The 2014 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM14)
Busan, Korea, August 24-28, 2014

Organic-inorganic hybrid of polyaniline-vanadium oxide nanocomposites and their electrorheological behaviour

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ABSTRACT

Organic/inorganic hybrid nanostructures comprised of polyaniline and vanadium oxide were synthesized *via* simple and feasible hydrothermal technique. The polyaniline/vanadium oxide hybrid morphology was tailored from rods to spheres by controlling the relative concentration of reactants. Field emission scanning electron microscopy (FESEM) has been conducted for morphological analyses of the nanocomposites. Electrorheological (ER) properties of these hybrid product materials suspended in silicone oil were investigated with a Bohlin rotational viscometer associated with a DC electric field source. The ER activity of the composite material suspensions showed higher ER effects for the product with rod-like structures than that for the sphere-like structures. The typical ER behaviour showed by the polyaniline-vanadium oxide nanocomposites demonstrated their potential application as an ER smart material.

1. INTRODUCTION

Electrorheological (ER) fluids are a kind of fascinating smart materials which are typically composed of polarizable particles dispersed in electrically non-conducting liquid media (like silicone oil) (Winslow 1949). Among numerous advanced ER materials *e.g.* inorganic nanomaterials, polymers, liquid crystals and others, conducting polymers have stimulated a great deal of interest as they have great advantages like a wide working temperature range, reduced abrasion of device, low cost, and relatively low current density.

Present work deals with such a conducting polymer namely polyaniline (PANI) in form of its hybrids with vanadium oxide to have synergic excellency in the ER performance. During this work, polyaniline/vanadium oxide (PANI/VO_2) nanocomposites with different morphologies (rods and spheres as main nano-building blocks) were synthesized through a subtle change in reagent concentration. Their electro-rheological properties have been investigated while suspended in the non-conducting media silicone oil. The interesting ER properties of as-prepared silicone oil

suspensions of the (PANI/VO_2) composites prove their excellence as a promising candidate in future ER fluid systems.

2. EXPERIMENTAL

Analytical grade aniline (Merck) was purified by distillation under reduced pressure prior to use. All other reagents like, commercial vanadium pentoxide (V_2O_5, Sigma Aldrich) powder and 30% hydrogen peroxide (H_2O_2, Sigma Aldrich) solution, were received as analytical grade and were used without further purification.

At first, V_2O_5 powder (0.36 g) was dissolved in 6 mL of 30% H_2O_2 solution, followed by the addition of 40 mL of deionized (DI) water with magnetic stirring to form an orange colour vanadic acid aqueous solution. This orange solution was aged for 12 hrs at room temperature. Then the acidic solution was mixed to 80 mL of 0.05 mol L^{-1} aniline aqueous solution. The mixed solution was autoclaved and maintained at 180ºC for 24 hrs and then cooled to room temperature naturally. The resulting precipitate was collected and washed with copious amounts of DI water and methanol for several times to remove the unused monomer and oligomers (if any) and then dried in vacuum at 60ºC for 24 hrs. The sample thus obtained was named as PAV. Anticipating some obvious changes in the morphology of the composites due to the variation in the molar concentration of the acidic solution during synthesis procedure, we have also tried different amounts of commercial V_2O_5 powder (in turn different molar concentrations of the vanadic acid solution), keeping the other reaction parameters (like, aniline concentration, temperature, time etc.) as before. Finally, to study the ER properties we have performed the rheological measurements only for the samples with large variation in their morphology (like, rods and spheres). The sample with rod-like morphology as constituents was named as PAV-R and that with sphere-like morphology as PAV-S. The ER fluid was prepared by suspending the samples (PAV-R or PAV-S, 2 wt%) in an insulating silicone oil via ultrasonication and its rheological properties were examined under an applied DC electric field (0−1.5 kV mm^{-1}) at 25^{o}C.

3. RESULTS AND DISCUSSIONS

Fig. 1 displays the FESEM images of the PANI/VO_2 structures we have obtained by simple hydrothermal syntheses. Sample PAV-R (Fig. 1a) is composed of flower-like structures which have rod-like components as their nanoscale building blocks. On the other hand, PAV-S (as shown in Fig. 1b) has small nano-dimensional spheres as the main feature of its morphology.

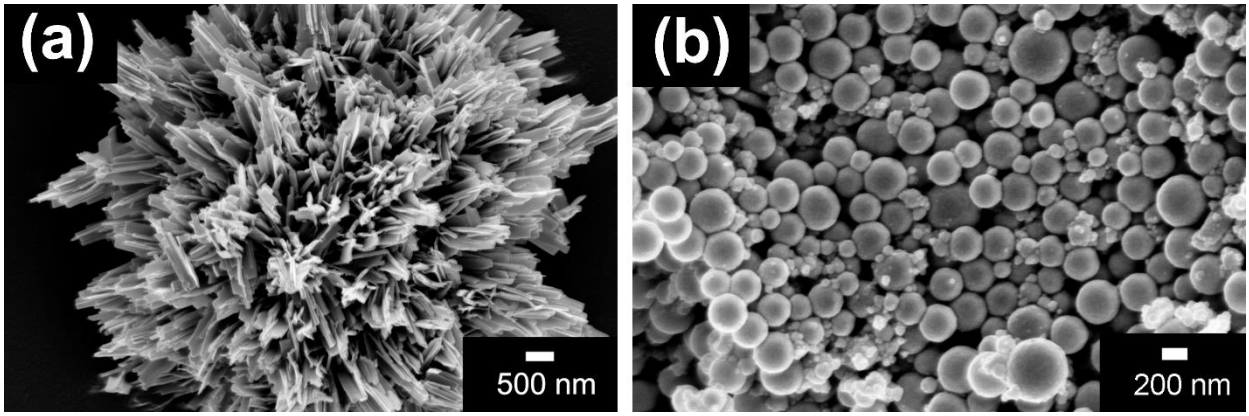

Fig. 1 FESEM images of (a) PAV-R and (b) PAV-S.

For electrorheological characterization both controlled shear rate (CSR) and controlled shear stress (CSS) modes were used to obtain the experimental findings. The typical ER behavior of PAV-R based fluid (CSR mode data) are depicted in Fig. 2.

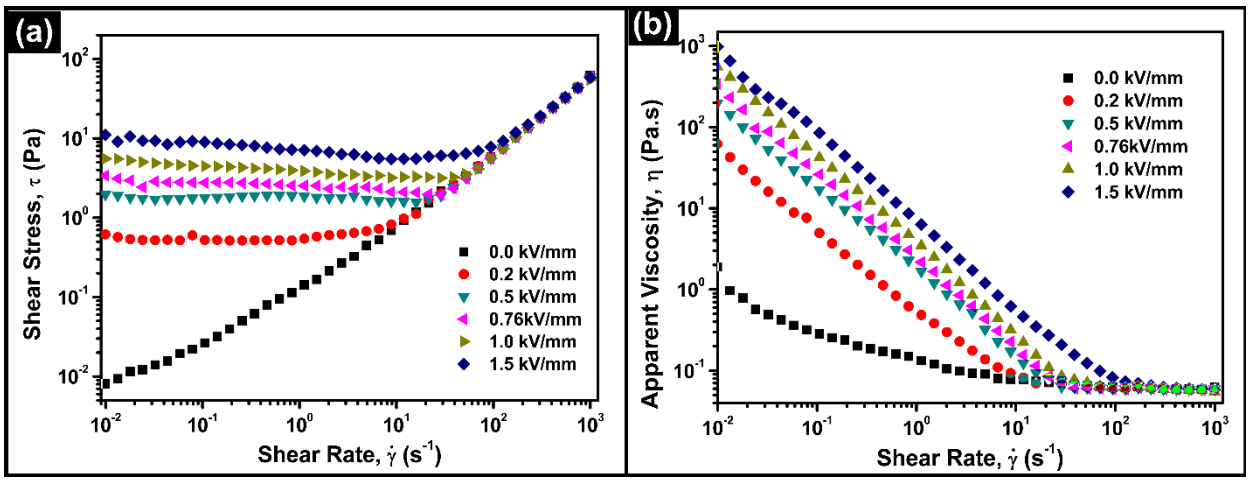

Fig. 2 The flow curves for the ER suspension with PAV-R as dispersed phase.

During the absence of electric field the shear stress increases almost linearly with the increasing shear rate i.e. a slight deviation from Newtonian-fluid like behaviour (Fig. 2a) is observed. In presence of an applied electric field, the shear stress increases abruptly and shows Bingham fluid (modified) like behavior. Such large increase in shear stress of the ER fluids is because the particles get polarized under the high field and form chain-like structures. Besides, from Fig. 2b it is clear that the apparent

viscosity exhibits a strong shear thinning behaviour. For the sphere-based suspension the same nature of the flow curves have been observed except that the viscosity and stress values were smaller than the ones of PAV-R. The ER efficiency (determined from the value of $(\tau_E-\tau_0)/\tau_0$, where τ_E and τ_0 are the shear stresses with and without electric field at low shear rate like 0.2 s^{-1}) was also higher for this PAV-R based fluid. Stronger inter-particle interaction and formation of robust dendrite-like network in presence of the applied field might have played the key role behind these higher values for the rod-like particles than the spherical one.

Fig. 3 represents the static yield stress as a function of the electric field strength for the two different types of ER fluids under the CSS mode.

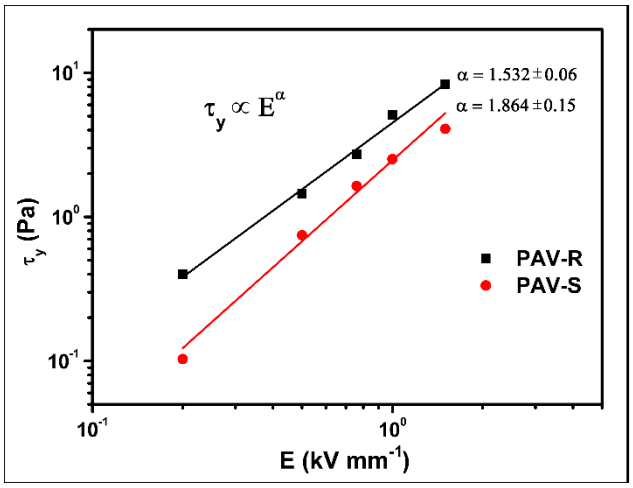

Fig. 3 Yield stress as a function of the applied electric field strengths.

For both fluids the yield stress increases with the increasing electric field strength which may be attributed to the increase in dipole-dipole interaction among polarized particles within the suspensions. However, at the same electric field, the yield stress of PAV-R based ER fluid is higher than that of PAV-S based ER fluid. The correlation between the yield stress (τ_y) and the electric field strength (E) at a fixed concentration can be represented by Eq. (1) as follows:

$$\tau_y \propto E^{\alpha} \tag{1}$$

where, the magnitude of the exponent term α is predicted to be 2 by the classic polarization model. As shown in Fig. 3, the magnitude of α is obtained by the linear fit of Eq. (2):

$$log(\tau_y) \propto \alpha \, log(\mathrm{E}) \quad (2)$$

The α-values for PAV-R and PAV-S suspensions are 1.532 and 1.864 respectively which differ from the theoretical prediction. The classic polarization model may be called the ideal case with the point-dipole approximation. But, in reality, in the case of multiphasic systems, there are many factors like particle concentration, particle shape, non-conductivity of the oil etc. which affect the electrorheological phenomena (Jianbo 2009). In our cases the shape of the particles can be mainly responsible for the deviation of α-values from the classical estimation. Especially, the deviation is higher for the fluid with PAV-R as the dispersed phase because of the rod-like structures of the suspended particles.

4. CONCLUSIONS

In this work, different hybrid structures of polyaniline-vanadium oxide nanocomposites have been tailored via a simple and feasible hydrothermal technique. The FESEM images have shown mainly two types of morphologies, rod-like and sphere-like. Both samples while suspended in silicone oil have exhibited excellent ER properties. Even though, the ER fluid with rod-like particles have qualitatively higher ER characteristics than that with the spherical one because of the stronger inter-particle interaction in presence of the applied electric field.

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ACKNOWLEDGEMENTS

This work was financed by the Portuguese Foundation for Science and Technology through the Project PEst-C/CTM/LA0025/2013.