both cases the conductivity mechanism is responsible for the formation of the internal structures [33].

In this case, the values of the yield stress could be controlled not only by the usual method of adjusting the intensity of the external electric field strength as is usual [16,18], but also by using the unique ability to fine tune the GO conductivity via controlled reduction during the SI-ATRP (see Fig. S3). Most importantly, ER performance was improved for sample GO-8500 above 100 Pa at

low concentration, due to increase of the conductivity to the appropriate value.

The ER performance was considerably enhanced compared to those obtained by other researchers using graphene oxide or modified GO particles as the dispersed phase [15,24].

In conclusion, the grafting of PGMA from the GO surface using the SI-ATRP technique gave rise to a polymer coating with simultaneous finely adjustable reduction of the GO particles within a one-step reaction. The reduction of the GO particles was confirmed using various techniques such as FTIR, TGA and conductivity investigations. The GO surface modification yielded not only the controlled GO reduction, but also finely tuned electro-responsive properties that can be effectively applied for ER suspensions with ER performance that was enhanced, compared to those of the common graphene-based ER suspensions.

Acknowledgments

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Appendix A. Supplementary data

Experimental procedure, details of synthesis of GO, GO-I and GO-PGMA particles and characterization techniques. Evaluation of the synthesis products (Table S1), FTIR spectra (Fig. S1), derivation of the TGA (Fig. S2) and the flow curves (Fig. S3). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.08.013>.

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