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Novel electro-rheological nanocrystalline dielectric particles modified with or embedded in organics

Shin-ichi Hirano[a,*], Toshinobu Yogo[b], Wataru Sakamoto[b], Kouichi Banno[a], Reimon Fukuzawa[a]

[a]*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
[b]*Center for Integrated Research in Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

Abstract

Inorganic-organic materials consisting of dielectric particles and organics were synthesized through in-situ processing of metal-organic precursors. $BaTiO_3$ precursor was synthesized from barium metal, titanium isopropoxide and 4-octyloxyphenol (OP). The modified Ba–Ti alkoxide could successfully afford OP-modified $BaTiO_3$ nano-particles below 100 °C. $KNbO_3$ precursor was synthesized by the reaction control of potassium ethoxide, niobium ethoxide and acetoacetoxyethyl methacrylate. The organic matrix included nanometer-sized crystalline particles depending upon the hydrolysis conditions. The nanocrystalline particles were identified by XRD, electron diffraction and energy dispersive X-ray analysis. The hybrid nanocomposites revealed an interesting electrorheological (ER) behavior on applying DC field. The yield stress increased with increasing applied voltage and volume ratio of nano-particles. The hybridization of nanocrystalline particles and organic matrix was found to give a pronounced effect on ER properties.

Keywords: Dielectric properties; Electrorheology; Nanocomposites; Perovskite; Sol-gel processing

1. Introduction

Inorganic/organic hybrid materials have been receiving growing attention because of their novel properties derived from the combinatorial effects of inorganic and organic phase.[1–3] The diversities of hybrid materials depend upon their nanostructures between inorganic and organic phase, such as size, layers and topology.[4] The crystalline phase and the size of inorganic particles are the key for the properties of inorganic particle/organic hybrid, such as superparamagnetism and quantum size effect. The molecular design of the precursors through chemical reaction plays an important role for synthesis of these materials.

The agglomeration of small particles during their blending into polymer matrix prevents the uniform mixing of two phases. Especially, nano-sized particles tend to agglomerate due to strong van der Waals force. One of the advantageous methods for the formation of such composites is the in situ synthesis of nano-sized particles in an organic matrix. The authors synthesized nanocrystalline $BaTiO_3$ particle/organic hybrids from a designed titanium-barium double alkoxide under controlled hydrolysis conditions below 100 °C.[5,6] Nanocrystalline $PbTiO_3$ particle/organic hybrid was synthesized from a lead–titanium organic modified with methacrylate group.[7] Magnetic iron oxide particle/organic hybrids were successfully synthesized from a derivative of iron acetylacetonate.[8–10] Magnetic particle/organic hybrid exhibited superparamagnetism and quantum size effect based upon the nano-sized magnetic particles.

Both $BaTiO_3$ and $KNbO_3$ belong to a perovskite structure, and are well-known dielectric and ferroelectric materials. $BaTiO_3$ and $KNbO_3$ are expected for applications in ferroelectric and electrooptical applications. Crystalline $KNbO_3$ was formed above 500 °C from amorphous oxo-hydroxide powder prepared by the reaction between niobium chloride and potassium chloride.[11]

This paper describes the synthesis and properties of nanocrystalline dielectric particle/organic materials

* Corresponding author. Tel.: +81-52-789-3343; fax: +8152-789-3182.
E-mail address: hirano@apchem.nagoya-u.ac.jp (S. Hirano).

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from designed metal-organic compounds. Modified $BaTiO_3$ (BT) precursor was synthesized from barium–titanium complex alkoxide and 4-octyloxyphenol, which was used as one of the polar organic ligands. $KNbO_3$ (KN) precursor was synthesized from potassium ethoxide, niobium ethoxide and acetoacetoxyethyl methacrylate (aaemH). AaemH was selected for the formation of polymer matrix. Both precursors were hydrolyzed under controlled conditions affording hybrid dielectric particle/organic nanocomposites. The electrorheological properties of modified BT particles and KN particle/polymer were investigated.

2. Processing and characterization methods of dielectric particle/organics

2.1. Processing of OP-modified $BaTiO_3$ nanoparticles

Barium metal was cut into an 2-ethoxyethanol solution of $Ti(OC_3H_7)_4$ with a molar ratio of Ba/Ti = 1. The reaction mixture was refluxed at 125 °C for 24h producing a clear solution. An equimolar amount of 4-octyloxyphenol (OP, $CH_3(CH_2)_7OC_6H_4OH$, mp 60 °C) was added to the solution, and then refluxed at 125 °C for 24 h. The solution was hydrolyzed with various amounts of CO_2-free water diluted with ethanol. After reflux from 6 to 40 h, the solvent was evaporated under vacuum yielding a brownish powder.

2.2. Processing of hybrid $KNbO_3$ particle/polymer nanocomposite

Potassium ethoxide and niobium ethoxide were weighed with a molar ratio of 1.0 and dissolved in anhydrous ethanol. The mixture was refluxed at 80 °C for 24 h producing a clear solution. After 1 equiv. acetoacetoxyethyl methacrylate (CH_3COCH_2COO-$C_2H_4OCO(CH_3){=}CH_2$, aaemH) was added to the solution, the solution was reacted at 60 °C from 0.5 to 24 h yielding a homogeneous precursor solution. The precursor was hydrolyzed with various amounts of CO_2-free water diluted with 10 ml of ethanol. The molar ratio of water to Nb changed from 1.0 to 20. Then, the solution was refluxed at 80 °C from 8 to 72 h. The solvent was evaporated in vacuo at 10 Pa at room temperature affording a solid product.

2.3. Characterization

The IR spectra of products were measured by a KBr method. ^{93}Nb NMR spectra of precursors were recorded at 61.14 MHz in ethanol solutions. The standard of chemical shifts of ^{93}Nb spectrum was tetramethylammonium hexachloroniobate $(CH_3)_4N[NbCl_6]$ in CD_3CN.

The organics of the product were analyzed by differential thermal analysis-thermogravimetry (DTA-TG). The particles in an organic matrix were observed by transmission electron microscopy (TEM) with an energy dispersive X-ray (EDX) analyzer. The dielectric properties of fluids were measured at room temperature using an LCZ meter equipped with a test fixture for liquid. $BaTiO_3$ or $KNbO_3$ nanoparticle/organic material was mixed with a 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 (ER) measurement. Hydrothermally prepared $BaTiO_3$ particles of about 0.1 μm were used as a reference of ER measurement. Authentic $KNbO_3$ powder was prepared from K_2CO_3 and Nb_2O_5 according to the literature.[12] The ER properties were measured with a rotational viscometer combined with a DC power supply. A concentric cylinder was used for the measurement of viscosity at room temperature and DC field from 0 to 5 kV/mm. The gap between inner and outer cylinder was 1 mm. The fluid including hybrid was observed with an optical microscope.

3. Synthesis and properties of OP-modified $BaTiO_3$ particles

3.1. Synthesis of OP-modified $BaTiO_3$ particles

4-Octyloxyphenol (OP) was selected as a ligand, because it consists of polar octyloxy group to the para sites of benzene ring of phenol. The electronic polarization is favored by the presence of aromatic ring.[13] OH group is used for the bond formation to barium or titanium in the precursor.

The formation of OP-modified BT precursor was analyzed by IR spectroscopy. 4-Octyloxyphenol showed an OH absorption at 3300 cm^{-1}. BT precursor measured using a Nujol method revealed characteristic absorptions of C–O from 1000 to 1200 cm^{-1} together with that of Ti–O at 550 cm^{-1}. After 4-octyloxyphenol was reacted with Ba–Ti complex alkoxide, OH absorption disappeared in the reaction product. The disappearance of OH indicates the coordination of octyloxyphenol to metal. ^{1}H NMR spectrum of the BT precursor revealed the disappearance of OH proton. ^{1}H NMR spectrum also supported the presence of both octyloxyphenoxy and 2-ethoxyethoxy group in the BT precursor. The latter was introduced to the precursor through the ligand exchange between isopropoxy and 2-ethoxyethoxy group. The results of IR and NMR spectra supported the formation of OP-modified BT precursor.

After hydrolysis, the absorption of OH group was not observed in the IR spectrum of OP-modified $BaTiO_3$ particles. Neither free hydroxyl group nor absorbed water was included in the product.

Fig. 1 shows the XRD patterns of the products synthesized through the hydrolysis of OP-modified BT precursor under various conditions. When the BT precursor was hydrolyzed with 6 equiv. water at 125 °C for 24 h, only broad diffractions were observed as shown in Fig. 1(a). The product obtained by hydrolysis with 40 equiv. water at 125 °C for 24 h showed a similar broad diffraction [Fig. 1(b)]. However, several diffractions appeared after hydrolysis with 40 equiv. water at 125 °C for 72 h as shown in Fig. 1(c). After heat treatment of the product shown in Fig. 1(c) at 800 °C in oxygen, crystalline $BaTiO_3$ was formed [Fig. 1(d)]. The diffractions shown in Fig. 1(c) were assigned to cubic $BaTiO_3$.

Fig. 2 shows the microstructure of the product from the OP-modified BT precursor after hydrolysis with 2 equiv. water at 125 °C for 24 h. Large particles around 10 nm were observed together with quite small particles below 5 nm. The electron diffraction of black particles revealed spots on the ring, which confirmed the particles to be crystalline. The d values from the diffraction were in good agreement with those of $BaTiO_3$. The EDX analysis also confirmed that the constituent elements were barium and titanium.

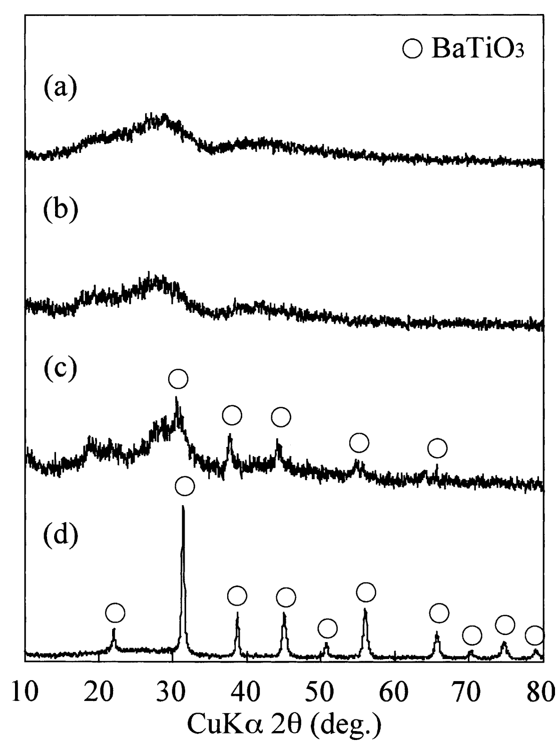

Fig. 1. XRD profiles of OP-modified $BaTiO_3$ particles synthesized under various conditions. (a) hydrolyzed at $H_2O/BT=6$ ratio and 125 °C for 24 h, (b) hydrolyzed at $H_2O/BT=40$ ratio and 125 °C for 24 h, (c) hydrolyzed at $H_2O/BT=40$ ratio and 125 °C for 72 h, (d) after heat treatment of (c) at 800 °C.

3.2. Electrorheological properties of OP-modified $BaTiO_3$ particles

The electrorheological (ER) properties were measured for the fluid of silicone oil dispersed with the hybrid powder. Fig. 3 shows the shear stress versus shear rate curves for 10 mass% OP-modified $BaTiO_3$ particles–silicone oil suspension at various DC fields. OP-modified $BaTiO_3$ particles were synthesized from OP-modified BT precursor by hydrolysis with 6 equiv. water at 125 °C for 24 h. At 1.0 kV/mm, almost no ER effect was observed. The stress began to increase at 2.0 kV/mm, and increased with increasing DC field from 3.0 to 4.0 kV/mm. The behavior is the characteristics of the Winslow fluid.[14,15] On applying electric field, the fluid revealed a typical behavior of Bingham plastic with a yield stress. The extrapolation of stress to zero shear rate does not intersect zero stress, but reveal a stress (τ_y). The yield stress (τ_y) was about 40 Pa at 4.0 kV/mm.

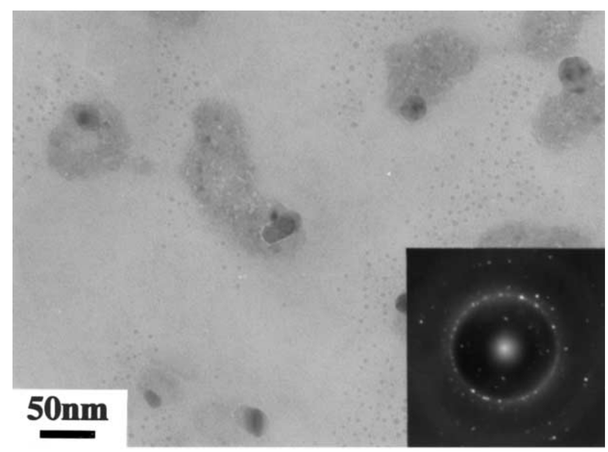

Fig. 2. Microstructure of OP-modified $BaTiO_3$ particles hybrid with a selected area diffraction of black particles.

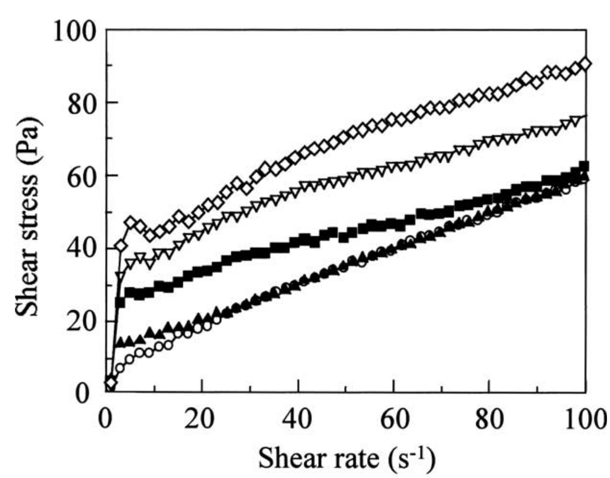

Fig. 3. Shear stress versus shear rate curves at various DC fields for fluids containing 10 mass% of hybrid synthesized by hydrolysis with 6 equiv. water. ○ 0 kV/mm, ▲ 1.0 kV/mm, ■ 2.0 kV/mm, ▽ 3.0 kV/mm, ◇ 4.0 kV/mm.

Fig. 4 shows the changes in shear stress with shear rate for fluids including various amounts of hybrid shown in Fig. 3. The applied DC filed was 4.0 kV/mm. No ER effect was observed for the fluid including 1 mass% OP-modified $BaTiO_3$ particles. The stress increases for the fluid including 5 mass% modified BT. The ER effect was clearly observed for the fluid including 10 mass% modified BT. The stress increases with increasing hybrid in amount. The maximum yield stress was about 90 Pa at 30 mass% modified BT in the fluid.

Fig. 5 shows the change of yield stress with the amount of water for hydrolysis. The maximum yield stress was obtained for the product hydrolyzed with 6 or 10 equiv. water. The crystallinity of $BaTiO_3$ particles increases with increasing hydrolysis water as shown in Fig. 1. The crystallinity of $BaTiO_3$ particles by hydrolysis with 40 equiv. water [Fig. 1(c)] was higher than that with 6 equiv. water [Fig. 1(b)]. The increase in yield stress does not agree with that in crystallinity of $BaTiO_3$ particles. The dielectric constant of $BaTiO_3$ particles depends upon the crystallinity, and increases with increasing crystallinity. The result suggests that the ER effect does not depend upon bulk polarization, but upon other polarizations at interfaces.

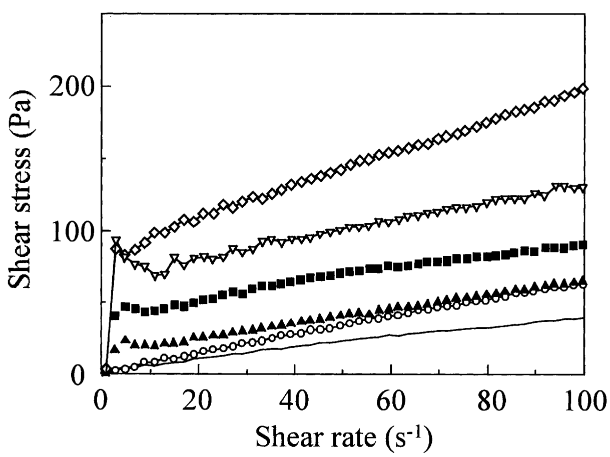

Fig. 4. Shear stress versus shear rate curves at 4.0 kV/mm for fluids containing various amounts of hybrid synthesized by hydrolysis with 6 equiv. water. ○ 1 mass%, ▲ 5 mass%, ■ 10 mass%, ▽ 20 mass%, □ 30 mass%, —— silicone oil.

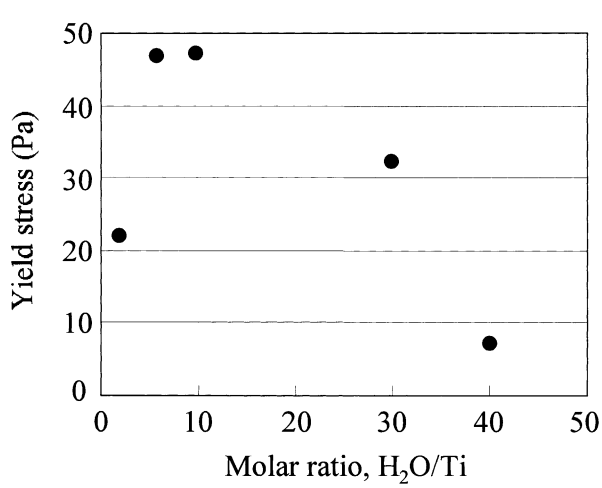

Fig. 5. Change of yield stress with amount of hydrolysis water for the synthesis of OP-modified $BaTiO_3$ particles.

Fig. 6 summarizes shear stress-shear rate curves of various suspensions. The applied field was 4.0 kV/mm. The amount of $BaTiO_3$ in each suspension is the same as that in the 10 mass% OP-modified $BaTiO_3$ particles–silicone oil suspension. The amounts of $BaTiO_3$ in the modified BT and hydrolysis product were calculated based upon TG analysis. Commercial $BaTiO_3$ powders of 0.1 μm were used for the BT powder–silicone oil suspension. The BT hydrolysis product was prepared from a complex alkoxide synthesized under the same conditions as those of OP-modified $BaTiO_3$ particles except that the BT hydrolysis product includes no OP. After the BT hydrolysis product was isolated, OP was mixed with the hydrolysis product yielding a blend of BT hydrolysis product and OP (BT–OP blend). The suspensions of BT powder and BT hydrolysis product revealed almost the same behavior to that of silicone oil. The suspensions including the BT–OP blend only showed slightly higher stresses than those of BT hydrolysis product. On the other hand, the prominent ER effect was observed for the suspension including OP-modified $BaTiO_3$ particles. The difference is attributed to the presence of the chemical bond between BT particles and OP as confirmed by IR in 3.1.

Fig. 7 shows the ER response of the fluid to DC field. The DC voltage of 4.0 kV/mm was applied on the fluid at a shear rate of 2.0 s^{-1}. OP-modified $BaTiO_3$ particles were synthesized from the precursor by hydrolysis with

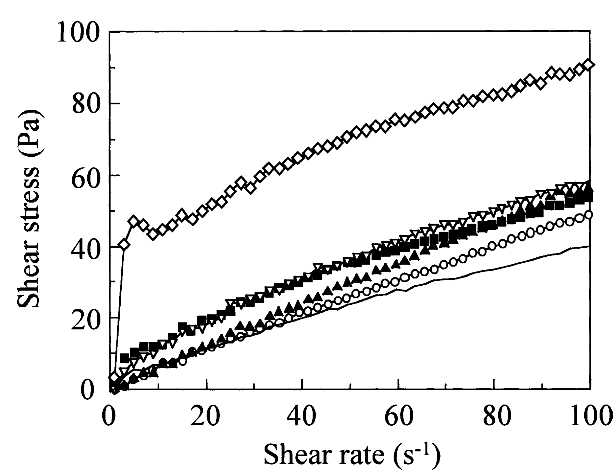

Fig. 6. Variations of shear stress with shear rate for fluid including various specimens at 4.0 kV/mm. ○ BT powder, ▲ BT hydrolysis product, ■ OP, ▽ BT hydrolysis product-OP, ◇ OP-modified $BaTiO_3$ particles, — silicone oil.

6.0 equiv. water at 125 °C for 24 h. The concentration of the hybrid in the fluid was 10 mass%. The stress of the fluid revealed a quick response to on-off switching of DC field, which leads to a novel switching device.

The fluid including OP-modified $BaTiO_3$ particles was observed by optical microscope without and with DC field. The fluid including the modified BT was spread over the transparent electrodes on a glass plate. The modified BT powders were distributed randomly in silicone oil before applying DC filed. When the DC filed was applied between the ITO electrodes, the power aligned and formed bridges between the electrodes. The bridged structure is the origin of the increased stress under DC field as reported for ER fluid.[15]

4. Synthesis and properties of hybrid $KNbO_3$ particle/polymer nanocomposite

4.1. Synthesis of $KNbO_3$ precursor and hybrid $KNbO_3$ particle/polymer nanocomposite

^{93}Nb NMR spectrum of $KNb(OEt)_6$ showed a single signal at −1000 ppm, which corresponds to the presence of niobium-ethoxy octahedra, $[Nb(OEt)_6]$, as reported for $K[Ta(OEt)_6]_x[Nb(OEt)_6]_{1-x}$.[16] The spectrum of KN/aaem precursor is composed of a broad signal at a different chemical shift of −900 ppm. The change in chemical shift suggests the coordination of aaem to $KNb(OEt)_6$. Aaem is a bidentate ligand, and coordinates to metal as a diketonate ligand. Since the signal comprises from at least two peaks at −720 and −910 ppm, the precursor is considered to be a mixture of isomers coordinated by aaem. This indicates the formation of KN precursor through the reaction of $K[Nb(OEt)_6]$ with aaemH.

The precursor was hydrolyzed with water from 1 to 20 equiv. at room temperature and then refluxed at 80 °C for 24 h in ethanol. During hydrolysis at 80 °C, the aaem ligand of the precursor undergoes polymerization, since aaemH itself is easily polymerized yielding a solid product at 80 °C. Microstructures of hydrolyzed products were analyzed by TEM. When the KN precursor was hydrolyzed with 2 equiv. water, fine particles below 10 nm were dispersed in the organic matrix. The black particles were confirmed to be $KNbO_3$ by electron diffraction. The ratio of K to Nb of the particles was found to be 1:1 by EDX analysis.

4.2. ER properties of hybrid $KNbO_3$ particle/polymer nanocomposite

The ER properties of KN particle/polymer material were investigated. The increase in shear stress was observed for the fluid of silicone oil including KN particle/polymer. No increase was observed for the fluid including less than 1 mass% KN/polymer. The fluid increased in stress clearly when the concentration of KN particle/polymer was above 10 mass%. The fluid showed a field-dependent stress. The yield stress increased from 50 to 200 Pa with increasing applied DC field from 2 to 4 kV/mm for the fluid including 10 mass% KN/polymer.

Fig. 8 shows the shear stress–shear rate curves for various fluids containing $KNbO_3$ particle/polymer, the hydrolysis product of $K[Nb(OEt)_6]$ and $KNbO_3$ ceramic powder. All dispersed specimens in silicone oil included the same amount of 4.6 mass% $KNbO_3$. Both $KNbO_3$ particle/polymer and the hydrolysis product were obtained by hydrolysis with 5.0 equiv. water. The $KNbO_3$ ceramic powder synthesized from K_2CO_3 and Nb_2O_5 at high temperature had the particle size from 0.1 to several μm. The stress of the fluid including the hydrolysis product or $KNbO_3$ ceramic powder is slightly higher than that

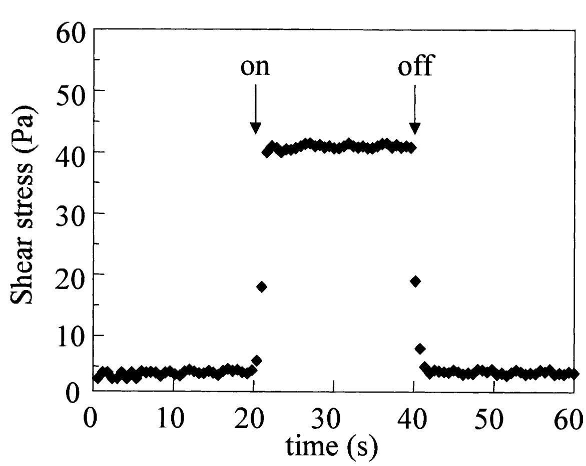

Fig. 7. Shear stress versus time curves at 2 s^{-1} for the suspension including 10 mass% hybrid synthesized by hydrolysis with 6 equiv. water.

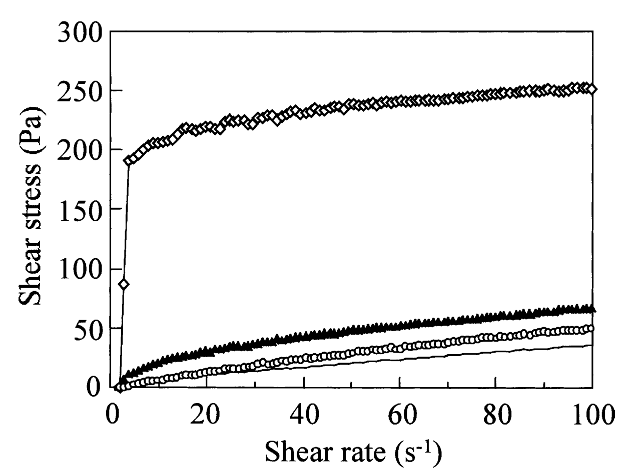

Fig. 8. Change of shear stress with shear rate for fluids including various solids. ◇ KN particle/polymer hybrid, ▲ hydrolyzed $K[Nb(OEt)_6]$, ○ KN ceramic powder, — silicone oil.

of silicone oil (JS 500) as shown in Fig. 8. The stress of $KNbO_3$ particle/polymer, however, is much higher than those of the hydrolysis product and $KNbO_3$ ceramic powder. The yield stress of the fluid including $KNbO_3$ particle/polymer is about ten times that of the product obtained from the hydrolysis of $K[Nb(OEt)_6]$ with 5 equiv. water. Similar to the case of OP-modified $BaTiO_3$ particles, the hybridization exhibited a prominent effect on the ER properties.

5. ER properties of OP-modified $BaTiO_3$ particles and $KNbO_3$ particle/polymer

The dielectric constant (ε_r) of the fluid including 20 mass% OP-modified $BaTiO_3$ particles was 2.3 at 100 kHz. Since the ε_r of silicone oil was 2.1, the fluid had a comparable ε_r to that of silicone oil. The ε_r of 4-octyloxyphenol measured at 60 °C was 6. The ε_r of OP-modified $BaTiO_3$ particles was about 30 at room temperature. Since the ε_r of OP-modified $BaTiO_3$ particles is much smaller than that of bulk $BaTiO_3$, the ER effect dose not reflect the dielectric constant of dispersoid in the fluid.

Ferroelectric materials have a spontaneous polarization, and is considered to be an ideal candidate for electrorheological materials based upon the polarization model.[17] Several workers have reported $BaTiO_3$-based ER fluids, which were prepared via mixing between $BaTiO_3$ particles (>0.1 μm) and host liquid.[18] However, the performance of $BaTiO_3$-based ER fluid is not so high as expected from the value of ε_r. The low stress indicates that interfacial polarization is more important than bulk polarization. Since the size of particles is as small as 10 nm in the present hybrids, the area of interface between nano particles and organic phase is considered to be quite large. In addition, the chemical bonds at the interfaces between in situ formed particles and organics are considered to play an important role for the ER properties. A similar behavior of KN particle/polymer to that of BT particle/OP reveals that the ER effect of the current hybrid reflects the interfacial polarization between nano particles and organic matrix.

The dielectric constants (ε_r) of $BaTiO_3$ ceramics is more than 1000 at room temperature,[19] and is higher than that of $KNbO_3$ ceramics (450).[12] However, the fluid of KN particle/polymer revealed a higher yield stress of 200 Pa than that of BT particle/OP. Although BT particles are chemically modified with OP, no network structure of organic is formed. The higher yield stress of KN particle/polymer is considered to be the effect of polymer matrix, in which nano particles were embedded through chemical bonds. The investigation of polymer matrix and functional groups including other polar ligands is now in progress in order to improve further the ER properties of the hybrid.

6. Conclusions

Inorganic–organic materials comprising from nano-sized $BaTiO_3$ or $KNbO_3$ crystalline particles and organics was successfully synthesized from modified metal–organic precursor under controlled hydrolysis conditions. The controlled hydrolysis yielded the uniform precipitation of nanocrystalline $BaTiO_3$ or $KNbO_3$ particles in the organic matrices. OP-modified $BaTiO_3$ particles revealed characteristic electro-rheological properties, which were superior to those of mixtures of hydrolyzed product and $BaTiO_3$ ceramic powder with the same organics. The polymerization of organic matrix was also effective for the ER effect of the hybrid. Hybrid $KNbO_3$ particle/polymer nanocomposite was superior in ER properties to OP-modified $BaTiO_3$ particles. As a guest of ER fluids, dielectrics/organics have advantages over inorganic particles, such as lower density and decrease in wear. In situ formation of dielectric nano-particles in organic matrices was found to be a key for the achievement of ER behavior. The developed hybrid dielectric particle/organics are expected as novel field-responsive materials.

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