

## MODIFICATION OF THE CARBONYL IRON PARTICLES USING SI-ATRP APPROACH WITH POLY(2-(1H-PYRROLE-1-YL)ETHYL METHACRYLATE

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### Abstract

This study is focused on the synthesis of core-shell type of magnetic particles, where magnetic core is carbonyl iron (CI) microparticles and conducting shell is poly(2-(1H-pyrrole-1-yl)ethyl methacrylate) (PPEMA) synthesized using atom transfer radical polymerization (ATRP) technique. In order to obtain core-shell particles the surface-initiated (SI)-ATRP is used, where both benefits, magnetic behaviour of core and conducting behaviour of shell, are advantages for their intended application as materials for electromagnetic shielding of piezo-resistors. Basic characterizations of the neat CI and CI-PPEMA particles such as magnetization saturation using and conductivity using dielectric spectroscopy are performed. Also the confirmation of the controllable coating using gel permeation chromatography and nuclear magnetic resonance are provided. The successful modification of CI with PPEMA is investigated using Fourier transform infrared spectroscopy. It is also proved by dielectric spectroscopy if such CI-PPEMA particles possess enhanced properties in comparison to neat CI particles and thus should exhibit the improved capability in electromagnetic shielding.

**Keywords:** Carbonyl iron, SI-ATRP, pyrrole, hybrids, electromagnetic shielding

### 1. INTRODUCTION

Magnetorheological elastomers (MREs) are special type of materials, those toughness can be tuned by application of external magnetic field and generally belong to the class of materials called smart materials [1-3]. These are usually composed of two phases represented by the filler and matrix, when filler is in the most cases carbonyl iron (CI) particles possessing excellent magnetic performance and elastomeric matrix mainly based on various polydimethylsiloxanes (PDMS) [4, 5] or synthetic rubbers such as SBR, NBR, etc. [6, 7].

Next to the already mentioned controllable toughness, also other properties of such materials can be achieved, such as magnetostriction or electromagnetic shielding [8, 9]. In this case the proper dispergation of the particles is necessary and also the off-state stiffness of the matrix play a crucial role in the case of magnetostriction [10] or proper dielectric and magnetic properties are necessary in case of electromagnetic shielding [11].

There are various approaches, how to reach the mentioned goals. In order to reach controllable off-state stiffness of the matrix, in case of PDMS, the lower cross-linking density can be achieved by establishing the ratio between the monomer and cross-linker [10] or addition of the silicone oil to the PDMS systems [12]. In case of electromagnetic shielding, the addition of various conducting fillers to the MREs can be used [13], or utilization of the hybrid fillers based on magnetic particles [14] or development of core-shell particles mainly based on non-covalent modification [15].

Therefore the main aim of this study is to prepare the magnetic particles covalently modified with conducting polymer poly(2-(1H-pyrrole-1-yl)ethyl methacrylate) (PPEMA) by utilization of atom transfer radical polymerization (ATRP) approach enabling us to prepare the core-shell particles with covalently bonded conducting polymer layer. Such particles were properly characterized by various spectroscopy techniques and magnetic capability and electrical conductivity were properly investigated.

## 2. EXPERIMENTAL

### 2.1. Materials

CI BASF, ES grade min. 97% iron contain. 2-chloroethanol (EtOCl, 97%), pyrrole (Py, 98%) methacryloyl chloride (98%), aminopropyl(triethoxy) silane as a coupling agent (APTES, 97%), initiator  $\alpha$ -bromoisobutryl bromide (BiBB, 98%) where the initiator bonding was performed in the presence of proton scavenger, triethyleneamine (TEA,  $\geq 99\%$ ), 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,  $\geq 99\%$ ) and sodium sulfate (anhydrous,  $\geq 99\%$ ) were used as a drying agent. All chemicals were purchased from Sigma Aldrich (USA) and were used without further purification. Tetrahydrofurane (THF, p.a.), dichloromethane (p.a.), isohexane (p.a.), ethylacetate (p.a.), acetone (p.a.), ethanol (absolute anhydrous, p.a.), toluene (p.a.), and potassium hydroxide (KOH, p.a.) were obtained from Penta Labs (Czech Republic). Deionized water (DW) was used during all experimental processes and washing routines.

### 2.2. Initiator bonding

The CI particles have been covalently modified with APTES according to the procedure described elsewhere [10]. The NH<sub>2</sub> functional groups presented on the surface of after APTES modification were used as active sites for attachment of BiBB molecules. In a simple procedure, the CI (5 g), dried THF (60 mL), and TEA (12 mL) were mixed under argon atmosphere at a temperature of  $\sim 5$  °C ensured by an ice/water bath, while BiBB (10 mL) was dropwise added. The product was washed with THF, acetone and DW several times and then decanted using permanent magnet. The excess of water from treated particles was removed by vacuum drying at 60 °C overnight.

### 2.3. Synthesis of 2-(1H-pyrrole-1-yl)ethyl methacrylate monomer

There is a two-step synthesis, when firstly freshly distilled Py reacts with EtOCl. The synthesis was performed as follows: Magnetic stirrer and KOH were evacuated for 30 minutes in 3-neck flask and backfilled with argon. Dried DMSO (100 mL) was added under argon atmosphere. Freshly distilled Py (4 mL) was bubbled with argon for 15 minutes and added to the mixture. Finally, 30 minutes bubbled EtOCl (1.6 g) with argon was added dropwise at velocity of 4 mL/hour. Reaction was carried out for 12 hour at ambient temperature. Mixture was extracted with dichloromethane and brine 3 times and dried over sodium sulfate. Then the column extraction was performed with eluent isohexane:ethylacetate in ratio 3:2, then again column extraction in isohexane:ethylacetate in ratio 2:1 and pure product, 2-(1H-pyrrole-1-yl)ethanol (HEP) (yellowish liquid) after evaporation of solvent excess using vacuum rotator has been obtained. Yield of this reaction was calculated as 75 %. The product was dissolved in CDCl<sub>3</sub> and characterized using nuclear magnetic resonance (NMR). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.70, 6.18 (t, C<sub>4</sub>H<sub>4</sub>N), 4.07 (t, NCH<sub>2</sub>CH<sub>2</sub>), 3.84 (t, HOCH<sub>2</sub>CH<sub>2</sub>), 1.75 (s, COH).

In the second step, the reaction was carried out in the 3-neck flask equipped with magnetic stirrer evacuated for 30 minutes and backfilled with argon. Dried dichloromethane (20 ml) was added to the mixture under argon atmosphere. HEP (1.5 g) with Et<sub>3</sub>N (2.8 ml) were bubbled 15 minutes with argon and added to the mixture and the temperature between 0-5 °C was maintained for 1 hour. Freshly distilled methacryloyl chloride (1.6 ml) was added dropwise at velocity 5 ml/hour. Then was the mixture further maintained for 2 hours between 0-5 °C. Reaction was carried out for another 14 hours at ambient temperature. First extraction was performed with dichloromethane to the water 3 times, in order to dissolve created ammonium salt. Second extraction was performed with dichloromethane to the brine 3 times to purify the product and dried with sodium sulfate. Product was obtained after evaporation of solvent excess with vacuum rotator. Finally, the product was cleaned through the neutral alumina using dichloromethane. Yield of this reaction was calculated at 72 %.

## 2.4. ATRP polymerization of PPEMA

In order to prove that prepared monomer PEMA can be synthesized using ATRP approach, the general procedure was utilized. Schlenk Flask (SF) equipped with magnetic bar was evacuated several times and then backfilled with argon. Then monomer PEMA (0.3 g; 1.3 mmol), PMDETA (0.0035 mL; 0.016 mmol), EBiB (0.0025 mL; 0.016 mmol) and anisole (0.3 mL; 50 vol. %), were stepwise injected into the SF under argon atmosphere. Several freeze-pump-thaw cycles with liquid nitrogen were performed to eliminate residual oxygen from the polymerization mixture and finally the flask was filled with argon. The polymerization was initiated by addition of CuBr catalyst (0.0023 g; 0.016 mmol) to polymerization mixture and placing the reaction flask into the oil bath pre-heated to 70 °C. The reaction mixture was stirred at 250 rpm for 4.5 hours and then the reaction was stopped by opening the flask.

## 2.5. Grafting of CI with PPEMA

The CI particles with bonded initiator (1 g) were transferred into a SF equipped with a gas inlet/outlet and a septum. The system was evacuated and backfilled with argon several times. Then the similar procedure as for polymerization of PEMA was used and same ratios as were described above were used. The reaction was performed in glove-box and mechanical stirring was used to achieve the proper particle dispersion during the synthesis. The resulting particles were washed with THF and acetone and collected using permanent magnet. Particles were dried in the vacuum oven under reduced pressure and 50 °C and further analyzed. The grafted polymer chains which grown similarly as the polymer chains from sacrificial initiator were investigated using gas permeation chromatography (GPC).

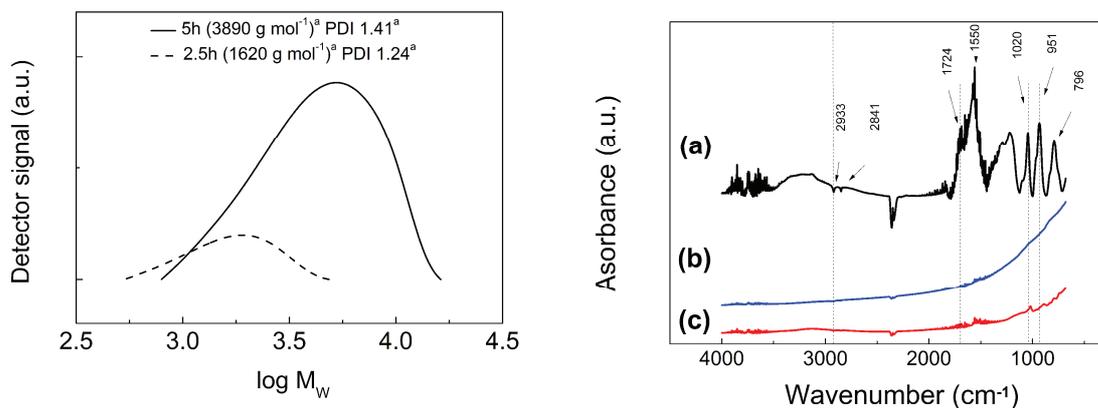
## 2.6. Characterization

<sup>1</sup>H 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 dispersity ( $\bar{D}$ ) of PPEMA chains were investigated using GPC technique on the GPC instrument (PL-GPC220, Agilent, Japan) equipped with GPC columns (Waters 515 pump, two PPS SDV 5 μm 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 GPC analysis were prepared by their dilution with THF, followed by the purification process, in which they were passed through a neutral alumina column. 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 attenuated total reflectance (ATR) technique with a Germanium crystal were employed. The spectra were recorded at room temperature. 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 which were performed by two-point method at laboratory temperature with the help of electrometer (Keithley 6517B, USA). Dielectric properties were investigated also on the pellets using impedance analyzer (Novocontrol, Concept 40, Germany).

## 3. RESULTS AND DISCUSSION

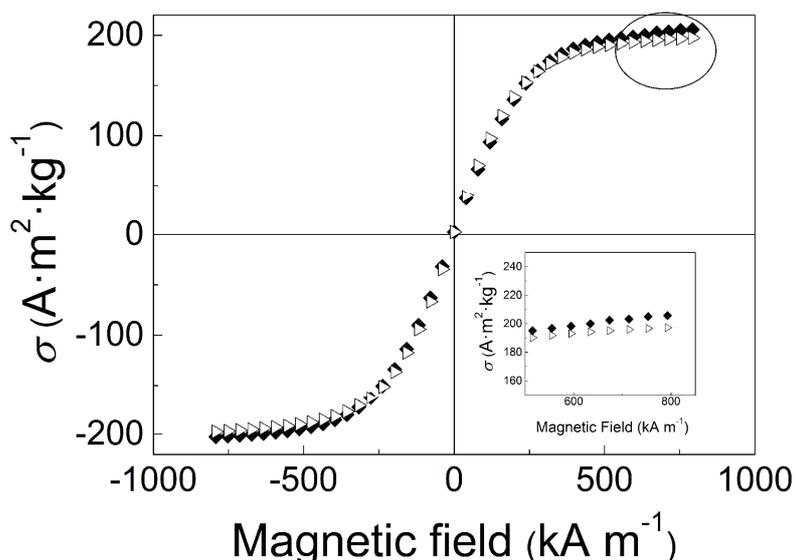
### 3.1. SI-ATRP of PPEMA from the surface of CI particles

The PPEMA was investigated using both GPC and FTIR. In addition, FTIR of the neat CI as well as CI-PPEMA particles were investigated and the spectra can be seen in the **Figure 1 right**. GPC of PPEMA (**Figure 1 left**) proved controlled radical polymerization and thus controllable thickness of the PPEMA shell on the surface of the particles similarly as was done elsewhere [10]. It can be seen that polymerization proceeded relatively quickly due to the presence of the CI particle those enhancing the catalysis of the ATRP process (**Figure 1 left**). The presence of the grafted polymer on the surface of CI was confirmed via FTIR (**Figure 1 right c**) where typical absorption bands for PPEMA also appears in the CI-PPEMA particles.



**Figure 1** (left) GPC spectra of the of PPEMA chains formed at various times during grafting process and (right) FTIR spectra of the (a) neat PPEMA, (b) neat CI, and (c) CI-PPEMA

### 3.2. Magnetic properties



**Figure 2** Magnetic properties of neat CI (◆) and CI-PPEMA (▷) particles

As can be seen in the **Figure 2**, the magnetization saturation of the neat CI particles is 198 emu/g and nearly negligible coercivity and magnetic remanence was measured. After covalent modification of the CI with PPEMA, the magnetization saturation just negligibly decreased to 192 emu/g probably due to the nano-size thickness of the PPEMA polymer layer, which was also seen in the case of utilization of ATRP for modification of CI particles elsewhere [10]. Thus the magnetic properties sustain on the same level, while the conductivity was considerably improved as was investigated further in the paper.

### 3.3. Conductivity and dielectric properties

In order to confirm the possibility of such CI-PPEMA particles for application as electromagnetic shielding material, the dielectric spectra were measured (see **Figure 3**). Since the both magnetic and electric properties play an important role in electromagnetic shielding, this investigation brings crucial information of the suitability of such particles. The magnetic properties were negligibly affected by PPEMA coating, while the conductivity increased in three orders of magnitude. Therefore, it can be stated that such improvement in the dielectric properties will lead also to enhance electromagnetic shielding.

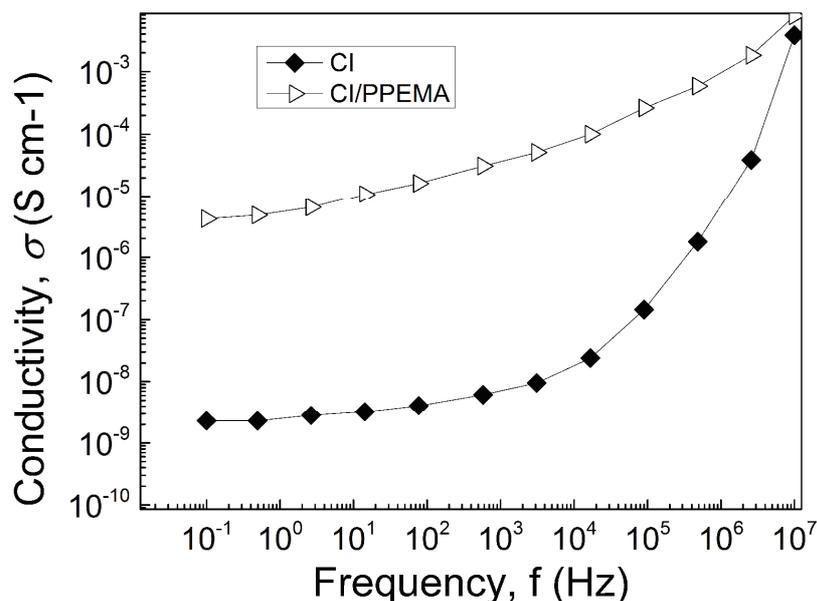


Figure 3 Dielectric spectra for neat CI (◆) and CI-PPEMA (▷) particles

#### 4. CONCLUSION

In this study, it was developed a novel approach how to synthesize the particles possessing both magnetic and electric activity, when the magnetic particles of CI were controllably coated with novel conducting polymer PPEMA. The monomer PEMA was synthesized and characterized via <sup>1</sup>H NMR. The polymerization was optimized and final product was characterized using GPC and conductivity measurements. Successful grafting and influence of the CI particles on the polymerization was investigated and confirmed via FTIR and GPC, respectively. Final properties of CI-PPEMA such as dielectric properties were correlated with bare CI in order to see the difference in the mentioned properties and it was proved that such modification can lead to the improved capability of such system in electromagnetic shielding.

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