

The Surface Modification of Magnetic Particles with Polyamidoamine Dendron

Michal Sedlacik^{1, a)}, Tomas Plachy^{1, b)} and Daniela Vaclavkova¹

¹Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, T. Bata Ave. 5678, 760 01 Zlín, Czech Republic

^{a)} Corresponding author: msedlacik@utb.cz

^{b)} plachy@utb.cz

Abstract. Magnetorheological elastomers are important kind of intelligent systems that can alter their properties upon an application of an external magnetic field. Crucial for their performance is interaction between polymer matrix and magnetic filler, thus, it is necessary to control the compatibility between the matrix and magnetic particles. In this study, polyamidoamine dendron was successfully introduced onto surface of carbonyl iron particles using divergent approach in order to provide novel magnetic particles for magnetorheological elastomers. The presence of a thin layer of polyamidoamine dendron on the carbonyl iron particles was confirmed by energy dispersive X-ray, infrared spectroscopy and transmission electron microscopy, which confirmed a thin layer in nanometers formed on the surface of the particles. The coated carbonyl iron particles exhibited superior chemical stability when compared to non-coated ones, while the saturation magnetization decreased only negligibly from 207.0 emu g⁻¹ to 203.5 emu g⁻¹ for pure carbonyl iron particles and polyamidoamine dendron-coated carbonyl iron particles, respectively.

INTRODUCTION

Materials significantly altering their properties according to external stimulus are called intelligent systems. Important part of current intelligent systems comprises magnetorheological elastomers (MRE) as a new group of materials exhibiting change of properties depending on external magnetic field applied¹. Depending on applied field strength such materials reversibly change their dimensions and stiffness (in controlled way) and thus they can be utilized in systems such as actuators². Their wider application is restricted by several aspects as low corrosion resistance of particles or insufficient wetting of particles by polymer matrix. Briefly to the latter case, magnetic particles have high surface free energy while polymers used for elastic matrix such as silicone, polyurethane or other thermoplastic elastomers possess low surface free energy which leads to the separation of magnetic particles into aggregates during the crosslinking process and, additionally, the wetting of formed aggregates with the matrix is worse leading to defects in the contact area particles–matrix hindering higher possible performance³. The modification of magnetic particles with polymers can decrease the surface free energy of particles and hence to improve the mutual compatibility between two discussed phases⁴. Moreover, the contact area of particles with polymer matrix can be even represented by chemical bonds when the corresponding shell layer is provided regarding to the elastomeric matrix used. However, an excessively thick shell/layer of magnetic particles can significantly decrease their magnetic properties resulting in lower performance.

Hence, the magnetic particles are modified with dendrimer shell layer via accurately controllable technique utilizing dendron surface modification in this study, since the technology of dendrites have been recently continuously

improved⁵. Here, the magnetic carbonyl iron microparticles are modified firstly with (3-Aminopropyl)triethoxysilane (APTES) in order to introduce $-NH_2$ groups on the surface of particles. Then, the as-obtained particles react through the vinyl group in methyl acrylate (MA), whose functional group further react with groups from ethylenediamine (ED) giving a rise a system with $-NH_2$ groups on its surface, again. Repeating described steps, the n-generation (Gn) dendrimer can be obtained. The influence of dendrimer structure generation on magnetic properties is further evaluated as an important factor for the future utilization of developed particles in novel MREs with improved performance.

EXPERIMENTAL

Materials

Carbonyl iron (CI) particles (SL type, $d_{90} = 9 \mu m$) were obtained from BASF company. Anhydrous methanol, APTES, ED and MA were purchased from Sigma Aldrich. Before use, methanol was further dried using a molecular sieves and ED was dried using a sodium. Methyl acrylate and APTES were used as delivered. Other common chemicals like ethanol, acetone, and toluene were purchased from Penta chemicals and used as delivered.

Synthesis of Polyamidoamine Dendron on Surface of CI Particles

Firstly, CI particles were treated with 0.05 M HCl in order to remove impurities and iron oxides from the surface and to activate the surface by introducing the hydroxyl groups ($-OH$)⁶. After the treatment, particles were washed in distilled water, ethanol and acetone and dried in a vacuum oven at 60 °C for 1 h. The APTES was introduced on the surface of particles in order to provide $-NH_2$ groups that can further serve as a place for the growth of the polyamidoamine (PAMAM) dendron. Briefly, activated CI particles (45 g) were mixed with redundant amount of toluene (200 ml) and APTES (5 ml) and the mixture was vigorously stirred for 6 h at toluene boiling temperature (ca 110 °C; STEP 1 in Fig. 1). After the treatment, particles were again washed in distilled water, ethanol and acetone and dried in a vacuum oven at 60 °C for 1 h and further stored in a desiccator.

The growth of the PAMAM dendron was done by repeating “step-by-step” synthesis when $-NH_2$ and $-CH_3$ -terminated ED and MA molecules, respectively, were alternately added into the structure. Thus, CI particles modified with APTES were further modified with MA. Briefly, CI particles modified with APTES were put into a 3-neck flask with dried methanol and MA dispersed in an excess of methanol was dropwise added to the mixture in the molar ratio of MA:APTES 2:1. The reaction was cooled at 5 °C for 1 h and then left at room temperature for 12 h. The particles were then washed with methanol and dried at 60 °C for 24 h (STEP 2 in Fig. 1). The methylene groups on the surface can further react with $-NH_2$ groups from an external source. Thus, to the system consisting of CI particles coated with APTES and containing MA on its surface was further added ED in methanol solution at a room temperature to give a rise of CI-PAMAM-G0 (G0 = the core of PAMAM dendron, Fig. 1). The reaction was vigorously mixed and run for 16 h in nitrogen atmosphere. By repeating the addition of ED or MA CI particles consisting of single layers CI-APTES-MA-ED-MA-ED-MA were obtained and are further labelled as CI-PAMAM-G1.5.

Particle Characterization

Morphology and size of the particles were observed using a scanning electron microscopy (SEM; Nova NanoSEM 450, FEI company) and qualitative elemental microanalysis was performed by the Octane SSD (area 30 mm²) energy dispersive X-ray (EDX) detector (AMETEC, Inc.) integrated into the SEM. Fourier-transform infrared (FTIR) spectra were measured via the DRIFT method in a range of 4000–500 cm⁻¹ on a Nicolet 6700 (Nicolet, USA). The particles were mixed with dry KBr to form pellets which were used for the measurement. A thickness of grafted layer was observed using a transmission electron microscope (TEM, JEM-2100Plus, Jeol, USA). The samples for TEM analysis were prepared by dispersing the particles in methanol and a dropping onto a copper grid. The magnetic properties of bare CI particles as well as their coated analogues were investigated in an external magnetic field in the range $\pm 780 \text{ kA m}^{-1}$ using a vibrating-sample magnetometer (VSM, Model 7404, Lake Shore, USA) at laboratory conditions. To observe resistance against the corrosion the particles under investigation were dispersed in a 0.05 mol L⁻¹ HCl, and the pH value of the solution as a function of time was recorded using the pH-meter (Greisinger electronic, GPRT 1400, AN, Germany).

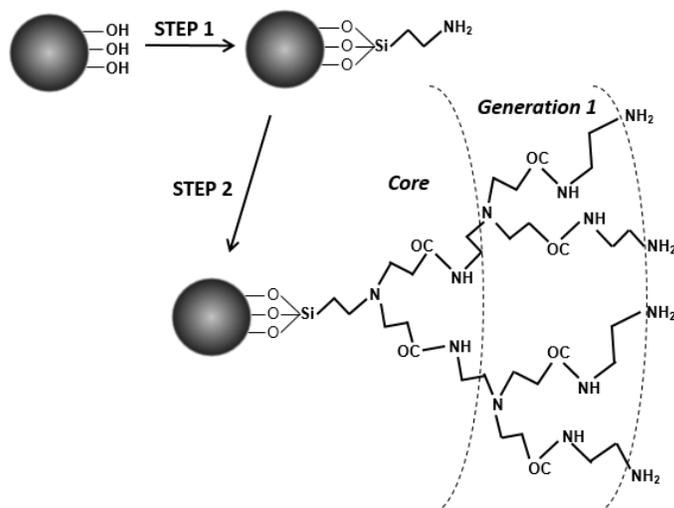


FIGURE 1. Diagram of synthesis of CI-PAMAM-G1.5.

RESULTS AND DISCUSSION

Carbonyl iron particles employed in this study are of spherical shape with size in micrometers and very high polydispersity (Fig. 2a). It can be seen that coating process did not affect the size of the particles reflecting the presence of very thin film created through introducing the PAMAM dendron on their surface (Fig. 2b).

In order to confirm the presence of PAMAM dendron on the surface of CI-PAMAM-G1.5 particles FTIR, EDX, and TEM were used. Energy dispersive X-ray spectroscopy (Tab. 1) confirmed the successful coating process with the presence of nitrogen and silicon elements. Besides the iron as a main element of the magnetic particles which was presented in the amounts over 94 wt.% in both samples, CI-PAMAM-G1.5 particles contains further low amount of silicon and nitrogen which are presented in the polymeric layer (Fig. 1). Presence of carbon and oxygen in pure CI particles come from as impurities from precursor of CI particles (pentacarbonyl iron) and possible oxidized layer on the particles.

The change on the surface of particles before and after the coating process was further investigated using FTIR spectroscopy. Even though the presented PAMAM layer is very thin, the peaks at 2921 cm^{-1} and 2856 cm^{-1} for CI-PAMAM-G1.5 representing $-\text{CH}_3$ groups in aliphatic substances were clearly observed (Fig. 3). The presence of these peaks at these wavelengths is typical for PAMAM dendrons or dendrimers⁵.

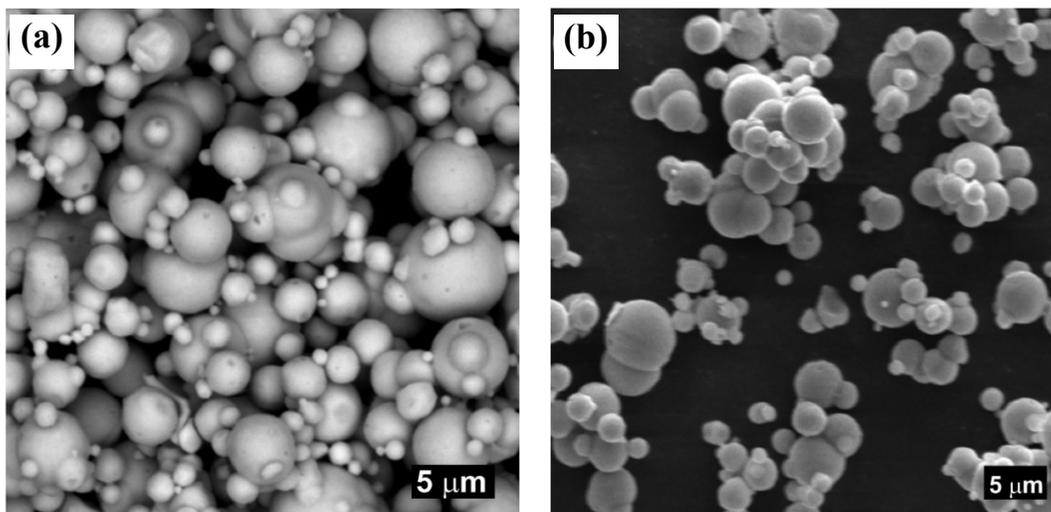


FIGURE 2. SEM images of (a) CI particles and CI-PAMAM-G1.5 particles.

Table 1. Element composition (expressed in weight ratio) of surface of CI and CI-PAMAM-G1.5 particles.

Element	CI	CI-PAMAM-G1.5
Fe	95.66 ± 0.20	94.94 ± 0.29
C	3.06 ± 0.18	3.37 ± 0.20
Si	—	0.13 ± 0.03
O	1.28 ± 0.09	1.13 ± 0.11
N	—	0.43 ± 0.19

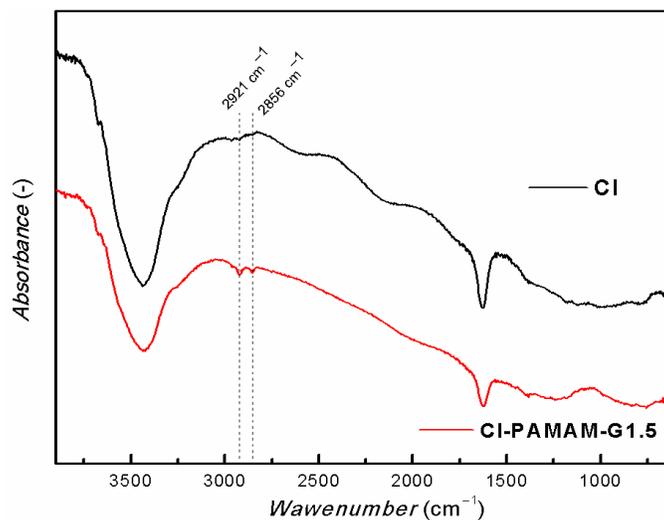


FIGURE 3. FTIR spectra of CI and CI-PAMAM-G1.5 particles.

Transmission electron microscopy is a commonly used technique to confirm growth of thin polymer layer on dense particles. While on surface of pure CI particles no polymeric or iron oxide layer can be observed (Fig. 4a), in the case of CI-PAMAM-G1.5 particles a thin layer in units of nanometers confirming the presence of polymeric layer can be seen. Such very thin layer can combine outstanding chemical and thermal stability of the magnetic particles without significantly affecting their magnetic properties.

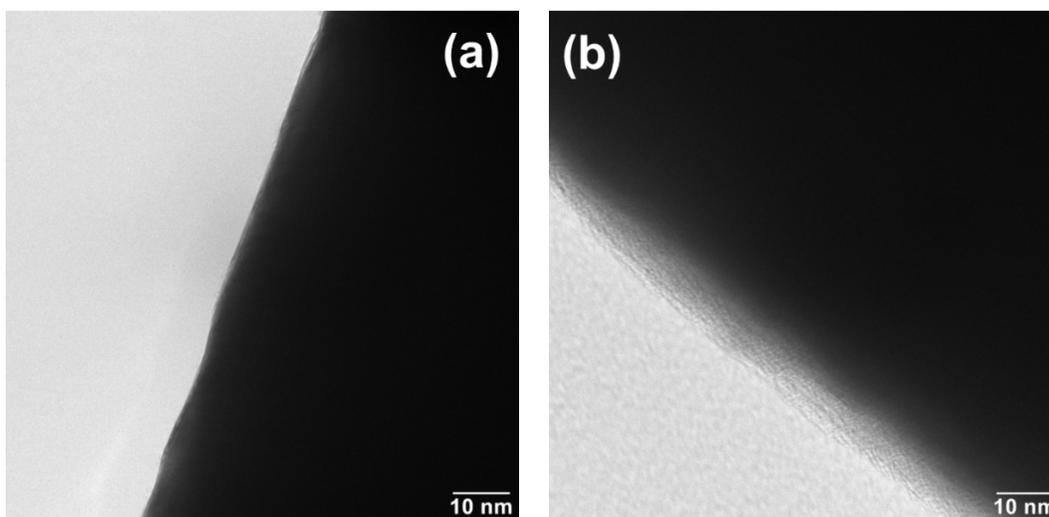


FIGURE 4. TEM images of (a) pure CI particles and (b) CI-PAMAM-G1.5 particles.

One of the important feature of magnetic particles for their real utilization is their saturation magnetization (M_s) which reflects their magnetic capabilities. Since both samples did not exhibit M_s in measured region, the obtained values of magnetization at 760 kA/m were taken as reference values close to the M_s . These values of magnetization were 207.0 and 203.5 emu g⁻¹ for pure CI and CI-PAMAM-G1.5 particles, respectively (Fig. 5). Many CI particles coated with various polymeric layer have been introduced in literature, however, uncontrolled coating often leads to a significant decrease in M_s values which further depreciates the utilization of such magnetic particles⁷. The possibility to control the layer thickness of the polymeric layer thus seems as a potential tool for preparation of magnetic particles with various functional polymeric groups on its surface which enables to preserve their original magnetic properties. The coating process further did not affect the remanence of the particles making them suitable candidates for use in magnetorheological systems such as suspensions or elastomers.

Chemical stability of magnetic particles is another feature determining their real utilization. Carbonyl iron particles tend to oxidize leading to a formation of iron oxides on their surface. This process can lead to undesirable loose of magnetic properties and further complications hindering utilization of CI particles in some applications. Both CI and CI-PAMAM-G1.5 particles were separately immersed in 0.05 M HCl and the change in pH of the solution was observed. In the case of pure CI particles the pH increased with increasing time due to neutralization of the solution represented by a decrease in the amount of H⁺ due to oxidation of the CI particles. On the other hand in the case of CI-PAMAM-G1.5 particles only slight increase in pH value of the solution was observed confirming superior resistance against the acid conditions.

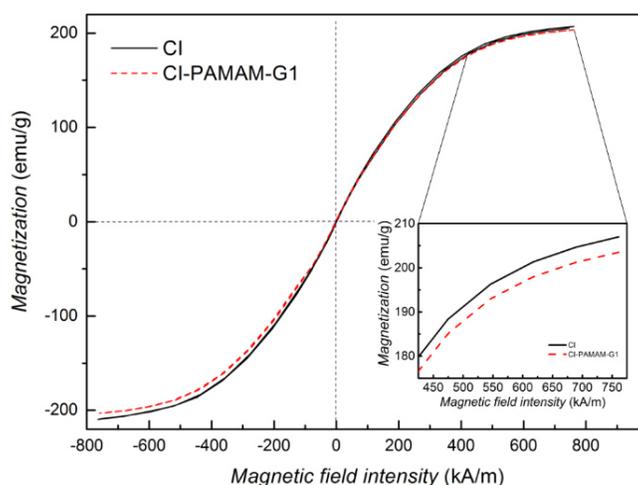


FIGURE 5. Magnetization curves of CI and CI-PAMAM-G1.5 particles.

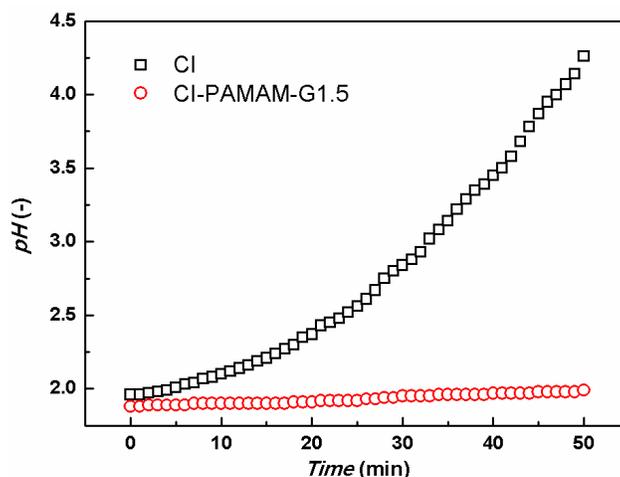


FIGURE 6. Oxidation of CI particles and CI-PAMAM-G1.5 particles in 0.05 M HCl.

CONCLUSIONS

A divergent growth approach was used in order to implement polyamidoamine dendrons on the surface of magnetic carbonyl iron particles. Using step-by-step synthesis when were alternatively grafted ethylenediamine and methyl acrylate enables a control of the created generation and thus to optimize the magnetic and functional properties together with the chemical stability of the particles. A presence of a thin layer formed of polyamidoamine dendrons was confirmed by transmission electron microscopy and qualitative spectroscopy techniques (infrared and energy dispersive X-ray). While pure carbonyl iron particles strongly oxidized in 0.05 M hydrochloric acid, their coated analogues exhibited superior stability in this solution. Moreover, the coating process only negligibly decreased the magnetization properties of the particles, which makes them a suitable candidate for the use as a dispersed phase in magnetorheological systems such as suspensions or elastomers.

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