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Electrorheological properties of poly(Li-2-hydroxyethyl methacrylate) suspensions

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Abstract

In this study, poly(2-hydroxyethly methacrylate), poly(hema), was synthesized by free radical polymerization using $K_2S_2O_8$ as an initiator. The polymer was characterized by FTIR, ^{1}H NMR and elemental analysis measurements. The molecular mass of poly(hema) was determined by osmometry, viscometry and end group analysis techniques approximately as 6×10^3 g/mol. Poly(hema) was partially hydrolyzed and converted to a lithium salt, poly(Li-hema) before the electrorheological (ER) measurements carried out. A series of particle size of poly(Li-hema) polymeric salt were prepared and average particle diameters were determined by dynamic light scattering (DLS) as 8, 13, 19 and 25 μm. Suspensions of poly(Li-hema) polymeric salts were prepared in four insulating oils namely silicone oil (SO), mineral oil (MO), dioctylphthalete (DOP) and trioctyltrimellitate (TOTM). ER properties of poly(Li-hema)/silicone oil suspensions were studied as a function of electric field strength, particle size, dispersed phase concentration, shear rate, shear stress, temperature, frequency and promoter. For these ER suspensions, yield stresses and excess shear stresses were determined. Further dielectric properties of poly(Li-hema) ionomer were also investigated.

Keywords: Electrorheological fluids; Poly(Li-2-hydroxyethyl methacrylate) ionomer; Colloidal suspensions

1. Introduction

Electrorheological (ER) fluids composed of a suspension of micron-sized particles in a non-conducting fluid form fibrillated particle structures, which are caused by the dielectric constant mismatch of the particles and the insulating oil, in strong electric fields [1,2]. Thus, it is quite natural that dielectric polarization theory appeared, because ER behavior was closely related to dielectric phenomena, and among various polarizations, interfacial polarization is assumed to be responsible for ER phenomena [3]. To overcome the shortcomings (thermal instability and corrosion) that wet-base systems possess, various dry-base systems have been investigated with anhydrous particles, including zeolite [4], carbonaceous particle, and intrinsically polarizable semi-conducting polymers [5]. Special attention has been paid to the polymer-based ER materials. Examples include: acene quinone radical polymers [6], polyaniline [7], copolyaniline [8], polyphenylenediamine [9], poly(2-acrylamido-2-methyl-1-propane sulfonic acid) [10], polypyrrole [11], polystyrene-*block*-polyisoprene [12] and polymer–diatomite composites with polyacrylonitrile [13] or polyaniline [14]. The difference between dry-base and wet-base systems is the carrier species for particle polarization. The particle chain structure is formed by the migration of ions in the absorbed water in wet-base ER fluids, whereas the electrons move inside the molecules of the particles in the dry-base ER fluids.

There is also a need for fluids with enhanced colloidal stability against sedimentation and sludge deposits formation [15]. Most of the studies on the literature are focused on the ER activity of acrylate salts and zeolitic materials, and very few of these researchers have investigated the influence of colloidal stability of suspensions. Another target is, for ER fluids, with long service stabilities, particularly at high temperatures and rigid environmental conditions [16].

Electrorheological active materials possess either branched polar groups such as amine (–NH_2), hydroxyl (–OH) and amino-cyano (–NHCN), or semi-conducting repeated groups. The polar groups may affect the ER behavior by playing a role of the elec-

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tronic donor under imposed electric field. The chemical structure of the organic materials is, therefore, an important factor in the ER performance.

There are very wide range of potential applications for ER fluids in such areas as vibration damping, robotics, hydraulics, couplings and automotive [17]. The patent literature on the subject suggests a growing interest in such devices after a period of research and assessment. A major limiting factor is still the need for fluids with better overall performance. Important factors influencing the ER effect are electric field strength, field frequency, shear rate, fluid composition, temperature, colloidal stability and presence of a polar promoter [18].

In this research, poly(Li-hema), as a new organic dispersed phase, was chemically synthesized; characterization, salt formation, and ER and dielectrical properties, pertaining to the ER behavior of poly(Li-hema) suspensions, in four insulating oil media, were investigated.

2. Experimental

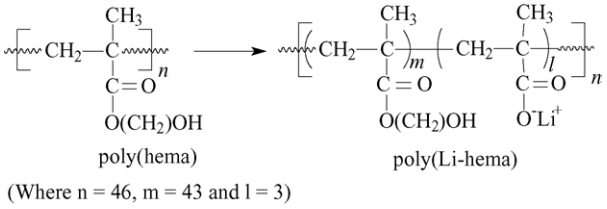
2.1. Materials

The monomer (2-hydroxy ethyl methacrylate) was purified by vacuum distillation and the initiator ($K_2S_2O_8$) was used as received. The insulating oils (silicone oil, SO, dioctaylphthalate, DOP, trioctyltrimellitate, TOTM and mineral oil, MO) were used after drying at 130 °C for 3 h in a vacuum oven, to remove any moisture present. The physical properties of four insulating oils are given in Table 1 [19]. All the chemicals were Aldrich (Aldrich Chemicals, Steinheim, Germany) products, with analytical grade.

2.2. Preparation of an ionomer from poly(hema)

Poly(2-hydroxyethyl methacrylate) was synthesized with suspension polymerization by radicalic mechanism at 60 °C, using $K_2S_2O_8$ as an initiator. $K_2S_2O_8$ was dissolved in distilled water and 2-hydroxyethyl methacrylate monomer was added drop-wise into this solution (containing poly(vinyl alcohol) as stabilizer) under $N_{2(g)}$ atmosphere. The polymerizing solution was kept stirring for 4h. Then poly(hema) was recovered by freeze-drying and vacuum dried at 25 °C for 48 h under 15 mmHg, and kept in a desiccator until use.

To prepare an ER active ionomer from poly(hema), it needs to be partially hydrolyzed and converted to a lithium salt, poly(Li-hema), by washing with 10% LiOH(aq) solution. Poly(Li-hema) was separated from the solvent by freeze-drying. It was then dried in a vacuum oven less than 15 mmHg pressure for 24 h at 50 °C. The reaction mechanism for the formation of ionomer (poly(Li-hema)) is described in Scheme 1.



Scheme 1.

2.3. Characterization

Poly(hema) and poly(Li-hema) were characterized before ER measurements to be carried out by elemental analysis, FTIR spectroscopy (Mattson Model-1000 FTIR spectrometer), ^{1}H NMR spectroscopy (400 MHz Brooker 400 DPX Avonce Spectrometer), intrinsic viscosity measurements (in *N*,*N*-dimethylformamide (DMF) using a Ubbelohde capillary flow viscometer at 25.0 °C ± 0.1 °C), and end-group analysis (by titrating acid units with 0.1 M $KOH_{(aq)}$ solution). Molecular mass of poly(hema) was also determined by a vapor pressure osmometer (Vapro Model 5520) in DMF at 90 °C.

Poly(Li-hema) ionomers were ground milled in a three-dimensional turbula shaker for 4, 8, 12 and 16 h and a series of various particle size of samples were prepared. Particle sizes of poly(Li-hema) were determined using a Malvern Mastersizer E, version 1.2b particle size analyzer according to Fraunhofer scattering. Some poly(Li-hema) samples were dispersed in ethanol and stirred at a constant temperature of 20 ± 0.1 °C. The data collected were evaluated according to Fraunhofer diffraction theory by the Malvern software computer [20].

The current–potential measurements were performed on an ionomeric salt disc (20 mm long, 5 mm wide, and 1 mm thick) with a Keithley 220 programmable current source and a Keithley 199 digital multimeter (Ohio) at the ambient temperature. The capacitance, *C*, of ER particles was measured with an HP 4192 A LF Impedance Analyzer at frequency of 1.0 MHz at constant temperature (20 ± 0.1 °C).

2.4. Preparation of suspensions

Suspensions of poly(Li-hema) ionomers were prepared in four insulating oils (SO, MO, TOTM and DOP) at a series of particle concentrations (c = 5–30 m/m, %), by dispersing definite amount of ionomers in calculated amount of insulating oils

Table 1
Physical properties of insulating oils

Oil	IUPAC name	Boiling point (°C)	Density (g/mL)	Viscosity (Pas)
DOP	Bis(2-ethylhexyl ftalate)	384	0.981	0.04
TOTM	Tris(2-ethylhexyl trimellitate)	163–165	0.821	0.08
Silicone oil	Poly(dimethyl-siloxane)	>140	0.963	0.08
Mineral	–	>110	0.862	0.04