Colloids and Surfaces A: Physicochem. Eng. Aspects 408 (2012) 57–63

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Synthesis of field-responsive $PbTiO_3$ particle/polymer hybrids from metal-organics

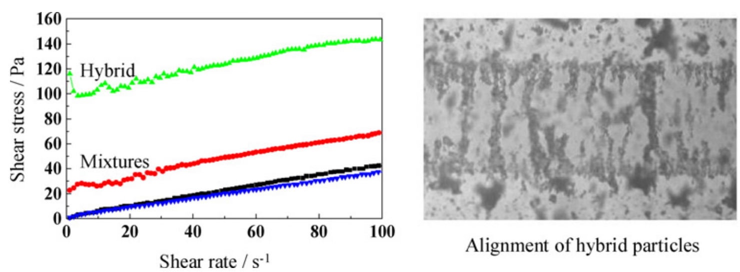
Yoshihiro Kato, Ken-ichi Mimura, Junji Umeda, Wataru Sakamoto, Toshinobu Yogo*

Division of Nanomaterials Science, EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

HIGHLIGHTS

- *In situ* synthesized $PbTiO_3$ nanoparticle/organic hybrid from metal-organics.
- Homogeneous dispersion of crystalline $PbTiO_3$ nanoparticles below 10 nm.
- The field-responsive properties of the hybrid to direct current field.
- Low $PbTiO_3$ content for electrorheological properties.
- A light-weight potential guest for electrorheological materials.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 March 2012
Received in revised form 29 April 2012
Accepted 13 May 2012
Available online 9 June 2012

Keywords:
Nanocomposite
Nanosized particle
Dielectrics
Sol–gel preparation
Electrorheology

ABSTRACT

A nanocrystalline $PbTiO_3$ particle/polymer hybrid was synthesized through controlled polymerization and the *in situ* hydrolysis of metal-organics. A $PbTiO_3$ precursor was synthesized from titanium isopropoxide, lead acetate, and 2-(methacryloyloxy)ethyl acetoacetate (MEAA). The $PbTiO_3$ precursor was coordinated by MEAA according to nuclear magnetic resonance and infrared spectroscopy analysis. The precursor was polymerized and hydrolyzed, yielding the $PbTiO_3$ particle/polymer hybrid. The polymer matrix was analyzed by transmission electron microscopy to include nanometer-sized crystalline particles that were confirmed to be lead titanate by electron diffraction and energy dispersive X-ray analysis. The suspension of the hybrid in silicone oil exhibited increased yield stress for an increased applied field and hybrid content. The suspension containing the synthesized hybrid showed a significantly increased yield stress compared with fluids containing $PbTiO_3$ ceramic particles and hydrolyzed $PbTiO_3$ precursors without MEAA modification.

1. Introduction

Nanoparticles attract special attention because of their unique size-dependent properties, such as superparamagnetism [1], quantum size effect [2], and surface plasmon resonance [3]. An inorganic nanoparticle/polymer hybrid is a composite between organic and nano-size inorganic materials. These hybrid materials exhibit novel properties that result from the synergetic effects based upon the unique properties of each material phase [4]. Despite these attractive material qualities, the uniform mixing of small magnetic or dielectric particles with a polymer to produce useful materials is extremely difficult because such particles agglomerate during processing through their magnetic moments and van der Waals forces.

The *in situ* formation of magnetic or dielectric particles in a polymer matrix is one of the most advantageous methods for the synthesis of inorganic particle/organic hybrids. The synthesis of $BaTiO_3$ nanoparticle/polymer hybrids using modified titanium alkoxide and barium alkoxide under controlled hydrolysis conditions below 100 °C was previously reported by the authors [5,6]. $PbTiO_3$ particle/organic hybrid was synthesized from a lead-titanium organic material modified with a methacrylate group [7]. The uniform formation of a nanocrystalline perovskite phase is attributed to the suitable reactivity of double metal-organic compounds. The molecular design of the precursors for controlled

* Corresponding author. Tel.: +81 52 789 2750; fax: +81 52 789 2133.
E-mail address: yogo@esi.nagoya-u.ac.jp (T. Yogo).

0927-7757/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2012.05.024

chemical processing is required for the synthesis of these materials. Hybrid materials synthesized in this manner are characterized by nanoparticles that are less than 10 nm in size and are well dispersed in the organic matrix.

Electrorheological (ER) fluids are suspensions of fine particles that can change their rheological properties in response to the strength of an external electric field [8,9]. The interfacial polarization between guest particles and host plays a crucial role in the appearance of ER properties [10]. Nano-sized particles possess the advantage of significantly higher surface area than micron-sized particles, allowing the high interface area between nanoparticle and polymer matrix to increase the level of interface polarization. In addition to the conventionally used micron-sized particles, nano-structured materials, such as nanoparticles and nanofibers [11–13], have been used as guest particle materials in ER fluids. The nanoparticles used in these studies generally form micron-sized agglomerates, although the primary particle size ranges from 20 to 100 nm. In addition, nanoparticles are mixed with host liquids at substantially high concentrations, often approaching 38 vol.% in order to achieve an optimum yield stress [14]. The high concentration of inorganic particles in these suspensions deteriorates fluid stability and causes the wear of metal vessels in ER devices.

$PbTiO_3$ is a perovskite oxide, and is a ferroelectric material. Both $PbTiO_3$ and $PbTiO_3$-based oxides are widely used as functional electroceramics owing to their excellent ferroelectric properties [15,16]. Nano-sized $PbTiO_3$ particles have been previously synthesized through various methods, such as the sol–gel process [17], tartaric acid precipitation [18], microemulsion process [19], and hydrothermal treatment [20]. Although 0.1 μm $PbTiO_3$ particles mixed with micron-sized silica dispersed in silicone oil are known to reveal ER properties [21], few reports of ER fluids using *in situ* synthesized $PbTiO_3$ nanoparticles have been documented. Even fewer have been documented using extremely small particle sizes below 10 nm. Preliminary results on the stress response of $PbTiO_3$ nanoparticle/polymer hybrids in DC electric fields were reported previously by the authors [22]. According to published research, field-responsive nanoparticle-based fluids were found to be optically transparent when modified $BaTiO_3$ nanoparticles of approximately 6 nm were highly dispersed in the fluid [23]. Based on these findings, the field-responsive properties of nanoparticle-based systems require further investigation for future applications in microfluids, nanofluids, and in particular in optofluids [24].

This paper describes the synthesis and properties of a $PbTiO_3$ nanoparticle/polymer hybrid synthesized from a metal-organic compound. The $PbTiO_3$ (PT) precursor was synthesized from lead acetate, titanium isopropoxide, and 2-(methacryloyloxy)ethyl acetoacetate (MEAA). MEAA has a methacrylate group for radical polymerization and a diketonate group for coordination to the metal as shown in Fig. 1(a). The synthesis conditions of the PT crystalline particle/polymer hybrid were investigated, and the electrorheological properties of the hybrid-based fluids were studied.

2. Experimental procedure

2.1. Synthesis of $PbTiO_3$ particle/polymer hybrid

Titanium isopropoxide ($Ti(O^iC_3H_7)_4$, $Ti(O^iPr)_4$) and anhydrous lead acetate ($Pb(OCOCH_3)_2$, $Pb(OAc)_2$) were commercially available (Kojundo Chemical, Saitama, Japan). 2-Methoxyethanol (ethylene glycol monomethyl ether, EGMME) was dried over molecular sieve and then distilled before use. 2-(Methacryloyloxy)ethyl acetoacetate ($CH_3COCH_2COOC_2H_4OCO(CH_3){=}CH_2$, MMEA) was purchased from Sigma–Aldrich Chemical (St. Louis, MO). $PbTiO_3$ powder (Kojundo Chemical) was used for the reference of electrorheological measurement.

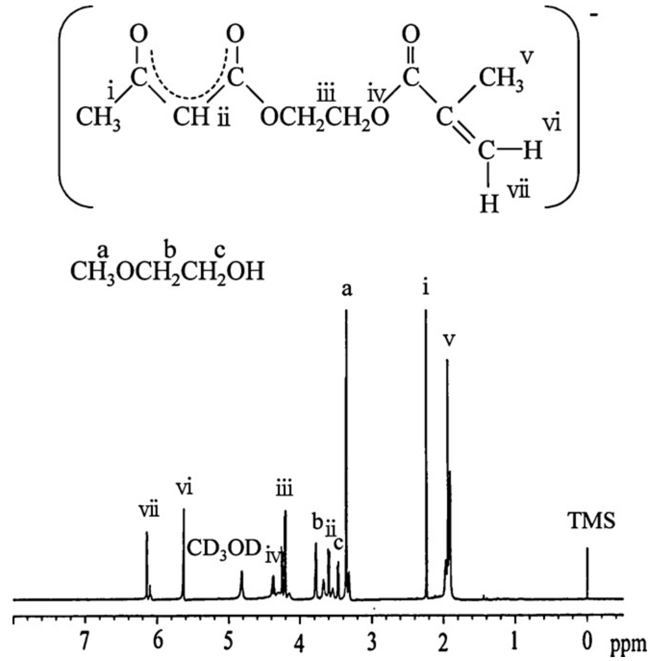


Fig. 1. Molecular structure of 2-(methacryloyloxy)ethyl acetoacetate (MEAA) and ^1H NMR spectrum of PT/MEAA precursor.

Since titanium isopropoxide is moisture sensitive, the synthesis was carried out in nitrogen atmosphere. Titanium isopropoxide (1.137 g, 4 mmol) and lead acetate (1.301 g, 4 mmol) were weighed with a molar ratio of 1.0 and dissolved in 40 ml of anhydrous EGMME. After 2 equiv. MEAAH (1.714 g, 8 mmol) was added to the solution, the solution was reacted at 50 °C for 2 h. The solvent and ester by-products were evaporated *in vacuo* from the solution affording a pale yellow solid. The solid was dissolved in 40 ml EGMME again yielding a pale yellow solution. The solution was hydrolyzed with deionized water (360 mg, 20 mmol, 5 equiv. to PT precursor) diluted with 10 ml of EGMME. The amount of water changed from 5 to 50 equiv. to PT precursor. Then, the solution was refluxed at 125 °C for 24 h. The solvent was evaporated *in vacuo* at 10 Pa at 60 °C affording a solid product.

$PbTiO_3$ particle/organic hybrid was mixed with silicone oil (JS500, 436 mPa s at 20 °C) with ultrasonication, and stirred for 24 h at room temperature yielding a suspension for the electrorheological measurement. The hybrid particles were shaped into a film using a press at 200 kg/cm^2 and 150 °C. The film was used for the measurement of dielectric properties. Authentic $PbTiO_3$ particles composed mainly of approximately 20 μm were commercially available (Kojundo Chemical).

2.2. Characterization

The ^1H NMR spectra of the products were measured with an NMR spectrometer (Varian, INOVA 500, Palo Alto, CA) in $CDCl_3$ using tetramethylsilane as the internal standard. The IR spectra of products were analyzed by a KBr method (Nicolet, Nexus 470). The organics of the product were analyzed by differential thermal analysis-thermogravimetry (DTA-TG, Rigaku, TAS-100). The particles in an organic matrix were observed by transmission electron microscopy (TEM, Hitachi H-800) with an energy dispersive X-ray (EDX) analyzer. The hybrid particles were shaped into a film using a press at 200 kg/cm^2 and 150 °C. The hybrid film was used for the measurement of dielectric properties. The dielectric properties of the films were measured at room temperature using an impedance analyzer (Solartron, SI 1260, Hampshire, UK) equipped with test