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LETTER

Preparation and electrorheology of new mesoporous polypyrrole/MCM-41 suspensions

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Encapsulation or self-assembly of conducting polymer within the channels of mesoporous silica is one of the ways to prepare new nanostructured materials [1]. The resulting materials may have unique nanostructures and properties controlled by host-guest interactions, as well as new potential applications, such as in nano-scale electronic, optical devices [2] and electrorheological (ER) fluids [3]. For example, stabilization of conducting polyaniline filaments with mobile charge carriers in mesoporous silica (MCM-41) represents a step toward the design of nanometer electronic devices [4]. In this area, Qiu [5] et al. found the impedance of polyaniline/SBA-15 (SBA-15 is another kind of mesoporous silica with larger pore size and thicker pore wall compared to MCM-41) composites more sensitive to humidity than that of bulk polyaniline, and Choi et al. [3] reported a composite material with conducting polyaniline in MCM-41 channels showing interesting ER properties.

Of conducting polymers, polypyrrole (PPy) as a promising conducting polymer has been widely studied because of its high polarizability, superior conductivity and electrorheological properties [6, 7]. Accordingly, incorporation of PPy in the pores of mesoporous silica is worth investigating, as it can be beneficial for further exploring electronic characteristics and applications of the resultant composite. On the other hand, ER fluids as one of the most promising smart materials for potential industrial applications have received wide interest. Recently, many studies on dry-based ER fluids have been reported, for example, poly- aniline/$BaTiO_3$ [8], polypyrrole/clay [9], polyaniline/clay [10] and polyaniline/MCM-41 [11] particles have been adopted as the dispersed phase of ER fluids.

In this work, a new type of anhydrous ER material based on conducting polypyrrole confined in MCM-41 channels was prepared and its ER behavior was also investigated for the first time. The preparation of mesoporous silica (MCM-41) followed the method described in literature [12]. To synthesize PPy/MCM-41 nanocomposite, the calcined MCM-41 was vacuumed at 200 °C for 4 h to remove air and water from the channels. Then the MCM-41 host was suspended above the pyrrole monomer in a flask under vacuum at room temperature for 24 h. The MCM-41 containing pyrrole was immersed in an aqueous solution of $FeCl_3 \cdot 6H_2O$ with continuous stirring in an ice bath for 24 h. The PPy/MCM-41 was washed with de-ionized water and acetone, and dried at 40 °C under vacuum. For ER behavior investigation, the PPy/MCM-41 particles were further dried at 120 °C and dispersed in silicone oil to form 10 wt.% suspension. Schematic of the synthesis of PPy/MCM-41 nanocomposite and ER tests are shown in Fig. 1.

FT-IR spectra were obtained on Nicolet Magna-550 spectrometer. N_2 adsorption/desorption isotherms were measured using Micromeritics ASAP 2010 system. High resolution transmission electron micrographs (HRTEM) were taken on a JEM 2100 F electron microscope. Scanning electron microscopy (SEM) was conducted on a JEOL JSM-6360 LV electron microscope. Measurements

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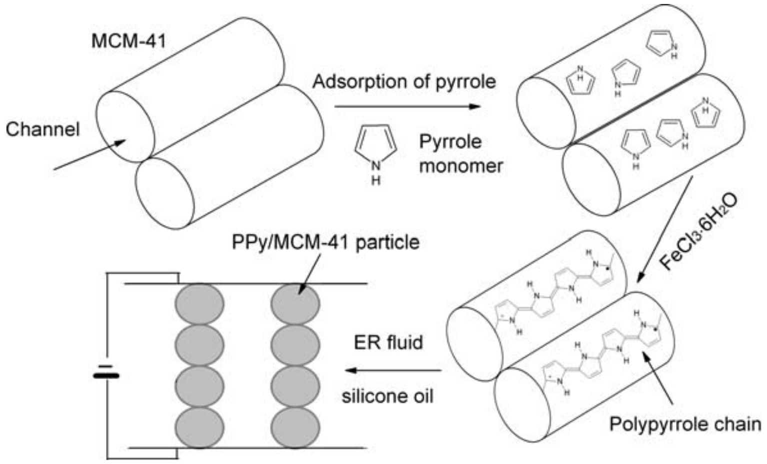
Fig. 1 Schematic of the synthesis of PPy/MCM-41 nanocomposite and preparation of ER fluids



of rheological properties were carried out using a coaxial cylinder viscometer (Bohlin Instruments, UK). All experiments were performed at 25 °C.

The presence of PPy in the channels of MCM-41 was confirmed by different techniques. The IR spectrum for PPy/MCM-41 clearly shows the characteristic peaks of PPy. The bands at 1549 cm^{-1} (C–C stretching vibrations), 1453 cm^{-1} (C–N stretching vibrations), 1090 cm^{-1} (in-plane deformation vibrations of N^+H_2), 787 and 673 cm^{-1} (C–H outer-bending vibrations) [13, 14] indicate that PPy chains have been successfully synthesized.

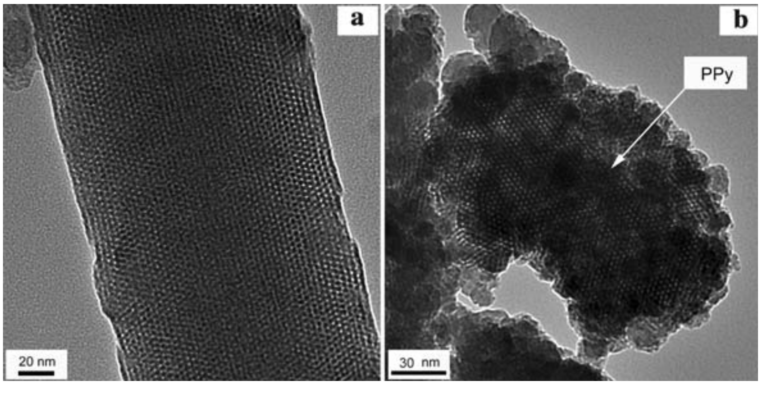
The N_2 adsorption/desorption measurements of the host and nanocomposite materials indicate that both provide type IV isotherm curves with an H_1 hysteresis loop, which are typical characteristics of mesoporous structure. The residual pore volume (calculated from the Kelvin equation using the Barrett–Joyner–Halenda formula [15]) of PPy/MCM-41 is reduced to 4.5×10^{-4} m^3/kg from 7.6×10^{-4} m^3/kg for the parent MCM-41 due to the incorporation of PPy in the channels.

This deduction can be confirmed by the HRTEM images (Fig. 2) of the materials. The channels of parent MCM-41 (a) show a well-ordered hexagonal structure with pore diameter of about 3 nm. In the nanocomposite (b), the black dots, indicated by the arrow, are chains of PPy. They are clearly encapsulated within the channels and no bulk aggregation of the polymer on the outer surface is observed. Moreover, the image of PPy/MCM-41 also reveals that the incorporation of PPy chains does not destroy the ordered structure of the channels.

The SEM images in Fig. 3 represent the surface morphological features of the particles before and after PPy incorporation. As can be seen, the particle size is less than 1 μm and most particles are nearly spherical, although some agglomerates are visible as well. Actually, particle surface morphologies of both samples are similar, which also implies that PPy is almost synthesized within the channels instead of coating the outer surface of MCM-41.

Figure 4 shows typical flow curves of the PPy/MCM-41 ER fluids under different electric field strengths. Without an electric field, the suspension behaves like a Newtonian fluid, with a slope of 1.0 for the shear rate versus shear stress dependence. In the presence of an electric field, the shear stress increases quickly and a yield behavior is observed (like a Bingham fluid). The yield stress increases significantly with stronger electric field. These changes suggest that the PPy/MCM-41 fluid displays a notable ER behavior. Figure 5 shows the shear viscosity of PPy/MCM-41-based

Fig. 2 HRTEM images of (**a**) MCM-41 and (**b**) PPy/MCM-41. The arrow in (**b**) identifies PPy chains confined in the pores of MCM-41 material



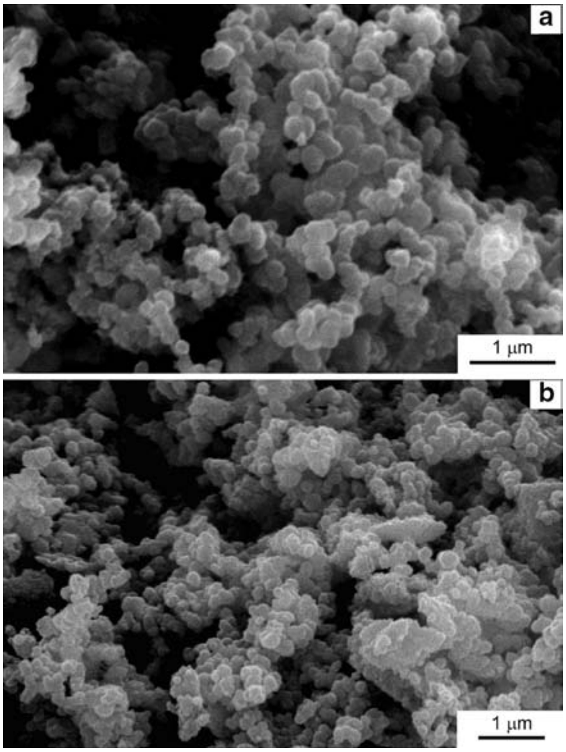


Fig. 3 SEM images of (**a**) MCM-41 and (**b**) PPy/MCM-41

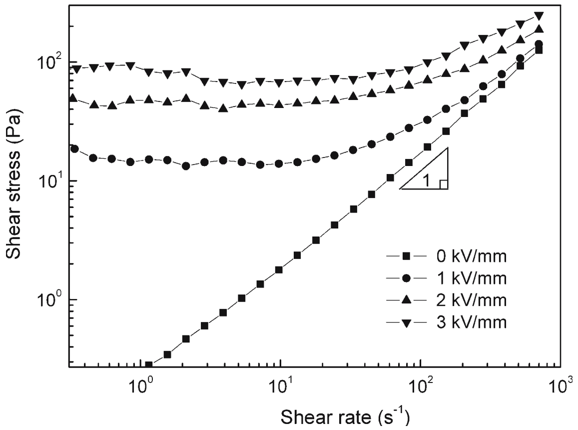


Fig. 4 Shear stress versus shear rate curves for 10 wt.% PPy/MCM-41 particles in silicone oil at different electric field strengths

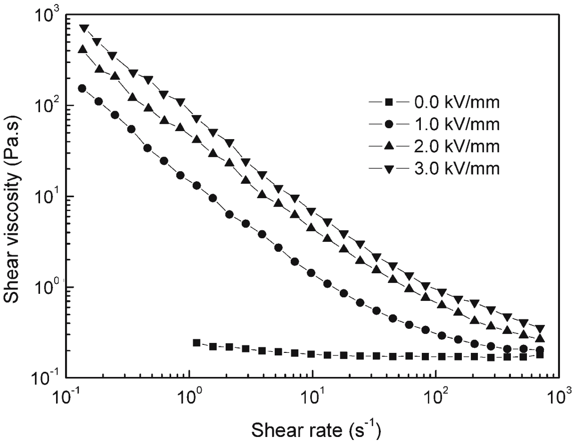


Fig. 5 Shear viscosity as a function of the shear rate at different electric field strengths for 10 wt.% PPy/MCM-41 in silicone oil

ER fluid with various electric fields. In the low shear rate region, the viscosity increases rapidly with electric field, while at high shear rates, the shear viscosity tends to reach the same value as in zero-field and shear thinning behavior is clearly observed. Furthermore, we can find that this ER fluid shows better ER performance compared to MCM-41 fluid [11], which shows ER behavior due to absorbed water in the channels (the water is the source of polarization). Hence, the experimental results clearly prove that conducting PPy in the channels of MCM-41 is more effective than water as polarizing species, which enhances the electrorheological performance of PPy/MCM-41 fluid. A similar effect has also been reported for polyaniline/MCM-41 fluid [3].

In conclusion, we have synthesized a new nanocomposite in which conducting PPy is confined in MCM-41 channels. The resultant nanocomposite retains hexagonally ordered mesostructure. This material is a novel anhydrous system which can be used for ER purposes, as it exhibits better ER performance than MCM-41-based suspensions.

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