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Carbonization of aniline oligomers to electrically polarizable particles and their use in electrorheology

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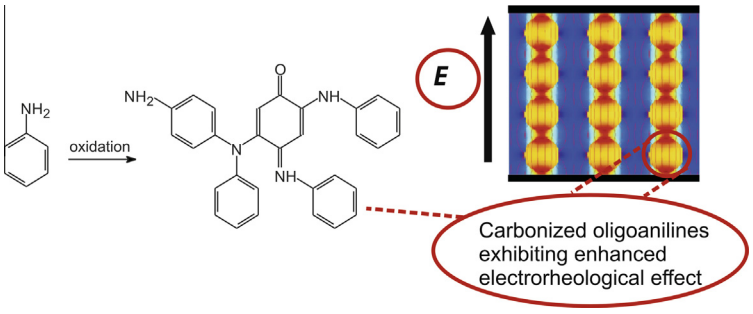
HIGHLIGHTS

- Aniline oligomers were prepared via the oxidation of aniline under alkaline conditions at various concentrations of ammonia.
- Carbonization process leads to the transition of particles' morphology from microspheres to two-dimensional plates.
- The electrorheological performance of suspensions increased with the carbonization of aniline oligomers particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Aniline oligomers prepared via the oxidation of aniline under alkaline conditions at various concentrations of ammonia were carbonized at 650 °C in inert atmosphere. Subsequently, the prepared particles were mixed with silicone oil and the suspensions were used as electrorheological fluids. After the carbonization, when the higher amount of ammonia was present during the synthesis, the transition of morphology of the particles from microspheres to two-dimensional plates was observed. This transition led to a significant increase of viscosity of silicone-oil suspensions in the presence of external electric field, while their field-off viscosity remained nearly unchanged. Thus, the carbonization had the desired effect on the treated particles leading to extremely high electrorheological efficiency of the suspensions based on such particles. The highest electrorheological efficiency was achieved for the suspension based on carbonized particles prepared in 0.2 M ammonia. The dielectric spectroscopy was used as an evaluative tool of electrorheological performance of suspensions, and data correspond well with the obtained results from electrorheological experiments.

1. Introduction

Electrorheological (ER) fluids are known as liquids altering their rheological parameters by application of an external electric field. Mostly, ER fluids are suspensions consisting of solid electrically polarizable particles dispersed in insulating liquid. In the absence of an external electric field, particles are randomly distributed within the suspension. However, when an electric field is applied, particles start to create highly organized structures due to the interaction of induced dipoles. This formation of chains and column-like structures spanning the gap between electrodes is accompanied by an abrupt increase in viscoelastic moduli and viscosity, and suspensions start to act as Bingham fluids because electrostatic forces start to dominate over hydrodynamic ones. These changes are completely reversible and fast (within milliseconds).

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In the presence of an external electric field, particles are oriented along the electric field direction thanks to dipole–dipole interaction. This phenomenon is called the ER effect. It is assumed that interfacial polarization and conductivity of the particles are dominant factors on the ER performance of ER suspensions [1]. Thanks to their unique properties, ER suspensions have been proposed for many applications, mainly in hydraulics and robotics, e.g., as dampers, clutches, torque transducers, in haptic masters for minimally invasive surgery systems [2] or haptic displays [3]. Both inorganic [4] and organic [5] materials have been used as a dispersed phase in ER suspensions. Also the composites consisting of combination of inorganic and organic materials were introduced [6,7]. The group of organic materials is particularly represented by conducting polymers. Among them polyaniline (PANI) [8,9] and polypyrrole [10] are of special interest. Polyaniline, as a material for electrorheology, has been reported in many scientific papers due to its easy and inexpensive synthesis [5,8,11–18]. Moreover, aniline-like oligomers with tuneable conductivities prepared by different reaction conditions or reaction substances have been introduced [19–21].

Conducting polymers, such as PANI, are unique among polymers in their ability to produce a variety of nanostructures [22,23]. Conducting PANI is produced by the oxidation of aniline with ammonium peroxydisulfate under acidic conditions. When oxidation of aniline is started under alkaline conditions, non-conducting aniline oligomers are produced as microspheres of several micrometres in diameter [24]. Their molecular structure is open to discussion but it is assumed that they are represented by condensed aniline molecules including oxygen atoms resulting from hydrolytic processes (Fig. 1). These are the objects of present study.

In recent studies, conducting polymers have been exposed to elevated temperature in inert atmosphere in order to obtain carbonaceous nitrogen-enriched structures [25–30]. In some cases, this treatment has positively influenced the ER performance of suspensions based on these materials.

Morávková et al. [31] have prepared carbonized aniline oligomers obtained by the oxidation of aniline under alkaline conditions. After the carbonization, the transition of morphology from microspheres into two-dimensional plates was observed. This phenomenon has been explained as a consequence of a transition, when the liquid content of the microspheres is rejected outside the microspheres above 200 °C and self-assembles into plates. In electrorheology, closely related aniline-like oligomers have been studied by Mrlik et al. [20]; however, there is no mention about their carbonized analogues.

Yin et al. [32] have introduced an ER suspension based on graphene-supported carbonaceous sheets, which has shown significantly higher increase in viscosity in the presence of the external electric field in comparison with carbonized PANI particles, which possess globular shape. However, there is a lack of studies which would describe ER behavior of two-dimensional carbonaceous enriched plates. Therefore, this study deals with aniline oligomers prepared under alkaline conditions and their subsequent carbonization at 650 °C, which lead in some cases to creation of two-dimensional plates.

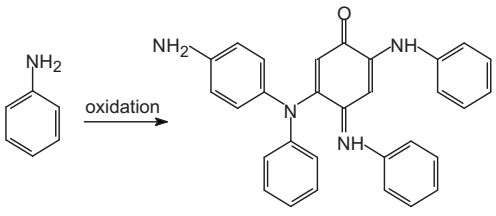

Fig. 1. A possible structure of aniline oligomers.

2. Experimental

2.1. Synthesis of aniline oligomers

Aniline (0.2 M; Sigma Aldrich) was oxidized with ammonium peroxydisulfate (0.2 M; Lach:Ner, Czech Republic) in the aqueous solutions of 0.1, 0.2, 0.5, 1 and 2 M ammonium hydroxide (NH_4OH; Lach:Ner, Czech Republic) or in water at room temperature. Solutions of the monomer and the oxidant in water were mixed at room temperature to start the oxidation. So-prepared particles are labelled as 0.1, 0.2, 0.5, 1, or 2 M regarding the amount NH_4OH presented during their synthesis. After the end of polymerization, the solids were collected on a filter after 2 h, rinsed with water, dried in air and then over the silica gel in a desiccator. A part of products deposited on silicon windows or in solid state was converted to bases by overnight immersion in 1 M NH_4OH, followed by separation and drying.

2.2. Carbonization

The carbonization of PANI base exposed up to 800 °C in air and in nitrogen atmosphere has been studied [33,34]. According to the Raman spectra it was found that G and D bands characteristic for carbon-like structure (representing the graphitic and disordered modes of carbon) are well developed after PANI exposition at 650 °C in inert atmosphere. Therefore, the second set of the samples was prepared by an exposure of the particles to the temperature 650 °C in nitrogen. When the temperature was reached, the oven was switched off and the particles were left to cool to room temperature. These samples are further labelled as carbonized particles prepared in 0.1 M, 0.2 M, 0.5 M, 1 M or 2 M NH_4OH solution.

2.3. Characterization

The course of oxidation was monitored by acidity changes recorded with a pH-meter. The morphology and dimensions of the particles were investigated using scanning electron microscopy (SEM; VEGA II LMU, Tescan, Czech Republic). UV–Vis spectra of the oxidation products dissolved in *N*-methylpyrrolidone (Sigma Aldrich) were collected with a Lambda 20 spectrometer (Perkin Elmer, UK). Infrared spectra in the range of 400–4000 cm^{-1} were recorded at 64 scans per spectrum at 2 cm^{-1} resolution using a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. Raman spectra excited in the visible range with a HeNe 633 nm laser were collected on a Renishaw inVia Reflex Raman microspectrometer. The scattered light was analyzed by the spectrograph with a holographic grating (1800 lines mm^{-1}). A Peltier-cooled CCD detector (578 × 385 pixels) registered the dispersed light. The conductivity of the original samples was measured by van der Pauw method using Electrometer Keithley 6517B (USA). The particles were pressed into the pellets of 13 mm diameter at pressure 15 MPa. Carbonized samples could not be pressed into pellets, thus their conductivity was not determined.

2.4. Preparation of suspensions

Experiments were performed with a fraction of samples grounded using a ball mill Lab Wizz 320 (Laarmann, The Netherlands), and sieved on a sieve with mesh diameter of 45 μm. Powders were mixed with silicone oil (Lukosiol M200, Chemical Works Kolin, Czech Republic, viscosity η_c = 194 mPa s,