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Nano titanium dioxide particles modified with poly(lauryl methacrylate) and its electrorheological and electrophoretic behavior

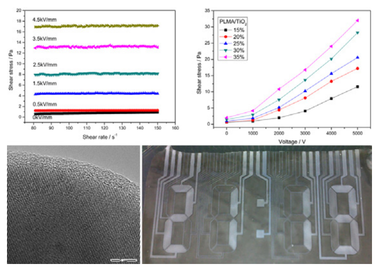
Yanping Jiang, Xianggao Li*, Shirong Wang, Yin Xiao

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- A novel ER fluid is prepared by PLMA/TiO_2 dispersed in low-viscosity isoparaffin.
- PLMA/TiO_2 ER fluid shows perfect electrorheological behavior under electric field.
- PLMA/TiO_2 ER fluid is successfully used for electrophoretic displays.
- The maximum contrast ratio of a micro-cup device is 6.2 and response time is 288 ms.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we reported a new non-aqueous electrorheological (ER) fluid structured by TiO_2 nano-particle modified poly(lauryl methacrylate) (PLMA/TiO_2) dispersed in low viscosity isoparaffin and studied its electrorheological behaviors. Moreover, the ER fluid was applied to electrophoretic display at the first time. PLMA/TiO_2 particles were prepared via graft copolymerization using γ-methacryloxypropyltrimethoxysilane and lauryl methacrylate, successively. The thickness of the cladding layer of nano titanium dioxide surface was about 2.9 nm. When an external electric field was applied to this dispersed system, from 0 to 4.5 kV/mm, the ER fluid showed a good rheological property and the viscosity of ER fluid was increased from 20 to 160 mPa s. The shear stress strengthened with PLMA/TiO_2 particles weight fraction increase in dispersed system. As a white medium, the ER fluid was mixed with carbon black to prepare a micro-cup electrophoretic display device, which could successfully realize electrophoretic display for white and black state under an electric field. The maximum contrast ratio of the micro-cup device was 6.2, and response time was 288 ms, and the clock micro-cup device could maintain display state than 24 h in the absence of electric fields.

1. Introduction

Electrorheological (ER) fluid is a suspension system which consists of insulating liquids and polarizable solid particles dispersed in it [1–3]. The behavior of ER fluids could be intensely influenced by an external electric field and surface properties of nano-particles. Under a given electric field, dielectric particles dispersed in ER fluids are polarized and attracted with each other to form chain or fibrillation structures in the direction of the field [4]. The viscosity of ER fluids suddenly increases as the strength of the external electric field enhancing while the variation is reversible [5,6]. In other words, the viscosity of ER fluids restores the initial value when the external electric field is canceled since the chain or fibrillation structures formed by polarized particles are destroyed in the absence of the electric field.

Various types of metal oxides have been used in ER fluids because they have wide types and different electric properties [7–10]. TiO_2 is a very good model in metal oxide materials. It

* Corresponding author. Tel.: +86 022 27404208.
E-mail address: lixianggao@tju.edu.cn (X. Li).

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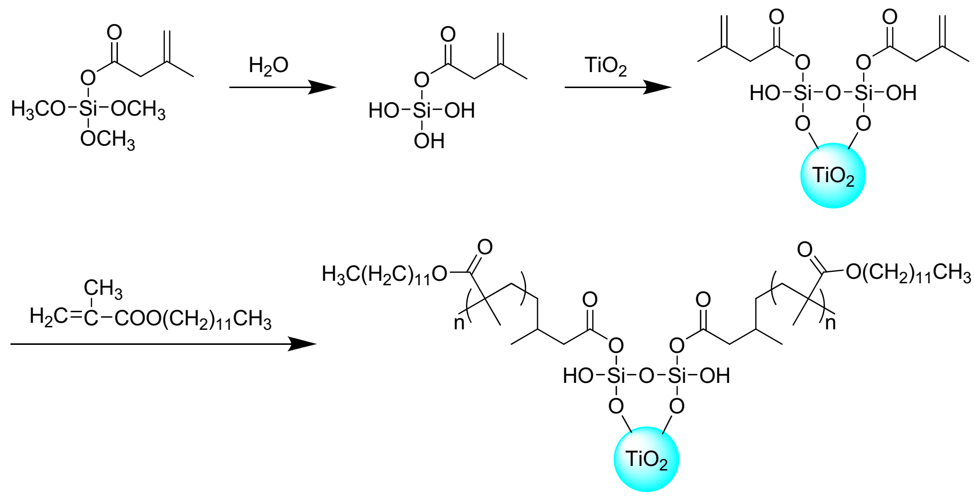

Scheme 1. Preparation of TiO_2 grafted with poly(lauryl methacrylate).

is considered to be a potential candidate material for high electrorheological performance. However, it is known that TiO_2 does not exhibit an appreciable ER effect due to its weak polarization [11]. In recent years, some researchers employed some effective doping methods or modification for TiO_2 surface to improve the polarization and conductivity of TiO_2 for obtaining its ER effect. For example, TiO_2 particles were modified by triethanolamine dispersed in silicone oil. Under 5 kV/mm external electric field, the yield stress was 50 times higher than that of unmodified TiO_2 [12]. Zhu [13] reported a type of non-aqueous ER system of copper phthalocyanine-doped mesoporous TiO_2 dispersed in silicone oil. The system performed well in electrorheological behaviors as the conductivity of TiO_2 particles was improved by CuPC.

In this article, a polarizable TiO_2 nano-particle covered with poly(lauryl methacrylate) (PLMA/TiO_2) was prepared and Scheme 1 showed the modification process. A new type non-aqueous ER fluid was obtained by dispersing PLMA/TiO_2 nano-particles in low viscosity isoparaffin. The ER fluid performed rheological properties under the action of the applied different electric fields and the relationship of electrorheological property between the electric field intensity and PLMA/TiO_2 particles weight fractions in isoparaffin were investigated. The ER fluid as a white medium was used in a micro-cup electrophoretic display device and showed the excellent display effect.

2. Experimental

2.1. Materials

Ethanol, glacial acetic acid, toluene and azobisisobutyronitrile (AIBN) were analytical grade and purchased from Guangfu Chemical Reagent Co., Ltd., China. Titanium dioxide (mean diameter 50 nm) was obtained from Beijing Mountain Technical Development Center. Lauryl methacrylate (LMA) and γ-methacryloxypropyltrimethoxysilane (KH570) were purchased from Liyang Kaituozhe Chemical Technical Service Center and Tianyang Additives Co., Ltd., respectively. Isoparaffin with a density of 0.76 g/cm^3, dielectric constant of 2.011, and viscosity of 1.336 mPa s at 20 °C was purchased from Shanghai Huishuo Chemical Development Co., Ltd., China.

2.2. Modification of TiO_2 with a silane coupling agent

In a typical synthesis, 93.06 g of ethanol and 6.94 g of H_2O were put into a 250 ml flask under gentle stirring, and then the pH value was adjusted to 4.5 with glacial acetic acid. After 20.00 g of TiO_2 and 5.00 g of KH570 were added, the temperature increased gradually to 60 °C for 8 h. The modification of TiO_2 (KH570/TiO_2) was obtained by centrifugation and washed with ethanol for several times until the unreacted silane coupling agents were removed completely. The quality of KH570/TiO_2 was 19.46 g.

2.3. Modification of KH570/TiO_2 with LMA

Titanium dioxide modified poly(lauryl methacrylate) (PLMA/TiO_2) was prepared via graft copolymerization. 8.96 g of LMA and 50.00 g of toluene were put into a 250 ml flask with nitrogen gas inlet, and then 7.00 g of TiO_2 coated KH570 and 0.10 g of AIBN were added under stirring at 300 rpm. The temperature increased to 80 °C and maintained for 12 h. PLMA/TiO_2 particles were collected by centrifugation and washed with tetrahydrofuran until the unreacted monomer and oligomer removing completely, followed by drying in a vacuum oven for 24 h and the quality of PLMA/TiO_2 was 6.44 g.

2.4. Preparations of ER fluids and rheological properties measurement

The novel non-aqueous electrorheological fluid could consist of PLMA/TiO_2 particles and isoparaffin. PLMA/TiO_2 particles were dehydrated for 1 h at 120 °C in vacuum oven. 15 g of isoparaffin was put into a 50 ml ball bottle and different weight fractions of PLMA/TiO_2 particles were dispersed in isoparaffin added with a few stabilizing agents for particles dispersing steadily. After ball-milling 24 h, ER fluid was prepared for tests.

ER effect was characterized at 20 °C by Physica MCR 301 concentric cylindrical rheometer (Anton Paar Inc., Austria) equipped with a high voltage power supply (HCP-Series, FuG Elektronik GmbH Inc., Germany). ER fluid was placed in the cylinder and the gap between the cylinder and measuring reservoir was 1.13 mm. Electrorheological effect of PLMA/TiO_2 was measured by different electric field intensities, from 0 to 4.5 kV/mm, offered by the high-voltage power generator while the shear rate changed from 80 to 150 s^{-1}.

2.5. Characterization methods and instruments

FT-IR spectroscopy of PLMA/TiO_2 particles was performed in potassium bromide pellet on a NICOLET 380 Fourier Transform Infrared Spectroscopy. TEM photos were collected utilizing JEM2100F with an accelerating voltage of 200 kV. TGA was