

ELECTRORHEOLOGICAL FLUIDS CONTAINING GRAPHENE OXIDE SHEETS GRAFTED WITH POLY(METHYL METHACRYLATE)

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Abstract

Electrorheological (ER) fluids are fascinating materials with a wide range of potential applications. However, low performance in electric field and poor sedimentation stability are the most serious limitations for these applications. To reduce the mentioned drawbacks various materials such as graphene were explored. Recent efforts to improve performance of the ER fluids led to the modification of the graphene with polymer substances. Herein, the proposed ER structures are based on the graphene oxide (GO) sheets controllably grafted with poly(methyl methacrylate) (PMMA). The oxygen-containing functional groups introduced by modified Hummers method enabled the immobilization of 2-Bromoisobutyryl bromide onto the GO. The controlled PMMA chain growth was performed by atom transfer radical polymerization resulting in the GO-*g*-PMMA entities. The reaction process was monitored via nuclear magnetic resonance spectroscopy and gel permeation chromatography. The successful grafting process was confirmed via infrared spectroscopy. Conductivity of the neat GO as well as the fabricated GO-*g*-PMMA structures was investigated using four-point method, while their reduction was examined via Raman spectroscopy. Such particles were further thoroughly dispersed in silicone oil (SO) and the ER performance of as-prepared ER fluids was investigated. The system containing the GO-*g*-PMMA exhibited superior dynamic yield stress and higher ER effects as the modified particles were able to develop more rigid field-induced internal structures, due to the enhanced particle conductivity and thus better response to external electric field. The results also showed that the presence of PMMA grafts enhanced the compatibility with SO, which was reflected in substantially improved stability against sedimentation.

Keywords: Electrorheology, steady shear, graphene oxide, surface modification, atom transfer radical polymerization

1. INTRODUCTION

Electrorheological (ER) fluids are colloidal systems consisting of electrically highly-polarizable particles dispersed in an insulating liquid. These systems exhibit fascinating rheological properties such as rapid and reversible viscosity changes when exposed to an external electric field. The transition from fluid-like to solid-like states, known as the ER effect, is a consequence of particle chain formation between the electrodes in a direction of applied field [1, 2]. The ER phenomenon triggered broad scientific and industrial interest which resulted in a proposal of novel ER clutches [3], dampers [4], haptic masters [5], displays [6] etc.

In order to develop high-performance ER fluid broad spectrum of materials has been investigated. Besides semi-conducting polymers [7] aniline oligomers [8], or titanium derivatives [9], the carbonaceous structures have been also recognized as promising ER materials [10]. Graphene and graphene oxide (GO) were a subject of recent studies, however they both were found to be unsuitable in their original forms [11]. While the former is characterized by too high conductivity ($\sim 10^{-6}$ S·cm⁻¹) causing the short circuiting during the ER experiments, the conductivity of the latter is rather low ($\sim 10^{-9}$ S·cm⁻¹) leading to insufficient ER performance of their silicone oil-based suspensions.

As graphene is considerably inert in various surrounding, the attention was paid to layered GO prepared via Hummer's or Brody's method owing oxygen-containing groups such as hydroxy, epoxy, carbonyl or carboxyl on its surface [12], which can be preferably used for post-modification of GO with various polymers to ensure the compatibility with carrier fluid and at the same time alter the electrical conductivity leading to the higher ER effect [10]. Nevertheless, this approach did not necessarily provide the optimal results, thus tuning the GO electrical conductivity is highly-challenging. Moreover, the early methods required two-step reaction synthesis employing the modification of the GO and its implementation into desired surrounding followed by its reduction via using primary and secondary amines [13] or hydrazine [14] in order to increase its conductivity to fulfill the requirements (from $\sim 10^{-5}$ to $\sim 10^{-9}$ S·cm⁻¹), which is according to Block et al. [15] a suitable range for the ER applications.

Recently, Ilcikova et al. [16] have shown more sophisticated method allowing the modification and reduction of GO within a single-step reaction. Their approach was based on the modification of GO surface with polystyrene using surface-initiated atom transfer radical polymerization (ATRP) in the presence of tertiary amine (*N,N,N',N',N''*-pentamethyldiethylenetriamine), which was responsible for the GO surface reduction. Moreover, following this procedure it was able to increase the GO electrical conductivity in eight orders of magnitude depending on the polymerization period. In our preceding study [17], we have verified that this approach is applicable also for modifying the GO sheets with poly(methyl methacrylate) (PMMA). This study is focused on the testing the ER performance perspectives of such material. As will be proven further in text, we believe, that this is a promising direction in the field of stimuli-responsive composites.

2. EXPERIMENTAL

2.1. Materials

Graphite (powder, < 20 μm, synthetic), sulfuric acid (H₂SO₄, reagent grade, 95-98 %), sodium nitrate (NaNO₃, ACS reagent, ≥99%), potassium permanganate (KMnO₄, 97%), hydrogen peroxide (H₂O₂, ACS reagent, 29.0-32.0 wt.% H₂O₂ basis), 2-bromoisobutyl bromide (BiBB, 98%), triethylamine (TEA, ≥99%), methyl methacrylate (MMA, 99%), ethyl 2-bromoisobutyrate (EBiB, 98%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, ≥99%), copper bromide (CuBr, ≥99%), anisole (99%) and diethyl ether (ACS reagent, anhydrous, ≥99%) were purchased from Sigma Aldrich (USA). 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 (Czech Republic). MMA was purified by passing through a neutral alumina column to remove inhibitor prior its use, while all other chemicals were used without further purification. Deionized water (DW) was used during the synthesis as well as the washing routines. A silicone oil (SO) M200 (conductivity of $\sim 10^{-11}$ S·cm⁻¹, dynamic viscosity of 197 mPa·s, density of 0.970 g·cm⁻³ at 25 °C) supplied by Lukosiol (Czech Republic) was used as a carrier liquid.

2.2. Approach from graphite to GO with PMMA chains

The modified Hummer's method based on weakening the van der Waals forces in graphite by introducing oxygen functional groups leading the exfoliation of graphite to GO sheets was performed [8]. Subsequently, the presence of functional groups was used to linkage with ATRP-initiator molecules of BIBB. The initiator-treated GO sheets were subjected to ATRP reacting system consisting of MMA, EBiB, PMDETA, and anisole, which represented monomer, sacrificial initiator, ligand, and a solvent, respectively. The reaction was catalyzed using CuBr. The final product was thoroughly purified and subjected to characterization [17].

2.3. Characterization

Monomer conversion and apparent molecular weights of PMMA grafts were characterized using ¹H nuclear magnetic resonance device (NMR, 400 MHz VNMR5 Varian, Japan) equipped with 5 mm ¹H-19F/15N-31P

PFG AutoX DB NB probe and calibrated (polystyrene standards) gel permeation chromatograph (GPC, PL-GPC220, Agilent, Japan) consisted of a Waters 515 pump, two PPS SDV 5 μm columns ($d = 8 \text{ mm}$, $l = 300 \text{ mm}$; 500 \AA + 105 \AA) and a Waters 410 differential refractive index detector, respectively. Both recordings were performed at a temperature of 25 $^{\circ}\text{C}$. 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 thermo-oxidation decomposition of the samples was on-line monitored using thermogravimetric analyzer (TGA) operating in oxygen atmosphere coupled with FTIR with a help of Nicolet iS10 equipped with TGA-IR module (Thermo Scientific, USA). The powders were compressed (pressure of 10 MPa, 1 minute) to the pellets (diameter of 13 mm, thickness of $\sim 1 \text{ mm}$) on a laboratory hydraulic press (Trystom Olomouc, H-62, Czech Republic) and their conductivity was characterized with the help of electrometer Keithley 6517B (USA) employing the Van der Pauw method with the four-point probe placed around the perimeter of the sample.

2.4. ER fluid preparation

The ER fluids were prepared following the protocol: (i) the moisture content of the components was eliminated by their heating at 60 $^{\circ}\text{C}$ overnight under decreased pressure; (ii) the appropriate amount of the GO particles or their PMMA-grafted analogues was mixed with SO in the sealable glass tubes to prepare the ER fluid containing 5 wt.% of the particles; (iii) before each experiment, the ER fluid was thoroughly stirred with a glass stick for $\sim 5 \text{ min}$ and subsequently the glass tubes were placed to an ultrasonic bath (K-12LE, Kraintek, Slovakia) for $\sim 5 \text{ min}$ at 25 $^{\circ}\text{C}$; (iv) finally, the freshly-prepared homogeneous ER fluids were subjected to ER characterizations.

2.5. Rheological measurements

The rheological behavior of the ER fluids was investigated under electric fields using a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) with parallel plate geometry (a diameter of 40 mm with a gap of 0.5 mm) at a constant temperature of 25 $^{\circ}\text{C}$. The controlled applied electric field was generated by a DC high-voltage source TREK 668B (Trek, USA). Two types of rheological tests were performed: (i) to characterize the steady-shear flow behavior, the ER fluid was pre-sheared at 50 s^{-1} for 1 minute in order to impose the same initial conditioning before each test run. Then, the rheological properties were collected within the shear rate range of 0.1-300 s^{-1} in the absence of electric field as well as at the applied DC field of the electric field strength of 0.5-2.5 $\text{kV}\cdot\text{mm}^{-1}$; (ii) the on/off tests were performed in order to show the repeatability of the processes during time. The experiment was performed under a constant shear rate of 1 s^{-1} , while the field of the 1.5 $\text{kV}\cdot\text{mm}^{-1}$ electric field strength was periodically applied in 300 s intervals.

3. RESULTS AND DISCUSSION

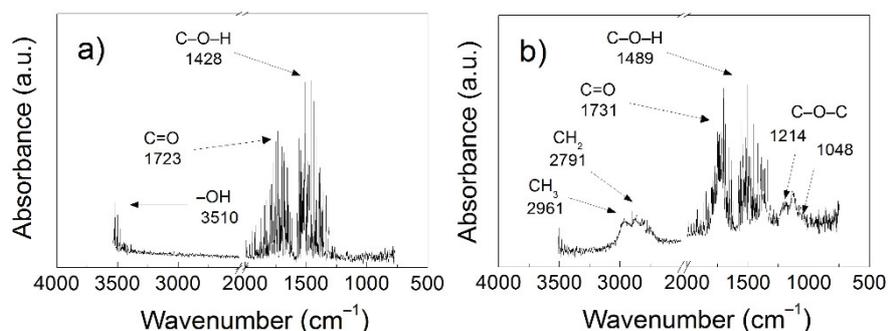


Figure 1 TGA/FTIR data for neat GO sheets (a) obtained in the temperature range from 180 to 270 $^{\circ}\text{C}$ and their PMMA-grafted analogues (b) obtained in the temperature range from 220 to 350 $^{\circ}\text{C}$ with denoted characteristic peaks

The ATRP was used as a precise and convenient technique to modify the GO surface with PMMA leading to enhanced compatibility with carrier fluid. As revealed by GPC, the weight-, and number-average molecular weights of PMMA grafts were found to be 6070 and 8170 g·mol⁻¹, respectively. Narrow dispersity of PMMA grafts (~1.35) indicated well-controlled ATRP. These characteristics were reached after 2 h polymerization and 82 % monomer conversion as detected by NMR. The TGA/FTIR spectra of neat GO and GO-*g*-PMMA structures are shown in **Figure 1** with denoted peaks characteristic for the certain functional groups releasing the samples at the investigated temperature range. In addition to hydroxyl groups and CO double bond groups occurring in neat GO (**Figure 1a**), the peaks representing CH₃ and CH₂ fractions were found in the spectrum of GO-*g*-PMMA (**Figure 1b**) confirming the presence of PMMA grafts

The modification of GO with PMMA grafts via ATRP was accompanied with simultaneous reduction of the GO substrate, which was investigated via Raman spectroscopy. The neat GO sheets were characterized by the D and G bands (**Figure 2a**) assigning the vibrations of disordered graphene sheets and vibrations of an ideal graphene sheets, respectively [19]. The Raman spectrum of GO-*g*-PMMA (**Figure 2b**) exhibited a slight shift of these bands due to reduction of GO due to induced reaction conditions (presence of PMDETA). The *I_D/I_G* ratio for neat GO was 0.90 due to harsh oxidation during Hummers method, which is a similar value as obtained Hafiz et al. [18]. The *I_D/I_G* ratio of GO-*g*-PMMA was 1.06 indicating that oxygen functional groups were diminished [20] due to modification. The 2D bands were assigned to decoupled multilayer graphene before as well as after the ATRP.

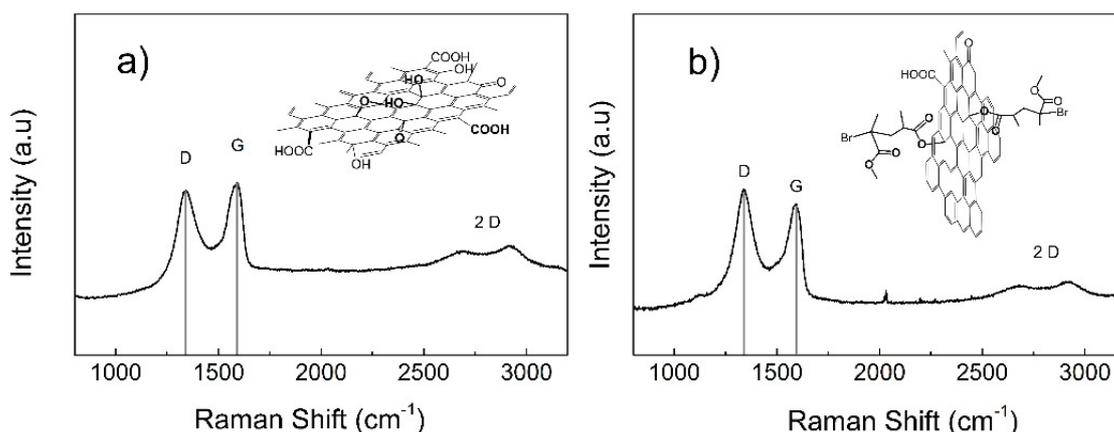


Figure 2 Raman spectra of neat GO sheets (a) and their PMMA-grafted analogues (b) with denoted characteristic bands

The electrical conductivity as a key property of the ER particles was investigated by four-point method. It was found, that the electrical conductivity of bulk GO was $(1.09 \pm 0.17) \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$, which is rather low value for ER material [11]. However, the value of $(6.90 \pm 0.83) \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ was obtained for GO-*g*-PMMA particles, which is more suitable value [15]. The conductivity increase was explained as a consequence of particle reduction during ATRP as the tertiary amine (PMDETA) was present in the reaction mixture. As we have shown previously [17], the PMMA-grafts substantially improved the wettability of the particles in hydrophobic media. Therefore, it is expected that SO-based ER fluids containing GO-*g*-PMMA particles are more stable when compared with their analogues containing neat GO. Further, **Figure 3** displays the ER behavior of prepared ER fluids. The both ER fluids exhibited similar rheological behavior in the absence of electric field with nearly Newtonian character. However, after the application of the electric field the shear stress significantly increased as the particles polarized and developed chain-like structures spanning the measuring geometry. The shear stress increase was superior in the ER fluid containing the GO-*g*-PMMA particles due to their higher electrical conductivity, which fell into optimal conductivity region for the ER materials [15]. According to a definition [1, 2], the ER phenomenon is a reversible process. This criterion must be fulfilled as the ER devices operate mainly

in switching on/off regime. Therefore, the reproducibility of the ER phenomenon was investigated (**Figure 3b**). As seen, both ER fluids were able to abruptly increase/decrease shear stress as a reaction on switching electric field through numerous operating cycles. Conclusively, the ER performance in terms of obtained shear stress values was significantly better for ER fluid containing GO-*g*-PMMA.

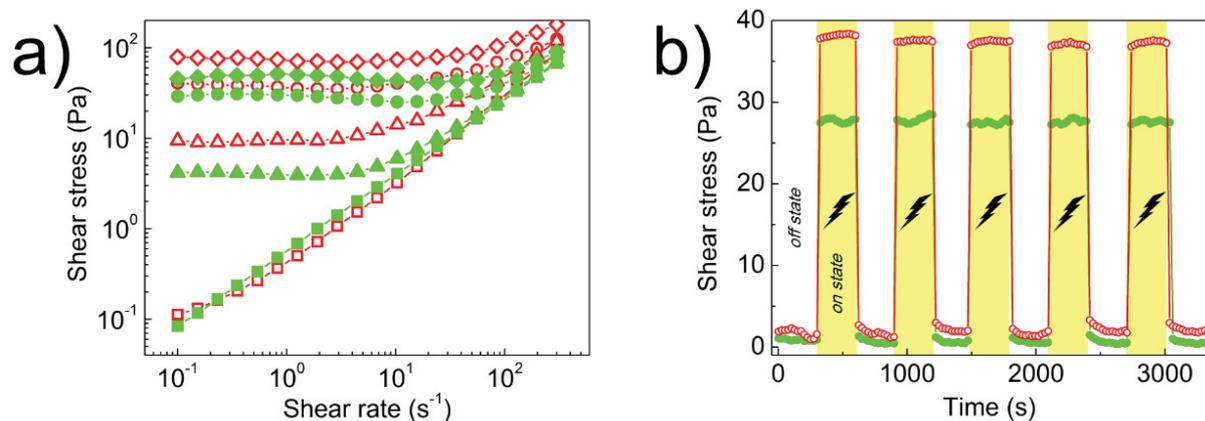


Figure 3 The ER-behavior of the SO-based ER fluids containing 5 wt.% of the corresponding particles. Shear stress versus shear rate dependences (a) for the ER fluid containing neat GO sheets (*solid symbols*) or their PMMA-grafted analogues (*open symbols*) at the off-state (*squares*) and in the presence of 0.5 (*triangles*), 1.5 (*circles*), and 2.5 $\text{kV}\cdot\text{mm}^{-1}$ (*diamonds*) electric field strengths. Shear stress as a function of time (b) during periodically switching on/off electric field ($1.5 \text{ kV}\cdot\text{mm}^{-1}$) at a shear rate of 1 s^{-1} for the ER fluid containing neat GO sheets (*solid circles*) or their PMMA-grafted analogues (*open circles*) with denoted off/on states (*white/yellow regions*)

4. CONCLUSIONS

The novel ER material of GO-*g*-PMMA was prepared using surface-initiated ATRP. The PMMA grafts possessed molecular weight of $8170 \text{ g}\cdot\text{mol}^{-1}$ and narrow dispersity of ~ 1.35 indicating well-controlled polymerization process. In a single-step reaction, the GO sheets modification and their reduction were performed. The presence of PMMA grafts was proved via TGA/FTIR analysis revealing the peaks corresponding for the molecular fractions, from which the PMMA grafts were consisted. Their reduction was further demonstrated through electrical conductivity measurements and Raman spectroscopy. The enhanced compatibility in hydrophobic media and suitably higher electrical conductivity (appropriate for ER fluids) of GO-*g*-PMMA sheets was reflected in superior ER performance of their SO-based suspension. The ER fluids containing GO-*g*-PMMA particles can develop more rigid field-induced structures, thus they have a potential to be used in practical applications.

ACKNOWLEDGEMENTS

The authors wish to thank the Grant Agency of the Czech Republic (GJ16-20361Y) for financial support. Author M. C. further thanks the Internal Grant Agency of Tomas Bata University in Zlin (project no. IGA/CPS/2017/004) for financial support. This work was also supported by the Ministry of Education, Youth and Sports of the Czech Republic - Program NPU I (LO1504). Authors M. I. and J. M. gratefully acknowledge APVV-15-0545 for financial support.

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