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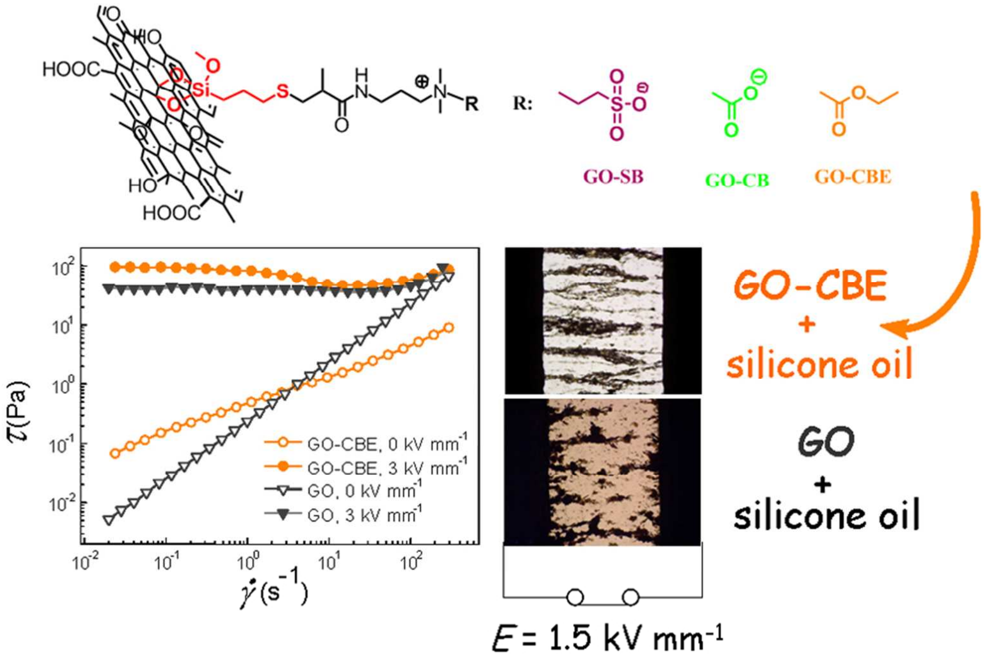

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Graphene Oxide Modified by Betaine Moieties for Improvement of Electrorheological Performance

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Abstract

Novel graphene oxide bearing betaine moieties as sulfobetaine (GO-SB), carboxybetaine (GO-CB) and carboxybetaine ester (GO-CBE) moieties were prepared in two simple fabrication processes based on silanization and thiol-ene click-reaction. Betaine modified particles showed appropriate electrical conductivity for electrorheological application and the electrorheological behavior was confirmed by on-line microscopic observation. Analysis of the dielectric data using Havriliak-Negami model showed that the suspension bearing carboxybetaine ester moiety (GO-CBE) in silicone oil had the highest dielectric relaxation strength and fastest relaxation time due to enhanced charge transfer caused by a specific carboxybetaine ester feature. Analysis of rheological data of the prepared suspensions at various external fields by power-law model revealed that conductivity mechanism is responsible for the electrorheological effect. Development of the internal structures was considerably improved for sample GO-CBE with yield stress up to 97 Pa at 5 wt. % GO-CBE particles in suspension.

Keywords: graphene oxide, sulfobetaine, carboxybetaine, zwitterions, electrorheology

1. Introduction

Smart materials represent a unique class of materials capable of dramatic change of their physical properties upon external stimulus. This stimulus can be temperature, pH, electric and magnetic field or UV radiation. These materials can find application in optics, electronics, (bio)engineering and (bio)sensing [1-5].

Electrorheological (ER) suspensions belong to smart materials whose repeatable transition from liquid-like to solid-like state is controlled by application of external electric field strength [6-8]. They are two phase systems consisting of an insulating liquid, mainly silicone oils and of solid organic or hybrid polarizable particles including dipoles [5, 9]. The ER suspensions change their Newtonian liquid-like behavior in the absence of the external electric field to a shear thinning solid-like behaviour upon application of electric field, due to formation of internal structures between particles aligned in the electric field strength direction. Various micro-structures of conducting materials in a dispersed phase, such as polymers [10-14], oligomers [15,16], hybrid particles in form of core-shell structures [17-19] and more recently two dimensional particles [20] in insulating liquids, have been used. The rheological quantities such as viscosity, viscoelastic moduli and yield stress are changed in several orders of magnitude as well. This unique characteristic has been utilized in automotive industry [21, 22], civil engineering [23] and medical applications [24, 25].

Materials based on graphene oxide (GO) possess unique characteristics combining two-dimensional shape, easy functionalization [26] and accessibility which make them attractive for smart applications [20, 27]. ER activity of GO [28] and GO based materials [29-35] can be modulated by their lower electrical conductivity comparing to graphene and by possible modification of their surface with polarizable or conductive feature. In the above mentioned studies the authors investigate the ER performance of neat GO particles [28], and the core-shell composite particles, when GO is used as a core [29, 31, 32] or as a shell component [30, 33, 34]. However in terms of yield stress, the ER performance of the GO based materials is rather low. The yield stress can be expressed as a rigidity of the created internal structures upon electric field application, and the values hardly reach 100 Pa for particles concentration more than 15 wt. % in silicone oil suspensions [29, 30].

Betaines belong to a specific type of compounds bearing permanent positive charge, which is usually a non-protonated ammonium group. If they contain covalently bound anionic group, they are zwitterions classified according to the anionic groups as phosphobetaines, sulfobetaines or carboxybetaines. Surface modification with betaine and betaine ester derivates was used predominately in bioapplication and biosensing [36-40].

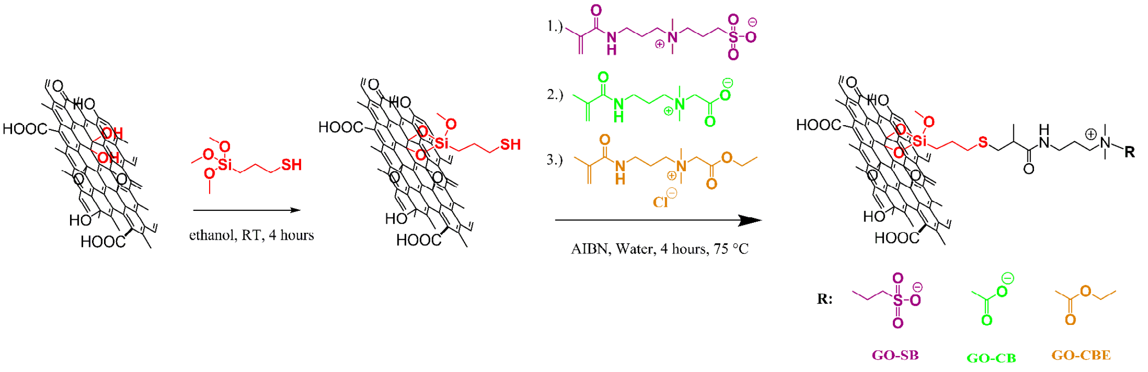
This study proposes a simple fabrication process for GO surface modification with betaines to improve the performance of ER suspensions. Fabrication process based on GO as a substrate for synthetic modification with betaine structures was applied for the first time in electrorheology. Modifications were confirmed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA). The dielectric relaxation strength as well as relaxation time was elucidated from dielectric data using Havriliak-Negami model to confirm the suitability of the prepared GO-based materials for ER applications. The improvement of internal structures rigidity of suspensions in silicone oil was investigated by rotational rheometry and also using on-line microscopic observation. The conductivity mechanism responsible for the ER effect was recognized by application of power-law model on the rheological data upon various electric field strengths in the range 0.5- 3 kV·mm^{-1}.

2. Experimental part

2.1 Materials

(3-Mercaptopropyl)trimethoxysilan and sodium hydroxide (NaOH) were obtained from BDH Laboratory Suplies (United Kingdom). Acetone and ethanol were purchased from Riedel-de Haën Laboratories Supplies (Germany). Azobisisobutyronitrile, Graphene Oxide (GO), Ethyl bromoacetate, N-(3-dimethylamino)propyl)methacrylamide, [3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide inner salt (SB), Amberlite IRA 400, dimethyl sulfoxide (DMSO), were purchased from Sigma-Aldrich (USA); used as received.

2.2 Synthesis



Scheme 1 Anchoring of betaine moieties onto GO surface

Synthesis of modified GO by 3-(trimethoxysilyl)propane-1-thiol (GO-SH)

GO (0.5134 g, 5 mmol hydroxyl and epoxy groups) was dispersed in ethanol (20 mL) and sonicated with ultrasonic probe (amplitude 20, cycle 0.5, 30s) UZ sonoplus HD 2070 (Bandeline, Germany) under argon atmosphere. Then (3-mercaptopropyl)trimethoxysilan (1 mL, 5 mmol) was added and the reaction mixture was stirred at room temperature for 4 hours under argon atmosphere. Later, the reaction mixture was transferred to centrifuge vials and low molecular weight side products were separated by centrifugation at 4100 *g* and washed with ethanol (3x 22mL). The GO- SH was dried at 80 °C and reduced pressure for 2 hours under argon atmosphere.

Synthesis of modified GO with sulfobetaine moiety (GO-SB)

GO- SH (0.255g, 0.09 mmol SH, based on TGA was dispersed in distilled water (30 mL) by using sonication probe (amplitude 20, cycle 0.5, 30s) under argon atmosphere. Then SB (0.5 g, 2 mmol) was added followed by addition of azobisisobutyronitrile AIBN (1 mol. %, 0.8 mg) dissolved in deoxygenated acetone (1 mL). Then the flask was immersed into an oil bath heated to 75 °C and the reaction mixture was stirred for 4 hours under argon atmosphere. The GO-SB was separated by centrifugation and washed with ethanol (3x 22mL). The GO-SB was dried at room temperature and vacuum overnight, then at 60 °C and reduced pressure for 4 hours.

Synthesis of modified GO with carboxybetaine ester moiety (GO-CBE)

GO-SH (0.215 g, 0.08 mmol SH) was dispersed in 25 mL of distilled water by using ultrasonic probe. Then CBE (0.53 g, 1.8 mmol) and catalytic amount of AIBN dissolved in 1 mL acetone was added. The reaction mixture was stirred at 75 °C for 4 hours under argon atmosphere. The product was separated by centrifugation at 4100 *g* and purified with dispergation and centrifugation in distilled water (28 mL) and ethanol (18 mL).

Synthesis of modified graphene oxide with carboxybetaine moiety (GO-CB)

GO-SH (0.136g, 0.05 mmol SH) was dispersed in 10 mL distilled water by using ultrasonic probe. Then CB water solution (0.311 g, 1.4 mmol) and catalytic amount of AIBN dissolved in 1 mL acetone was added. The reaction mixture was stirred at 75 °C for 4 hours under argon atmosphere. The product was separated by centrifugation at 4100 *g* and purified with dispergation and centrifugation in distilled water (28 mL) and ethanol (18 mL).

2.3. Methods

Characterization

Modification of the GO particles with betaine moieties was analysed using the FTIR spectroscopy, FTIR Nicolet 760 (Thermo Scientific, USA) in ATR mode. Element surface analysis was performed by scanning electron microscopy (SEM EDS; Quanta 200, FEI, Japan) equipped with energy-dispersive spectroscopy (EDS) microanalysis system. The amount of attached organic substances was determined by thermogravimetric analysis TGA/SDTA 851e (Mettler Toledo, Switzerland), heating rate 10 °C min^{-1}, in nitrogen atmosphere. ^{1}H NMR was performed on a 400 MHz VNMRS Varian NMR spectrometer (Varian, USA) equipped with 5mm ^{1}H-19F/15N-31P PFG AutoX DB NB probe at 25 °C in deuterium oxide as a solvent. The conductivity was measured at room temperature on three pellets prepared from each sample using four points van der Pauw's method after deposition of silver coating on both sides of pellets. The pellets were prepared from powders of modified GO under compression at 7 MPa in 13 mm diameter and 0.1–0.3 mm thickness.

Suspension preparation

Suspensions (1 and 5 wt. %) were prepared by mixing neat GO and modified GO particles with corresponding amounts of silicone oil (Lukosiol M200, viscosity η_c = 196 mPa.s, density d_c = 0.970 cm^{-3}, Chemical Works Kolín, Czech Republic). Before each measurement, the suspensions were stirred at first mechanically and then sonicated for 30 s.

Electrorheology

Rheological measurements were performed under controlled-shear-rate (CSR) mode using a rotational rheometer (Bohlin Gemini, Malvern Instruments, United Kingdom) in the range from 0.02-300 s^{-1}. The averaging and waiting time for datapoint was used to be 100 s for low shear rates and was decreased for datapoints at higher shear rates. The rheometer was modified for ER experiments and connected with DC high-voltage source TREK (TREK 668B, USA) to generate electric field strengths 0–3.0 kV·mm^{-1}. The suspensions were placed into parallel-plate geometry 40 mm in diameter with a 0.5 mm gap. Before each measurement step, the previously built-up particulate structures were destroyed by shearing the sample at the shear rate 50 s^{-1} for 80 s.

The yield stress τ_y was estimated by fitting of the rheological data with the Cho-Choi-Jhon model (ESI Tables S1-S4.) widely used in the literature in relation to ER suspensions [30, 31]. Furthermore, the data in the double-logarithmic plot of yield stress, τ_y, and electric field strength, E, were applied to power-law model, where $\tau_y = q \cdot E^a$. Parameter q is related to the stiffness of the internal structures, and parameter a characterizes the response of the particles to the application of an electric field.

Dielectric spectroscopy

The dielectric properties were measured with Impedance dielectric spectroscopy analyser, Novocontrol Concept 50 (Novocontrol, Germany) connected to the cylindrical sample cell BDS 1307 for liquid materials. Dielectric properties such as relative permittivity, ε', and dielectric loss factor, ε'', were investigated in a frequency range from 0.5 Hz to 2 MHz. The dielectric spectra were analyzed using the Havriliak-Negami model [41]

$$\varepsilon^*_{HN}(\omega) = \varepsilon'_\infty + \frac{\Delta\varepsilon'}{\left(1 + (i\omega \cdot t_{rel})^a\right)^b} \qquad (1)$$

where $\Delta\varepsilon' = \varepsilon'_s - \varepsilon'_\infty$ is dielectric relaxation strength, ε'_s, and ε'_∞, are relative permittivities at zero and infinite frequencies, f, respectively, ω, is angular frequency ($= 2\pi f$), t_{rel} is the relaxation time, and a and b are shape parameters which describe the asymmetry of the dielectric function.

Optical microscopy

Suspensions consisting of 1 wt. % particles in silicone oil were placed between two copper electrodes deposited on glass with a gap of 1 mm connected to a DC high-voltage source (Keithley 2400, USA). The formation of ER structures was observed with the help of an optical microscope (N 400M, China) linked to a digital camera.

3. Results and discussion

Synthesis and characterization

Introduction of betaine modification to GO was carried out in two steps fabrication as it is depicted in Scheme 1. In the first step, silanization of free OH groups from GO with thiolated silane derivate was performed [42] and in the second step thiol-ene click-chemistry between GO-SH and double bond of betaine alkene derivates was performed [43]. The size of the GO particles was just negligibly affected by the modification, since the size of the GO particles is in order of μm (Fig. S4) while the length of betaine moieties is in order of nm. The modification of graphene oxide was confirmed by FTIR. In spectra of all samples GO-SB, GO-CB and GO-CBE new peak at 1035 cm^{-1} characteristic absorption for stretching vibration N^+CH_3 bond and absorption at 1630 cm^{-1} for C=O stretching vibration in amides appeared after modification. The GO-SB spectra a new band appeared at 1153 cm^{-1} corresponding to sulphonate group. In carboxybetaine ester GO-CBE, the characteristic C=O vibration of ester appeared at 1740 cm^{-1}. It should be pointed out that the GO-CBE can be easily transformed from GO-CBE to GO-CB after hydrolysis in 0.1 M aq. NaOH in 1 hour. This characteristic allowed this material to be considered as pH responsible.

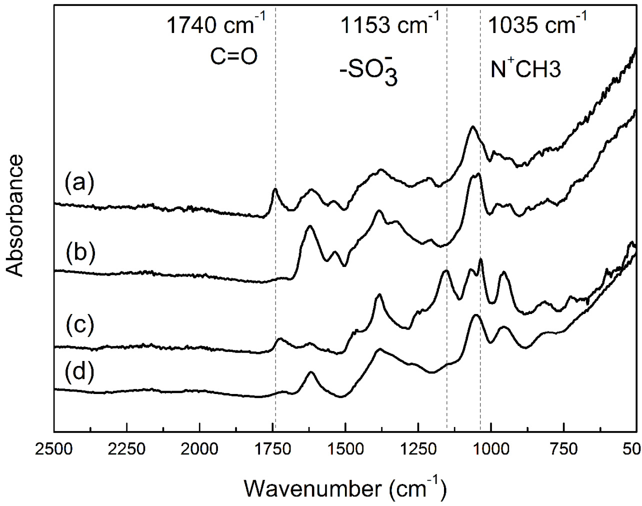


Figure 1 FTIR spectra for (a) GO-CBE (b) GO-CB (c) GO-SB (d)GO.

The presence of betaine modification was proven by atomic composition analysis performed by SEM EDS and summarized in Table 1. Compared to neat graphene all samples contain nitrogen atom, silicon and sulphur from silanization step. The sulphur content is higher in GO-SB sample due to sulfobetaine functionality. Small discrepancies at low at.% contents of elements can most like be attributed to the limitations of semi-quantitative SEM EDS investigations.

Table 1 Atomic composition of surface of neat GO and modified GO particles determined by SEM EDS analysis

	at.%			
	GO	GO-SB	GO-CB	GO-CBE
C	66.26	64.41	65.15	65.45
O	33.74	31.15	30.28	30.44
N		3.50	4.44	3.53
Si		0.11	0.09	0.36
S		0.83	0.04	0.22

The quantification of modification was estimated by TGA (Figure 2). At Around 100 °C the weight loss corresponds to water content, followed by decomposition of oxygen containing functionalities, such as hydroxyl, epoxy and carboxyl groups [44]. The weight loss of organic modifications occurs at 250 °C to 400 °C. The determination of modification for GO-CB, GO-CBE and GO-SBE respectively was assumed 9 wt. %, 9 wt. % and 11 wt. % respectively.

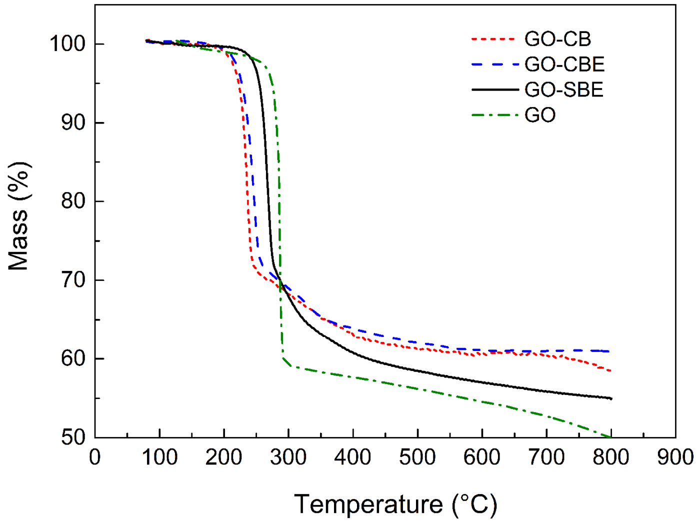


Figure 2 TGA analysis of neat GO and GO modified with betaine moieties

Electrical conductivity investigation

The electrical conductivities of GO-CBE, GO-CB and GO-SB in form of pellets reach values between 2.92 -6.62 x 10^{-8} S cm^{-1} (Table 2) which allows to consider these materials suitable for electrorheological suspensions [32]. The modification of the GO surface with betaines moieties increased the conductivity in order of one magnitude in comparison to neat GO 2.02x10^{-9} S cm^{-1}. This slight increase can be attributed to the various structures of negatively charged counterions. All three modifications contain positively charged quaternary ammonium group. In GO-SB the negatively charged counterion is sulphonate group with low pKa, which means that all the positive charge is compensated with sulphonate group resulting in restricted overall ion movement. On the other hand the carboxybetaine is derivative of carboxylate which has higher pKa, therefore some of the carboxyl groups are present in protonated form, and the positive charge in not fully compensated, which facilitates the charge movement. In both cases the negative charges are present on atoms covalently fixed in the betaine structure contrary to carboxybetaine ester, where the negative charge is present on chloride counterion, which interacts with the structure by electrostatic forces. This probably allows the most effectively the charge transport between the neighbouring structures, similar to the role of methanesulfonic anions in aniline oligomers [45].

Table 2: The conductivity, σ, of the GO and GO modified particles

Sample code	GO	GO-SB	GO-CB	GO-CBE
$\sigma\,[\times 10^{-8} \mathrm{S\ cm^{-1}}]$	0.20 ±0.05	2.92±0.52	4.54±0.72	6.22±0.36

Development of internal structures

The electrical conductivities data suggests these materials should be suitable components in electrorheological suspensions. The development of internal structures is related to the phase transition from the liquid-like to the solid-like behaviour of electrorheological suspensions after application of the external electric field. 1 wt. % of GO, GO-SB, GO-CB and GO-CBE, respectively were suspended in silicone oil and all systems showed formation of the chain like structures along the external electrical field strength of 1.5 kV mm^{-1}. This transition in performance is illustrated in on-line microscopic investigation in Figures 3-6.

In the absence of the external field the particles are randomly dispersed in the system (Figures 3-6a). It can be clearly seen that modification of the GO particles with betaine moieties, especially in case of the GO-CBE sample (Fig. 6a), improved dispersibility of the GO in silicone oil compared to the neat GO ones, which further positively influence the behaviour upon external electric field and partially contribute to the enhanced ER response. After the application of external electric field strength of 1.5 kV mm^{-1}, the particles are polarized and create induced dipoles oriented in the direction of the external field, resulting in formation of chain-like structures perpendicular to the electrodes (Figure 3-6b). For the neat GO samples in electric field (Fig. 3b) particles create only partial chain-like structures. Zwitterionic modification GO-SB and GO-CB samples (Fig. 4b and 5b) improves the chain-like structures and those are fully created between the electrodes with thin alignment which can be attributed to enhancement of charge motion within the system. The columnar structures observed in GO-CBE sample (Figure 6b) indicate the most promising enhancement of electrorheological performance of the system.

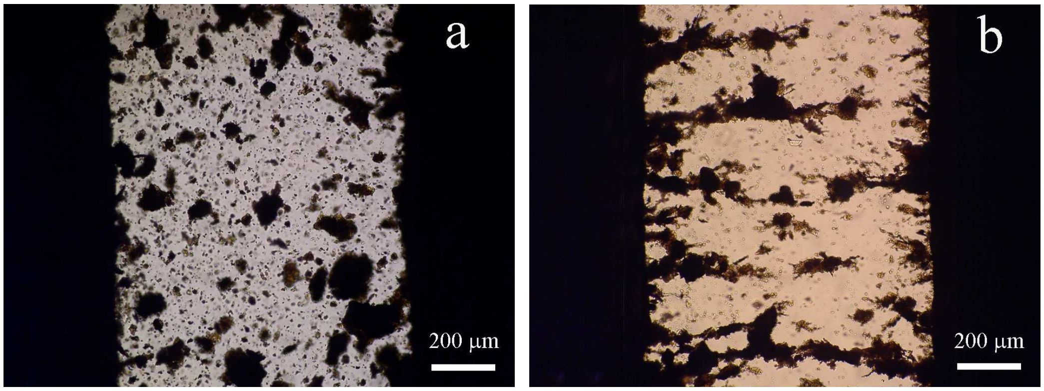


Figure 3 Optical microscopy of 1 wt. % silicone oil suspension of GO particles under various electric field strengths, E, (kV·mm^{-1}): (a) 0, (b) 1.5.

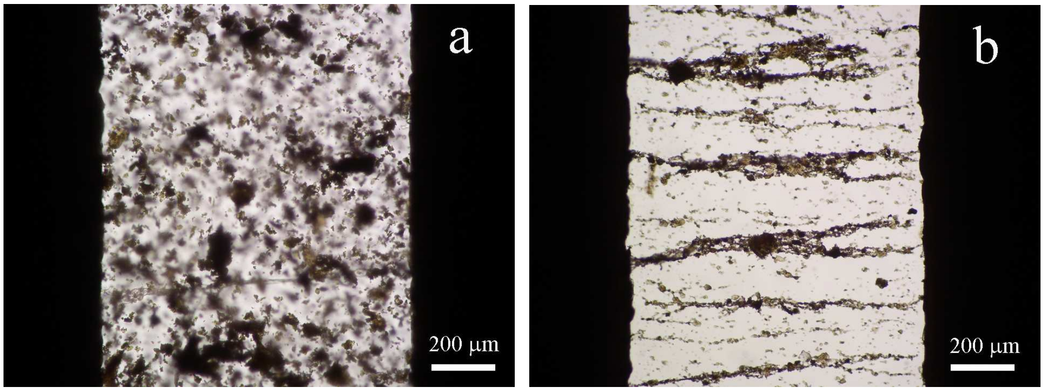


Figure 4 Optical microscopy of 1 wt. % silicone oil suspension of GO-SB particles under various electric field strengths, E, (kV·mm^{-1}): (a) 0, (b) 1.5.

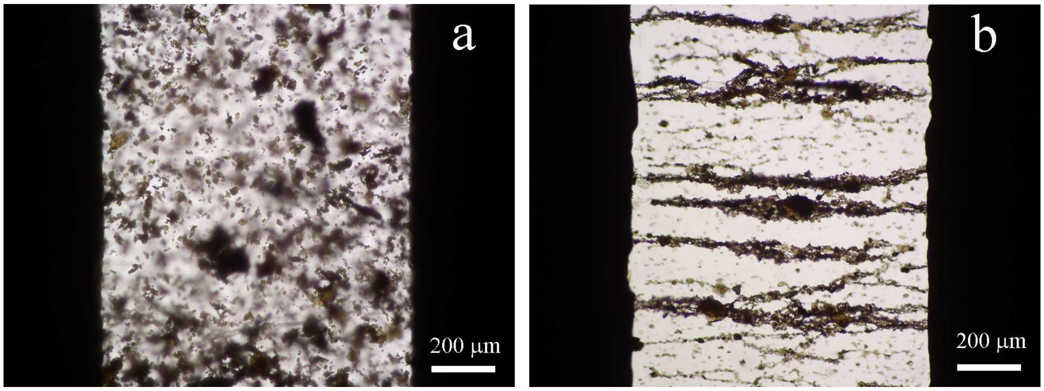


Figure 5 Optical microscopy of 1 wt. % silicone oil suspension of GO-CB particles under various electric field strengths, E, (kV·mm^{-1}): (a) 0, (b) 1.5.

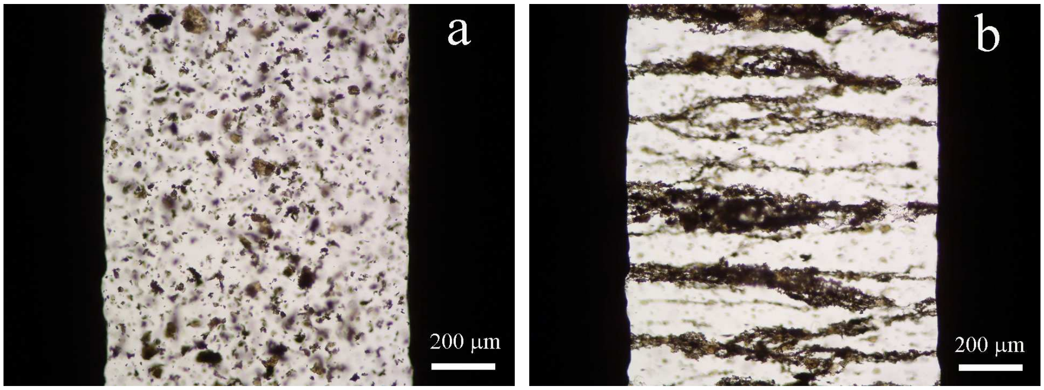


Figure 6 Optical microscopy of 1 wt. % silicone oil suspension of GO-CBE particles under various electric field strengths, E, (kV·mm^{-1}): (a) 0, (b) 1.5.

Electrorheology

Electrorheological behaviour was investigated in 5 % wt. suspensions of GO, GO-SB, GO-CB and GO-CBE in silicone oil in the range of 0-3 kV mm^{-1} and shear stress dependence on shear rate is summarized in Figure 7. In all cases electrorheological response was observed and increased gradually with electric field strength.

Suspensions of GO-SB similarly as neat GO (Figure 7a-b) particles exhibit nearly Newtonian behaviour in the absence of the external electric field strength. After the application of the external electric field, the particles are polarized resulting in the dramatic change from the Newtonian to pseudoplastic behaviour exhibiting the yield stress. Further, with increasing electric field strength, up to 3 kV mm^{-1}, the yield stress increases for GO and GO-SB, up to 40 Pa and 63 Pa, respectively and is consistent with previous observations [30].

Suspensions of samples GO-CB and GO-CBE (Figure 7c-d) exhibit slightly Non-Newtonian behaviour in the absence of the external field, due to the enhanced compatibility between particles and silicone oil. This effect can be assumed by weak acidity of the GO-CB particles and ethyl groups presented on GO-CBE particles, which allow hydrophobic interaction with silicone oil. On the other hand, in the presence of the external field, suspensions of modified GO particles exhibit considerably improved ER performance in the line of GO-SB, GO-CB and GO-CBE. The highest yield stress of suspension was observed for sample GO-CBE reaching 97 Pa.

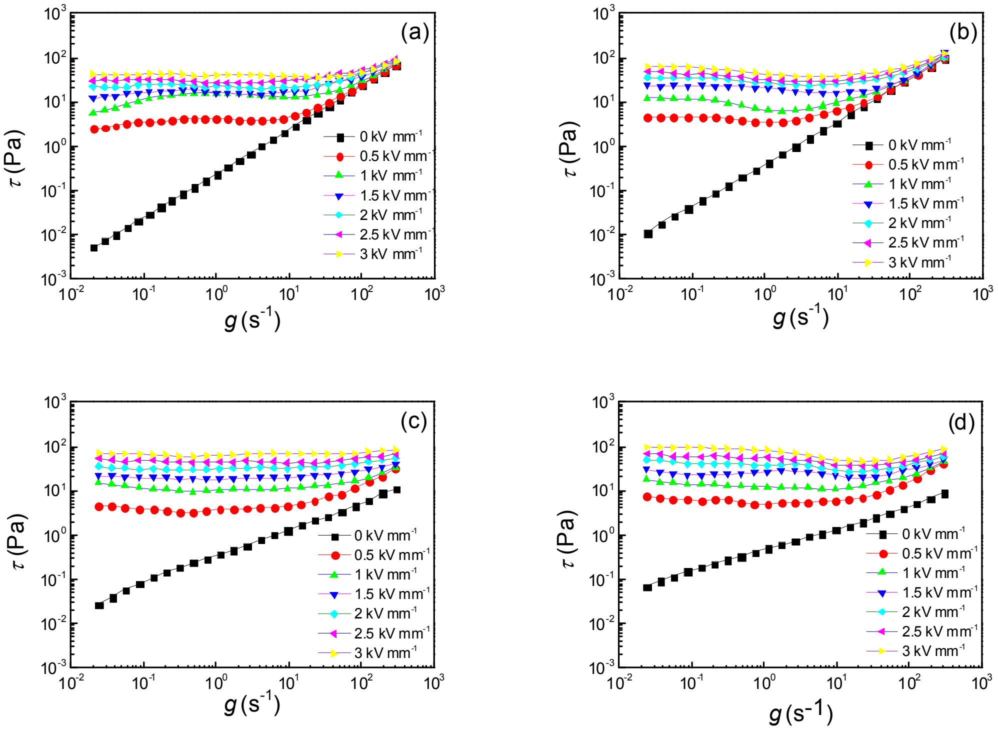


Figure 7. Dependence of shear stress on shear rate at various electric field strengths for suspensions of GO (a), GO-SB (b), GO-CB (c), GO-CBE (d), solid line between experimental points represents Cho-Choi-Jhon model fit.

In order to investigate the mechanism of the structure formation in GO-SB, GO-CB and GO-CBE samples, the calculated rheological data such as yield stress as a measure of rigidity of created internal structures, were plotted against external electric field strength and the data were fit with power-law model (Figure 8). The parameter *q* is related to the stiffness of the internal structures, and parameter a characterizes the response of the particles to the application of an electric field. The results from the fitting are summarized in Table 4. Since the parameter a is in all cases nearly 1.5, the τ_y increases with 1.5 as well. Therefore, behaviour of samples can be described by conductivity mechanism, where the conductivity mismatch between the particles and the medium is responsible for ER effect. Furthermore, parameters q and a increases in the line, GO, GO-SB, GO-CB and GO-CBE indicating improved ER performance, when higher values of the parameter q and values of the parameter a reaching 1.5 reflect more developed internal structures. This result is also confirmed by the higher values of the τ_y as a measure of the rigidity of the internal structures created after application of the external electric field in the same line (GO, GO-SB, GO-CB and GO-CBE).

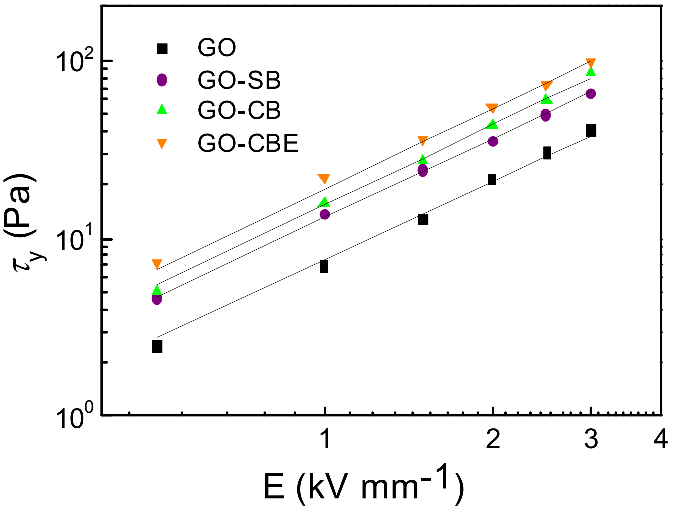


Figure 8. Dependence of yield stress on electric filed strength of neat GO and modified GO particles suspensions. Solid red lines represent Power-law model fits.

Table 4. Parameters of Power-law model fits of neat and modified GO particles suspensions

Sample Code	q [Pa]	a
GO	7.6	1.466
GO-SB	13.1	1.475
GO-CB	15.4	1.487
GO-CBE	18.8	1.510

Dielectric spectroscopy

In order to confirm the appropriate ER properties of GO, GO-SB, GO-CB and GO-CBE suspensions, the dielectric properties were analysed in the broad frequency range between (0.5 - 2 x 10^6) Hz (Figure 9) because the dielectric properties are closely related to the formation of the internal structures and ER suspensions performance [28, 32, 46]. The yield stress of the ER suspensions is closely related to the crucial parameters such as dielectric relaxation strength and relaxation time. These parameters were obtained from the fitting of the measured data with H-N model (Eq. 1). All parameters of this model are summarized in the Table 5. The increase of dielectric relaxation strength of the samples can be seen in the line GO, GO-SB, GO-CB and GO-CBE reaching values 0.47, 0.62, 1.03 and 1.72, respectively (Figure 10a). Also the relaxation time corresponding to the peak position (Figure 9b, Table 5) as a response of the particles to the external electric field is shorter in the same line GO, GO-SB, GO-CB and GO-CBE reaching 0.29 s, 0.26 s, 0.14 s and 0.04 s, respectively that corresponds to interfacial polarization between particles and silicone oil. Differences in ER performance are attributed to the character of surface modification. All modified structures have quaternary ammonium group, however the difference is in the terminating moiety (Scheme 1). In case of GO-SB, the terminating sulphonate group is strongly acidic with low pKa and protonization of ions and subsequent motion is restricted. In case of GO-CB the carboxybetaine structure with higher pKa, if compared to sulphonate moiety, allows protonization of carboxylate moiety and enhance charge motion. GO-CBE is terminated by carboxybetaine ester and contain Cl^- ion as a counterion to the quaternary ammonium group, which most effectively contributes to enhanced charge transport. Therefore it can be stated that simple fabrication process for modification of the GO is a synthetic platform for tune ability of ER performance of the resulted systems.

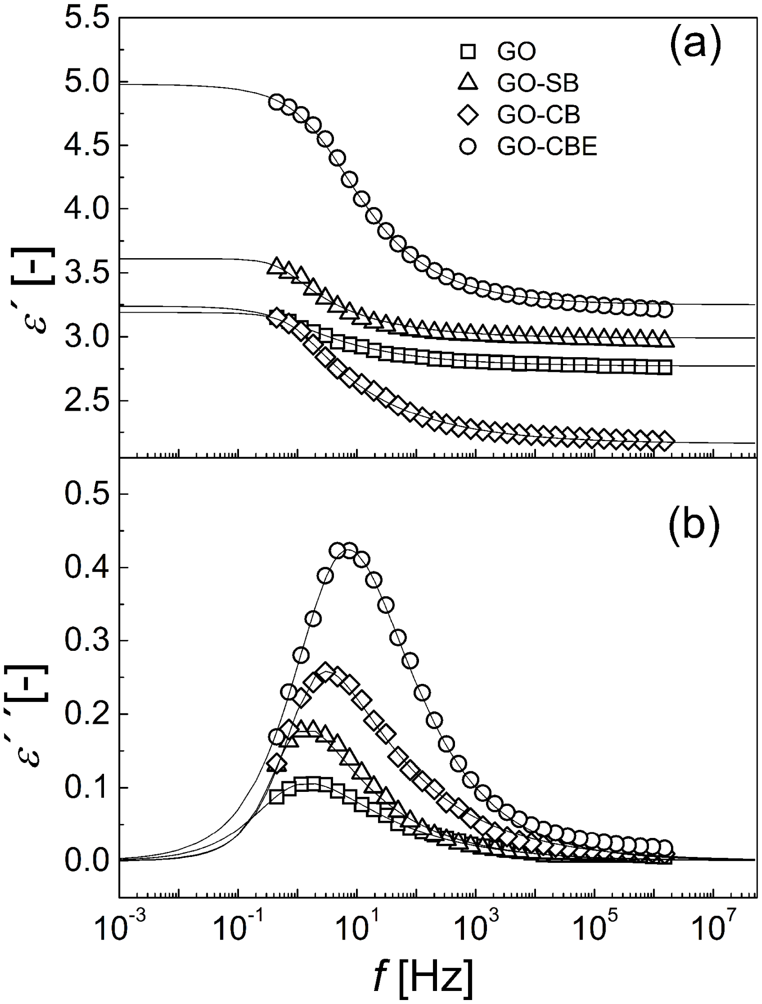


Figure 9 Havriliak-Negami fit of ε‘ and ε‘‘ on frequency dependence of suspensions of neat GO and modified GO particles

Table 5: Parameters of Havriliak-Negami model for GO and modified GO suspensions

Sample Code	ε'_s	ε''_∞	$\Delta\varepsilon'$	t_{rel} [s]
GO	3.24	2.77	0.47	0.29
GO-SB	3.61	2.99	0.62	0.26
GO-CB	3.19	2.16	1.03	0.14
GO-CBE	4.98	3.25	1.73	0.04

4. Conclusion

In this study the GO particles were successfully modified with sulfobetaine, carboxybetaine and carboxybetaine ester moieties using simple fabrication process based on silanization and thiol-ene click-chemistry. Electrical conductivity measurement reveals appropriate values for ER systems. Chain-like structures of synthesized particles were observed in the silicone oil suspensions under on-line microscope investigation in the presence of the external field in all cases. ER investigation in the absence as well as in the presence of the external field was performed and the conductivity mechanism was recognized to be responsible for development of the internal chain-like structures. The yield stress reached up to 97 Pa for 5 wt. % GO-CBE suspension, which is considerably higher than that observed by other research groups. Dielectric spectroscopy showed that two crucial factors considerably influencing the ER performance, dielectric relaxation strength and relaxation time, were improved in the same line as conductivity (GO, GO-SB, GO-CB and GO-CBE). The simple fabrication process offers tune ability in applied alkene derivates with different distance between charged group in betaines and in case carboxybetaine esters character of ester group and counterion.

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