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## ELECTRORHEOLOGICAL PERFORMANCE OF GRAPHENE OXIDE PARTICLES GRAFTED WITH POLY(ALPHA-METHYLSTYRENE) USING SI-ATRP APPROACH

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### Abstract

Electrorheological (ER) suspensions are a special class of systems, whose physical properties, such as viscosity, can be tuned using an external electric field strength. Generally, they are two-phase systems consisting of solid polarizable particles and a liquid insulating medium. After application of the external electric field, the particles are polarized and create chain-like structures in the direction of the electric field streamlines. Such internal structure development results in a significant increase in viscosity, usually by four orders of magnitude or more. This phenomenon is reversible, repeatable, and once the electric field is switched off, the suspension returns to its initial state. However, due to the usually various nature of the dispersed phase and liquid medium, the sedimentation stability of the suspensions is the main issue. In addition, the ER performance of various systems based on conducting polymers is not sufficient, thus the development of novel dispersed phases is still attractive. Moreover, graphene oxide (GO) particles and their hybrids were recently recognized as suitable materials for ER suspensions. Hence, we performed the SI-ATRP from the GO surface as a novel approach to provide GO-polymer particles with tunable conductivity and a polymer layer in a single step and thus solve the main drawbacks such as sedimentation stability as well as proper ER performance.

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

### 1. INTRODUCTION

Graphene was recently recognized as a very promising material, due to its simple preparation, low fabrication cost, and excellent physical properties (excellent thermal and electrical conductivities) [1, 2]. Unfortunately, graphene is relatively inert to the surrounding environment [3]. From its potential applicability point of view, the presence of graphene platelets or graphene oxide in various surroundings such as hydrogels [4], elastomers [5] or silicone oil [6] leads to interesting utilizations in intelligent systems [7, 8]. In order to be effectively applied in such systems, proper dispersion is a crucial factor, and such systems respond to magnetic [9] or electric field [10], pH [11] and light [12].

In this case, electrorheological (ER) suspensions are two-phase systems consisting of polarizable particles and a liquid medium [13], and are a class of materials belonging to the group of smart systems, and their physical properties such as viscosity or viscoelastic moduli can be tailored using an external electric field [14, 15]. Based on two fundamental models, the ER performance depends on the mechanism upon which particles are able to create internal chain-like structures, the conductivity mechanism and the polarization mechanism [16]. Various materials have been investigated, such as inorganics [17], conducting polymers [18], or other inorganic polymer hybrids [19].

Recently, our group recognized that GO particles can be reduced within a 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 a concept is also working for other monomeric systems such as poly(glycidyl methacrylate) [21] and its application as a smart system in electrorheology.

This study is focused on the verification of such technique, utilizing SI-ATRP and another monomer, alpha-methyl styrene ( $\alpha$ -MeS), is still valid and how the monomer nature influences the final product from the final properties as well as GO reduction point of view. The  $\alpha$ -MeS polymer chains were analyzed using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Successful modification was proved by FTIR. ER performance was investigated using rotational rheology in the steady shear mode, and finally the compatibility of GO and GO- $\alpha$ -MeS particles with silicone oil was elucidated.

## 2. EXPERIMENTAL

### 2.1. Materials

Graphite (powder, < 20  $\mu$ m, synthetic) was used as a precursor for GO sheets. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, reagent grade, 95-98 %), sodium nitrate (NaNO<sub>3</sub>, ACS reagent,  $\geq$ 99%), potassium permanganate (KMnO<sub>4</sub>, 97%) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, ACS reagent, 29.0-32.0 wt. % H<sub>2</sub>O<sub>2</sub> basis) were employed as chemical reagents to set the proper exfoliation conditions to form GO sheets.  $\alpha$ -bromoisobutyryl 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%). alpha-methyl styrene ( $\alpha$ -MeS, 99%), ethyl  $\alpha$ -bromoisobutyrate (EBiB, 98%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA,  $\geq$ 99%), copper bromide (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 H<sub>2</sub>SO<sub>4</sub> (100 mL) and the mixture was cooled down to  $\sim$ 5  $^{\circ}$ C using an ice/water bath. Subsequently, NaNO<sub>3</sub> (2.5 g) and KMnO<sub>4</sub> (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  $^{\circ}$ C. Finally, concentrated H<sub>2</sub>O<sub>2</sub> 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  $^{\circ}$ 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  $^{\circ}$ 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  $\mu$ m). The excess of water from treated particles was removed by filtration with diethyl ether (3x60 mL).

## 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  $\alpha$ -MeS (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 [ $\alpha$ -MeS]:[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 (3x100 mL) 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 ( $\bar{M}_w/\bar{M}_n$ ) of  $\alpha$ -MeS 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 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. Suspensions (5 wt. %) were prepared by mixing of neat GO and GO- $\alpha$ -MeS powders with corresponding amount of silicone oil (Fluid 200, Dow Corning, UK; viscosity  $\eta_e = 108$  mPa.s, density  $\rho_c = 0.965$  g.cm<sup>-3</sup>). Before each measurement, the suspensions were stirred at first mechanically and then sonicated for 30 s.

Rheological measurements were performed under controlled-shear-rate (CSR) mode using rotational viscometer (Bohlin Gemini, Malvern Instruments, UK). The suspensions were placed into the parallel-plate geometry 40 mm in diameter and 0.5 mm gap. The instrument modified for ER experiments was connected to DC high-voltage source TREK (TREK 668B, USA) to generate electric field strengths 0-2.0 kV.mm<sup>-1</sup>. Before each measurement step, the previously built-up particulate structures were destroyed by shearing the sample at the shear rate 50 s<sup>-1</sup> for 80 s.

## 3. RESULTS AND DISCUSSION

### 3.1. SI-ATRP of $\alpha$ -MeS from GO sheets

The prepared GO sheets were grafted with  $\alpha$ -MeS polymer chains using SI-ATRP technique. The resulting  $\alpha$ -MeS was analyzed from the reaction mixture by GPC. It was found that polymer has relatively low molecular

weight, due to the short time of polymerization, which is important in case of slight reduction of the GO substrate. The  $M_n$  of the PBA brushes was  $5680 \text{ g}\cdot\text{mol}^{-1}$  and polydispersity index (PDI) was 1.28. The monomer conversion in this case was 48% calculated from  $^1\text{H}$  NMR which well-correlates with the GPC results. The successful grafting process was confirmed by FTIR investigations. In the **Figure 1** the presence of the hydroxyl groups at  $3300 \text{ cm}^{-1}$ , carbonyl groups broad at  $1713 \text{ cm}^{-1}$  and epoxy groups at  $819 \text{ cm}^{-1}$ . The presence of the  $\alpha$ -MeS polymer brushes can be clearly seen as a several absorption bands corresponding to the aromatic ring from styrene, where C=C bending can be seen around  $1714 \text{ cm}^{-1}$  and C-H stretching around  $2934 \text{ cm}^{-1}$  and  $2902 \text{ cm}^{-1}$ . All these finding confirmed successful implementation of the  $\alpha$ -MeS brushes on the surface of the GO particles.

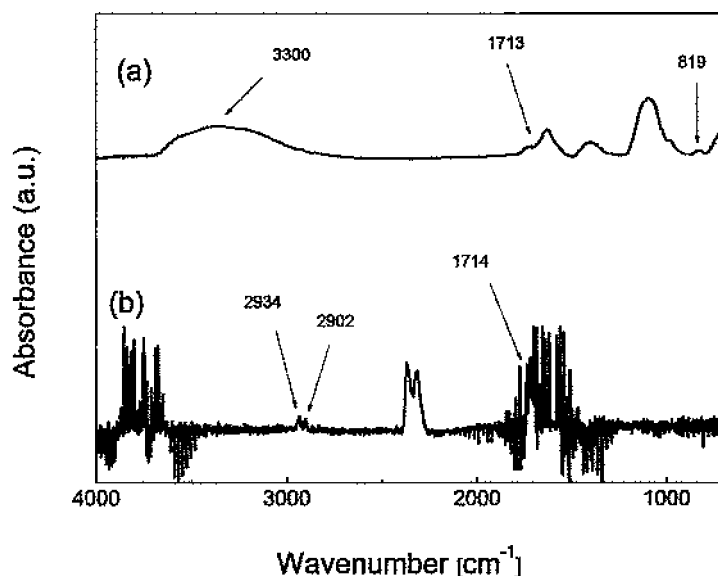


Figure 1 FTIR spectra of the neat GO (a) and GO- $\alpha$ -MeS (b) particles

### 3.2. Electrorheological performance of GO-grafted particles with $\alpha$ -MeS

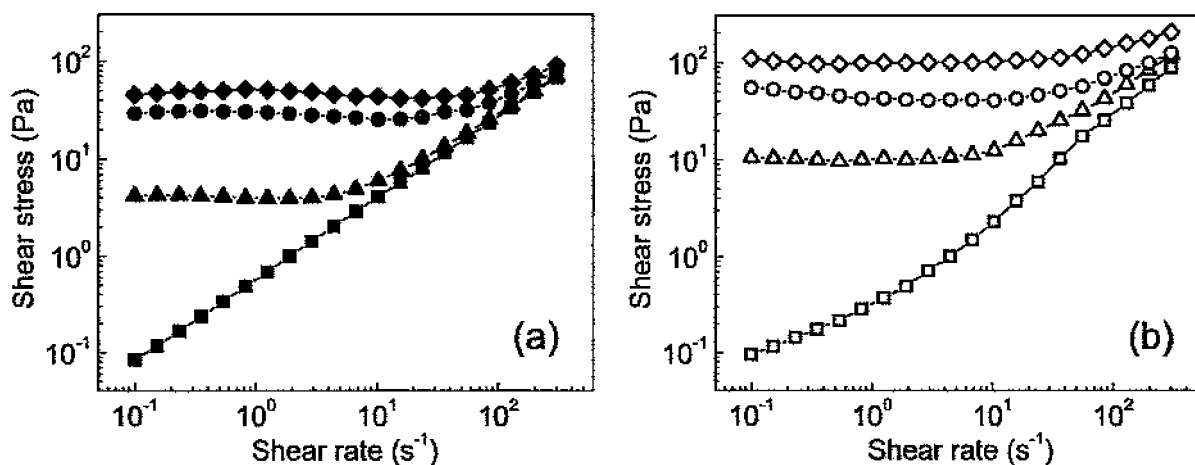
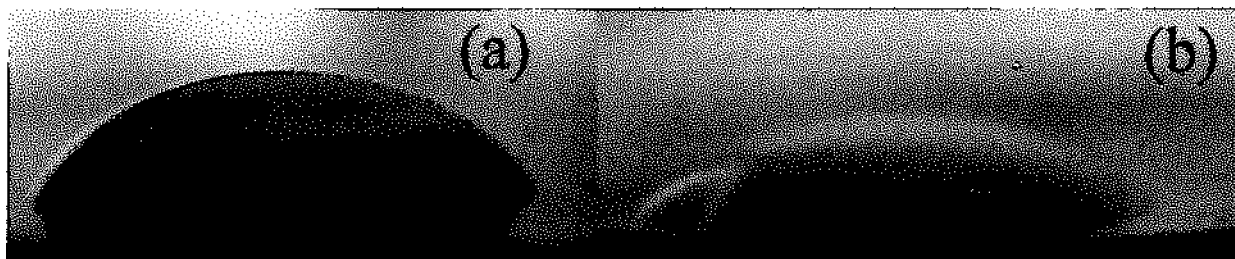


Figure 2 Dependence of the shear stress,  $\tau$ , on the shear rate,  $g$ , for 5 wt. % silicone suspensions of aniline oligomers particles prepared in (a) neat GO and (b) GO- $\alpha$ -MeS, at various external electric field strengths,  $E$ , ( $\text{kV}\cdot\text{mm}^{-1}$ ): 0 (■, □), 0.5 (▲, △), 1.5 (●, ○), 2.5 (◆, ◇)

In order to confirm the suitability of the synthesized particles for implementation as a dispersed phase in ER suspensions, the rheological properties of their silicone oil suspensions have been investigated. As can be seen in the **Figure 2**, both suspensions of neat GO and GO- $\alpha$ -MeS exhibit neatly Newtonian behaviour in the absence of the external electric field. Slight deviation from such behaviour can be seen for GO- $\alpha$ -MeS based suspensions, due to the enhanced compatibility with silicone oil in comparison to the neat GO. During the polymerization, also, slight GO reduction has been achieved and thus performance upon external electric field was enhanced. In this case the shear stress at  $0.1 \text{ s}^{-1}$  was 74 Pa and 109 Pa, for neat GO and GO- $\alpha$ -MeS, respectively. Thus we can conclude that suspensions based on modified GO grafted with  $\alpha$ -MeS polymer brushes, provide the system with tunable ER performance, by both external electric field and by reaction conditions, where the ratio between the GO and catalyst, play an important role similarly as was already proved elsewhere [21].

### 3.3. Compatibility of the GO sheets and GO- $\alpha$ -MeS with silicone oil

Compatibility of the GO particles with the surrounding in case they are dispersed is a crucial role for their potential applications as dispersed phase in ER suspensions [23-25]. Since, silicone oil is a most utilized continuous phase the compatibility between the neat GO and GO- $\alpha$ -MeS and silicone oil 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 polymer backbone with benzene ring as the bearing moiety decreases the contact angle to  $35.4^\circ \pm 2.1$  indicating improved interactions between the surface of the GO- $\alpha$ -MeS with aliphatic moieties from silicone oil in comparison the neat GO, where only hydroxyl, carbonyl, carboxyl and epoxy groups are present.



**Figure 3** Images from CCD camera of the silicone oil droplets on the GO (a) and GO- $\alpha$ -MeS (b) pellets

## 4. CONCLUSION

This study was aimed on the synthesis of GO- $\alpha$ -MeS hybrids using SI-ATRP approach, allowing the simultaneous modification of GO surface with  $\alpha$ -MeS polymer chains and tailorable chemical reduction in the range suitable for ER applications. The successful modification of GO with polymer brushes was proved using FTIR spectroscopy. In order to prove the potential applicability of such systems in ER application the rheological investigation shows that GO- $\alpha$ -MeS particles are very promising. Also compatibility with silicone oil was elucidated and it was found that GO particles with  $\alpha$ -MeS polymer chains provide enhanced compatibility with investigated which indicate also better long-term stability properties.

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## REFERENCES

- [1] LEE, C., WEI, X., KY SAR, J. W., HONE, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 2008, vol. 321, no 5887, pp. 385-388.
- [2] NOVOSELOV, K. S., GEIM, A. K., MOROZOV, S. V., JIANG, D., KITNELSON, M. I., GRIGORIEVA, I. V., DUBONOS, S. V., FIRSOV, A. A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 2005, vol. 438, no. 7065, pp. 197-200.
- [3] PARK, S., AN, J. H., PINER, R. D., JUNG, I., YANG, D. X., VELAMAKANNI, A., NGUYEN, S. T., RUOFF, R. S. Aqueous Suspensions and Characterization of Chemically Modified Graphene Sheets. *Chemistry of Materials*, 2008, vol. 20, no. 21, pp. 6592-6594.
- [4] USMAN, A., HUSSAIN, Z., RIAZ, A., KHAN, A. N. Enhanced mechanical, thermal and antimicrobial properties of poly(vinyl alcohol)/graphene oxide/starch/silver nanocomposite films. *Carbohydrate Polymers*, 2016, vol. 153, pp. 592-599.
- [5] GAN, L., SHANG, S. M., JIANG, S. X. Impact of vinyl concentration of a silicone rubber on the properties of the graphene oxide filled silicone rubber composites. *Composites Part B-Engineering*, 2016, vol. 84, pp. 294-300.
- [6] ZHANG, W. L., LIU, Y. D., CHOI, H. J., KIM, S. G. Electrorheology of Graphene Oxide, *ACS Applied Materials and Interfaces*, 2012, vol. 4, no. 4, pp. 2267-2272.
- [7] ZHANG, W. L., CHOI, H. J. Fast and facile fabrication of a graphene oxide/titania nanocomposite and its electro-responsive characteristics, *Chem. Commun.*, 2011, vol. 47, no. 45, pp. 12286-12288.
- [8] ILCIKOVA, M., MRLIK, M., BABAYAN, V., KASAK, P. Graphene oxide modified by betaine moieties for improvement of electrorheological performance. *RSC Advances*, 2015, vol. 5, no. 71, pp. 57820-57827.
- [9] ZHANG, W. L., CHOI, H. J. Silica-graphene oxide hybrid composite particles and their electroresponsive characteristics. *Langmuir*, 2012, vol. 28, no. 17 pp.7055-7062.
- [10] ZHANG, W. L., TIAN, Y., LIU, Y. D., SONG, Z. Q., LIU, J. Q., CHOI, H. J. Large scale and facile sonochemical synthesis of magnetic graphene oxide nanocomposites and their dual electro/magneto-stimuli responses. *RSC Advances*, 2016, vol. 6, no. 81, pp. 77925-77930.
- [11] MRLIK, M., SPIREK, M., AL-KHORI, J., AHMAD, A. A., MOSNACEK, J., ALMAADEED, M. A. S. A., KASAK, P. Mussel-mimicking sulfobetaine-based copolymer with metal tunable gelation, self-healing and antibacterial capability, DOI: 10.1016/j.arabj.2017.03.009.
- [12] ILCIKOVA, M., MRLIK, M., SEDLACEK, T., SLOUF, M., ZHIGUNOV, A., KOYNOV, K., MOSNACEK, J. Synthesis of photoactuating acrylic thermoplastic elastomers containing diblock copolymer-grafted carbon nanotubes. *ACS Macro Letters*, 2014, vol. 3, no. 10, pp. 999-1003.
- [13] MARINS, J. A., SOARES, B. G. Ionic liquid-based organically modified silica for the development of new electrorheological fluids, *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 2017, vol. 529, pp. 311-319.
- [14] MIN, T. H., CHOI, H. J. Synthesis of poly(methyl methacrylate)/graphene oxide nanocomposite particles via Pickering emulsion polymerization and their viscous response under an electric field, *Macromolecular Research*, 2017, vol. 25, no. 6, pp. 565-571.
- [15] ZHANG, W. L., CHOI, H. J., LEONG, Y. K. Facile fabrication of graphene oxide-wrapped alumina particles and their electrorheological characteristics, *Materials Chemistry and Physics*, 2014, vol. 145, no. 1-2, pp. 151-155.
- [16] RANKIN P. J., GINDER, J. M. Electro- and magneto-rheology, *Current Opinion in Colloid and Interface Science*, 1998, vol. 3, no. 3, pp.373-381.
- [17] WANG, J. H., CHEN, G. W., YIN, J. B., LUO, C. R., ZHAO, X. P. Enhanced electrorheological performance and antisedimentation property of mesoporous anatase TiO<sub>2</sub> shell prepared by hydrothermal process, *Smart Materials and Structures*, vol. 23, no. 3, pp. 035036.
- [18] KIM, M. H., SEA, D. H., CHOI, H. J., SEO, Y. Synthesis of semiconducting poly(diphenylamine) particles and analysis of their electrorheological properties, *Polymer*, 2017, vol. 119, pp. 40-49.
- [19] OZKAN, S., UNAL, H. I. Enhanced dielectric and electrorheological properties of needle-like TiO<sub>2</sub>/polyrhodanine core/shell hybrid nanostructure, *Journal of Applied Polymer Science*, 2016, vol. 133, no. 13, pp. 43240.

- [20] ILCIKOVA, M., MRLIK, M., SPITALSKY, Z., MICUSIK, M., CSOMOROVA, K., SASINKOVA, V., KLEINOVA, A., MOSNACEK, J. A tertiary amine in two competitive processes: reduction of graphene oxide vs. catalysis of atom transfer radical polymerization. *RSC Advances*, 2015, vol. 5, no. 5, pp. 3370-3376.
- [21] MRLIK, M., ILCIKOVA, M., PLACHY, T., PAVLINEK, V., SPITALSKY, Z., MOSNACEK, J. Graphene oxide reduction during surface-initiated atom transfer radical polymerization of glycidyl methacrylate: Controlling electro-responsive properties. *Chemical Engineering Journal*, 2016, vol. 283, pp. 717-720.
- [22] HUMMERS, W. S., OFFEMAN, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.*, 1985, vol. 80, no. 6, pp. 1339-1339.
- [23] LI, Y. Z., GUAN, Y. G., LIU, Y., YIN, J. B., ZHAO, X. P., Highly stable nanofluid based on polyhedral oligomeric silsesquioxane-decorated graphene oxide nanosheets and its enhanced electro-responsive behavior, *Nanotechnology*, 2016, vol. 27, no. 19, pp. 195702.
- [24] STENICKA, M., PAVLINEK, V., SAHA, P., BLINOVA, N. V., STEJSKAL, J., QUADRAT, O. The effect of compatibility of suspension particles with the oil medium on electrorheological efficiency, *Journal of Intelligent Materials Systems and Structures*, 2012, vol. 23, no. 9, pp. 1055-1059.
- [25] BELZA, T., PAVLINEK, V., SAHA, P., QUADRAT, O. Electrorheological properties of suspensions of silica nanoparticles modified by urea and N,N-dimethylformamide, *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 2007, vol. 297, no. 1-3, pp. 142-146.