Electrorheology of polyaniline, carbonized polyaniline, and their core–shell composites

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Abstract

In the search for a new electrorheological system, silicone oil suspensions of polyaniline base, carbonized polyaniline base, and core–shell particles of carbonized polyaniline base coated with polyaniline base have been investigated. The conversion of the materials was followed by Raman spectroscopy. Although the apparent viscosity of the suspensions measured via rotational rheometer in the presence of an electric field was the same for all three samples, the core–shell structured particle-based electrorheological system showed considerably lower field-off viscosity, which resulted in higher electrorheological efficiency.

Keywords: Polyaniline; Carbonization; Carbonized polyaniline; Core–shell structure; Electrorheology; Electrorheological efficiency

1. Introduction

Conducting polymers, such as polyaniline (PANI), are often used in applications that do not require their fundamental property, electrical conductivity, but other features, such as responsivity to external stimuli, antimicrobial performance, catalytic activity, etc. [1, 2]. When placed in an electric field, the particles of conducting polymers suspended in an insulating liquid become polarized and organize into chain-like structures due to interactions between the induced dipoles. Furthermore, the viscosity of their suspensions increases. This process is reversible when the electric field is switched off. Such suspensions are called electrorheological (ER) fluids [3–5].

The use of PANI in ER fluids was reviewed several years ago [3]. Recent applications concentrate on various morphological forms of PANI [6] or composite particles containing PANI [7, 8]. Furthermore, the conversion of a conducting polymer to nitrogen-containing carbons above 600 °C in an inert atmosphere has become the way to prepare new materials with controlled morphology [9, 10]. The present study combines both approaches, i.e. (1) the preparation and ER performance of PANI base and (2) its conversion to carbonized PANI particles followed by (3) the *in-situ* deposition of an overlayer of PANI base.

2. Experimental

2.1. Preparation

Polyaniline was prepared by the standard oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in an aqueous medium at room temperature [11]. The resulting PANI hydrochloride was converted to PANI base by immersion in excess of 1 M ammonium hydroxide. After that the particles were separated by filtration, and dried in air.

A portion of the PANI base was carbonized at 650 °C in a nitrogen atmosphere, keeping the target temperature for 1 h [9]. Then, the heating was switched off, and the sample was left to cool down to room temperature still under nitrogen flow (sample designated as carbonized PANI base).

4.5 g (or 4.0 g) of carbonized PANI base were dispersed in 25 mL (or 50 mL) of a freshly prepared reaction mixture used above for the preparation of PANI. Under such conditions, PANI is preferentially deposited over the surface of an immersed substrate rather than as a separate phase [12]. Polyaniline

hydrochloride coating was converted to PANI base again and dried in air. Such a sample contained 10 wt.% (or 20 wt.%) of PANI base and was denoted as PANI-BC10 (or PANI-BC20).

2.2. Raman spectroscopy

Raman spectra excited with a HeNe 633 nm laser were collected on a Raman spectroscope (inVia Reflex, Renishaw, UK). A research-grade microscope (Leica DM LM, Germany) with an objective magnification ×50 was used to focus the laser beam on the sample placed on an X–Y motorized sample stage. The scattered light was analyzed by the spectrograph with holographic grating 1800 lines mm^{-1}. A Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light.

2.3. Electrorheology

Prepared powders were sieved to obtain particle sizes smaller than 45 μm and dried in a vacuum oven at 60 °C for 24 h. Suspensions containing 10 wt% of particles in silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic, viscosity η_c = 200 mPa·s) were used as ER fluids. The ER properties were measured using a Bohlin Gemini rotational rheometer (Malvern Instruments, UK) with parallel plates 40 mm in diameter and a gap of 0.5 mm, modified for ER experiments. A direct current (DC) voltage was generated by a TREK DC high-voltage source (TREK 668B, USA). A DC voltage was applied for 60 s to generate an equilibrium chain-like structure of particles in suspension prior to shearing. The temperature was kept at 25 °C.

3. Results and Discussion

3.1. Preparation

Three types of materials were analyzed and tested with respect to their ER efficiencies (Fig. 1). The first was a standard PANI base. It was subsequently converted to a carbonized analogue at an elevated temperature. This is the morphology-retaining process associated with *ca* 50 wt% mass loss [9]. In the next step, the carbonized particles were coated with an overlayer of PANI base in order to modify their electrical polarizability.

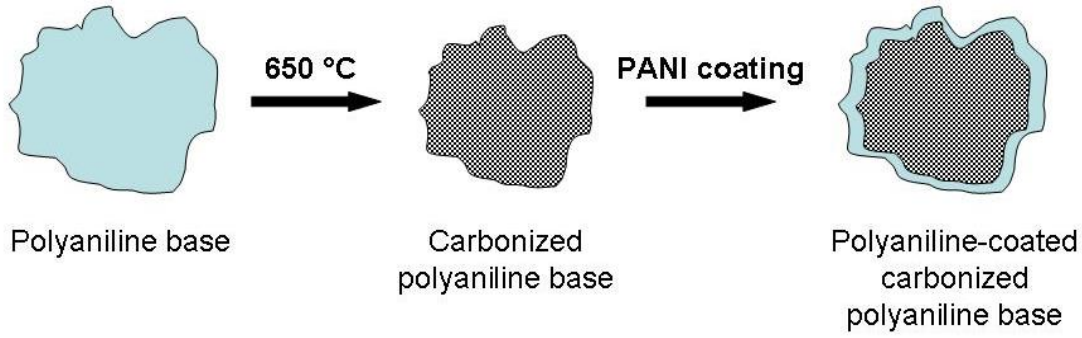

Fig. 1. A standard PANI base was carbonized at 650 °C in a nitrogen atmosphere and subsequently coated with a PANI overlayer.

3.2. Raman spectroscopy

The Raman spectrum of the PANI base corresponds to the spectrum of the typical emeraldine form [10]. The following bands are present in the spectrum (Fig. 2): 1595 cm^{-1} (C=C stretching vibrations of the quinonoid ring), 1470 cm^{-1} (C=N vibration in quinonoid units), a small band at 1330 cm^{-1} ($C\sim N^{+\bullet}$ stretching vibrations typical of protonated form but still present in PANI base), 1218 cm^{-1} (C–N stretching vibrations), 1163 cm^{-1} (C–H bending vibration of quinonoid rings), broad structural band with weak local maxima at 840, 780 and 747 cm^{-1} (deformations of variously substituted aromatic rings), and 525 cm^{-1} (out-of-plane deformations of the benzene ring).

In the Raman spectrum of carbonized PANI base, a band at 1570 cm^{-1} (emerged from the 1595 cm^{-1} band of PANI assigned to C=C stretching vibrations of the quinonoid ring) and a broad band due to an overlap of bands at 1330 and 1390 cm^{-1} (emerged from the 1330 cm^{-1} band of PANI assigned to $C\sim N^{+\bullet}$ stretching vibrations and from the stretching of aromatic rings) are observed. These bands can be considered as G-band ("graphitic" band, C=C stretching of any pair of sp^2 sites, 1585 cm^{-1}) and D-band ("disorder" band, breathing of aromatic rings activated by any defect including a heteroatom, 1350 cm^{-1}) defined for graphitic material [13] and proved to be applicable for nitrogen-containing graphitic material [14]. The spectrum corresponds to a disordered nitrogen-containing graphitic material [9].

The Raman spectrum of the PANI-CB20 composite sample is almost identical with the spectrum of the PANI base, with an observable slightly increased background at higher wavenumbers. Since the PANI base has local absorption maximum at the wavelength used, the penetration depth of the laser beam is

small and the carbonized substrate does not contribute significantly to the spectrum. This also illustrates the complete coating of carbonized substrate with the PANI base.

In the Raman spectrum of the PANI-CB10 sample, both the typical bands of the PANI base and the carbonized material are observed. In this case, the PANI overlayer is thinner than the Raman penetration depth.

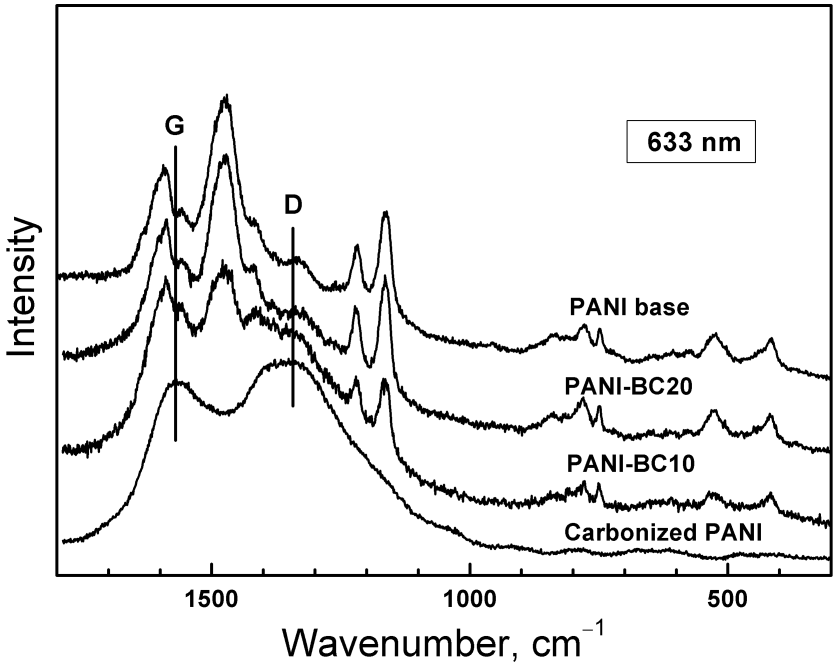

Fig. 2. Raman spectra of the PANI base, the PANI base carbonized at 650 °C in a nitrogen atmosphere, and subsequently coated with a PANI overlayer to obtain PANI-BC10 and PANI-BC20 core–shell particles.

3.3. Electrorheology

The strength of formed chain-like structures in ER suspensions is generally evaluated by steady-shear-flow experiments [15]. The role of particle surface composition in the suspension rheology in the absence of an external electric field is shown in Fig. 3a. The silicone oil suspensions of the PANI base and carbonized PANI base exhibit a strong pseudoplastic behaviour (Fig. 3a), while the system of core–shell particles has almost Newtonian behaviour with a shear viscosity independent of the shear rate. The pseudoplastic behaviour of the suspensions of the PANI base and its carbonized analogue could be caused by the formation of particle aggregates due to the difference between the high surface energy of the dispersed particles and the low surface tension of the silicone oil used as a carrier liquid. Such aggregates

are gradually destroyed as hydrodynamic forces resulting from the increasing shear rate. Composite PANI-BC10 particles are more compatible with silicone oil, which is reflected in the lower pseudoplastic behaviour of their suspension in the absence of an electric field. The best compatibility of particles with silicone oil resulting in the lowest viscosity is observed for particles of PANI-BC20, which were completely coated with PANI base.

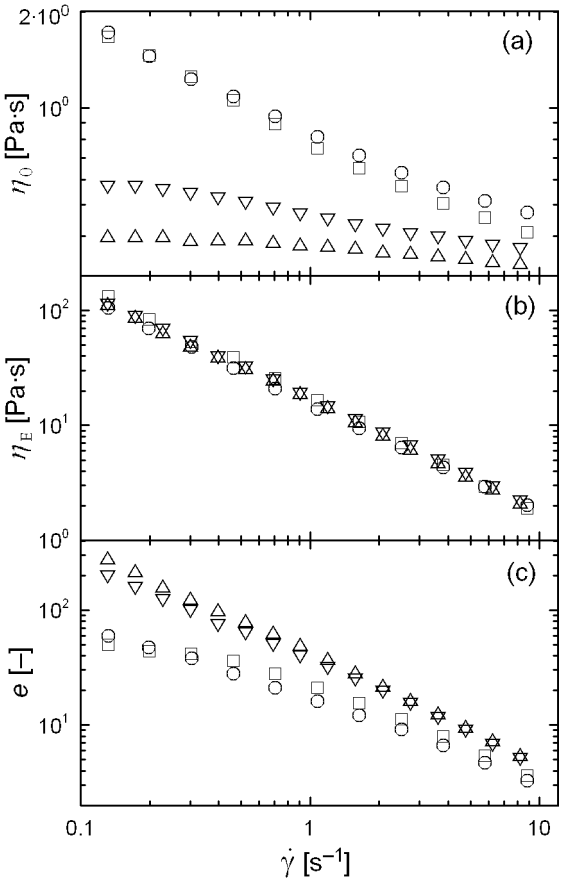

Fig. 3. Double-logarithmic plot of the apparent viscosity, η_0, (a) in the absence of an electric field, the apparent viscosity, η_E, (b) in the presence of an electric field of 1 kV mm^{-1}, and (c) electrorheological efficiency, *e*, *vs* shear rate, $\dot{\gamma}$, for 10 wt% silicone oil suspensions of the PANI base (○), carbonized PANI base (□), PANI-BC10 (▽), and PANI-BC20 (△) particles.

When an external electric field was applied (Fig. 3b), the polarized particles in suspension form chain-like structures of comparable stiffness (viscosity) for all samples. In addition to the viscosity of the suspension reached at certain electric field strength, however, a field-off value must be considered for an

evaluation of the practical ER efficiency. The efficiency can be expressed as $e = (\eta_E - \eta_0)/\eta_0$, where η_E is a viscosity of the suspension in the presence of electric field and η_0 is the field-off viscosity [16, 17]. It is obvious that the ER efficiency is significantly higher for suspensions based on PANI-CB10 and PANI-CB20 particles due to their lower field-off viscosity in comparison to the PANI base and carbonized PANI base particle suspensions (Fig. 3c).

4. Conclusions

Core–shell particles of carbonized PANI base particles coated with a PANI base overlayer can be used as a dispersed phase in a novel ER fluid. The composite structure lowers the interactions between the carrier liquid and the particles, resulting in an increase of the fluidity (reduction of viscosity) of the suspension in the absence of an electric field. As a consequence, the ER efficiency is significantly higher in comparison with suspensions of the PANI base and carbonized PANI base in silicone oil.

Acknowledgements

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