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In situ processing of electroceramic fine particles/polymer hybrids

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Abstract

Electroceramic fine particles/polymer hybrids have been receiving great attention in emerging areas. The conventional blending of fine particles into polymer or oligomer causes the particle agglomeration, leading to the degradation of properties. The newly developed method is based on the nucleation and growth control of crystalline oxide particles in organic matrix through the reaction control of a metallorganic precursor with a combination of the hydrolysis and polymerization below 100°C. The selection of reaction conditions does influence the size and crystallinity of ceramic particles in the organic matrix. The nano-sized magnetic particle/polymer hybrid exhibits the interesting feature of superparamagnetics and quantum size effect. The crystalline particles of $BaTiO_3$/, and $PbTiO_3$/polymer hybrids behave to be dielectric and show the typical electro-rheological behavior, which affords emerging areas. © 2001 Published by Elsevier Science Ltd.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Ferrites; Magnetic properties; Nanocomposites

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1. Introduction

Inorganic/organic hybrid materials have received great attention as newly emerging materials. The inorganic and organic phases constitute the nanostructure of the hybrid through chemical bonding. Various hybrids such as Ormocer, Ormosil and Ceramer have been synthesized from metalorganics including Si,Ti and Zr-based systems.[1–5]

Nano-sized crystalline magnetic particles show unique phenomena of superparamagnetism and quantum size effect.[6,7] The magnetic properties depend strongly on the crystalline phases, crystallinity, and particle size. Magnetic particle/organic hybrids have various potential applications in magnetic and medical uses, such as magnetic recording, magnetic fluid, magnetic ink, magnetic resonance imaging, drag carrier, and hyperthermia for cancer. The blending of magnetic particles into polymers has inevitable problem of particle agglomeration during processing.

The authors developed the novel method to synthesize successfully the nanocrystalline α-Fe_2O_3 particle/, and magnetic particle/organic hybrids by polymerization of iron(III) 3-allylacetylacetone (IAA), followed by in situ hydrolysis below 100°C. The hybrids exhibit typical superparamagnetic behavior.

The properties of dielectric particles also depend upon the size and crystal regularity. Usually, crystalline $BaTiO_3$ particles above 0.1 μm were dispersed in organic media using a conventional mixing method in order to fabricate dielectric/organic composites, which encounter agglomeration. The nucleation and growth control in organic matrix by the newly developed method afford crystalline dielectric particles of $BaTiO_3$ and $PbTiO_3$ of much smaller size bonded to organic matrix.[8–10] Nano-sized ferroelectric particles in polymer matrix do behave as superparaelectrics and show the electro-rheological behavior.

This article reviews the results on the author's recent works on the processing and characters of magnetic and dielectric particle/organic hybrids through the reaction control of designed metalorganics with vinyl bonds.

2. Processing and characterization of magnetic particle/organic hybrids[6,7]

2.1. Processing

The basic concept to process hybrids is shown in Fig. 1. The process starting with the polymerization

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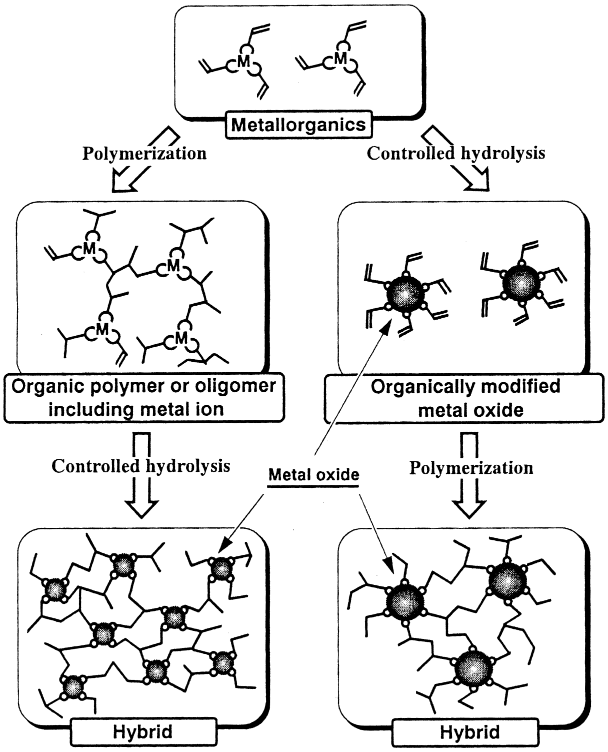

Fig. 1. Processing scheme of hybrid.

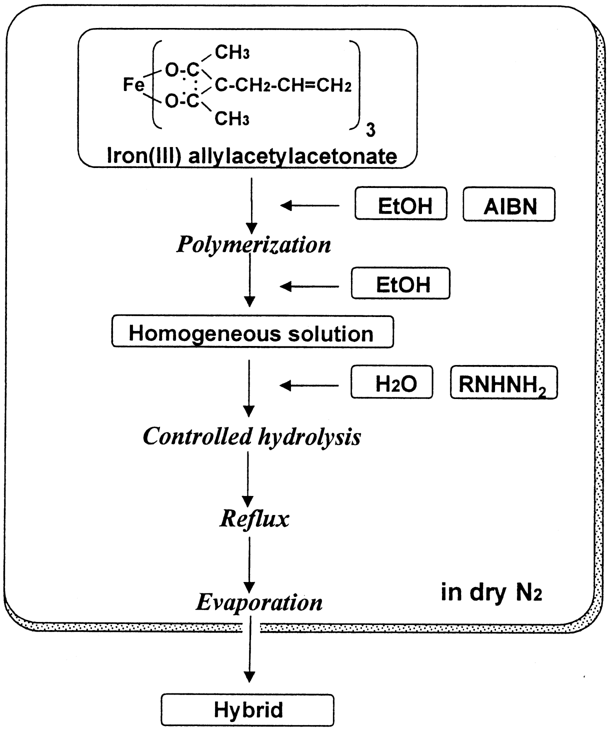

Fig. 2. Reaction flow of iron oxide/organic hybrid.

followed by the hydrolysis gives a hybrid composed of smaller size of particles in polymer, while initial hydrolysis prior to the polymerization affords the hybrids with larger particle size.

The processing procedure is shown in Fig. 2 for preparing a magnetic particle/polymer hybrid. Iron(III) tris(3-allylacetylacetonate)(IAA) were prepared by the method described in the literature.[11] Ethanol was dried over magnesium ethoxide and distilled before use. Commercial hydrazine monohydrate($NH_2NH_2{\cdot}H_2O$) and methylhydrazine(CH_3NHNH_2) were used as reducing agents. IAA was polymerized by solution polymerization with 2,2′-azobis (isobutyronitrile)(AIBN) as a radical initiator. IAA, ethanol and 3 mass% of AIBN were weighted in a glass tube, which was sealed under vacuum after freezing-melting treatments to remove oxygen. The sealed glass capsule was heated at 100°C for 42 h. After evaporation of ethanol, an IAA oligomer was obtained as a brownish solid.

The IAA oligomer was dissolved in O_2 free ethanol and then hydrolyzed with a mixture solution of hydrazine and water. The product was aged below 80°C from 0.5 to 24 h.

2.2. Characterization

The crystallization depends on the hydrolysis condition, especially on the ratios of hydrazine/Fe and H_2O/Fe. Fig. 3 illustrates nano-sized crystalline particles finely dispersed in an organic matrix, which was synthesized at a molar ratio of hydrazine/Fe = 4. The mean particle size is 10 nm. Fig. 4 shows the XRD profiles of hybrids prepared under various hydrazine/Fe ratios at H_2O/Fe = 10 and 80C. The XRD diffractions are in good agreement with those of spinel (Fe_3O_4 or γ-Fe_2O_3) of which identification is difficult by XRD, because the lattice constants are quite similar each other. The ratio of γ-Fe_2O_3 to Fe_3O_4 was analyzed by X-ray photoelectron spectroscopy (XPS) on the hybrid prepared at a molar ratio of hydrazine/Fe = 4 and H_2O/Fe = 10. The result revealed the hybrid included not only Fe(III) but also Fe(II). The

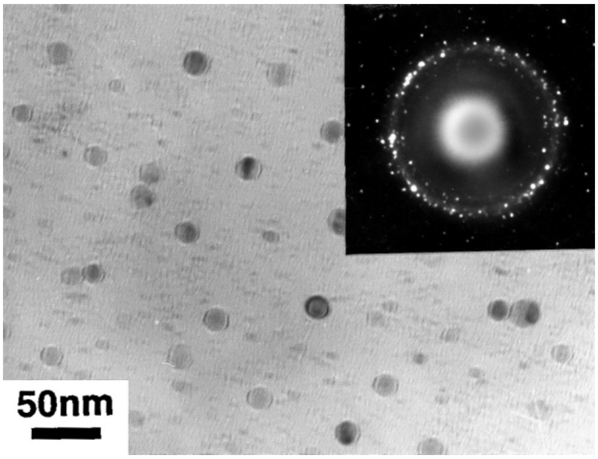

Fig. 3. Microstructure of iron oxide/organic hybrid with a selected area diffraction of black particles.

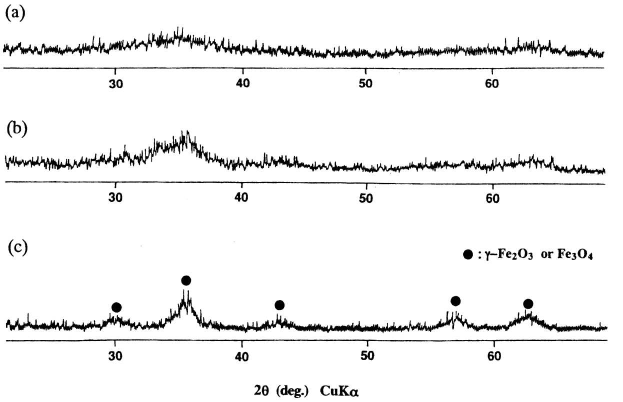

Fig. 4. XRD profiles of iron oxide/organic hybrid prepared at various NH_2NH_2/Fe ratios at H_2O/Fe ratio of 10 at 80°C for 24 h. (a) NH_2NH_2/Fe = 2, (b) NH_2NH_2/Fe = 3, (c) NH_2NH_2/Fe = 4.

ratio of γ-Fe_2O_3 to Fe_3O_4 in the hybrid was determined to be 1:1 based on the peak area of each spectrum.

Fig. 5 shows the room-temperature magnetization versus applied magnetic field for the hybrids prepared at various hydrazine/Fe ratios. The magnetic induction increases with increasing the applied field, although no hysteresis is observed. The saturation magnetization increased with increase in the ratio of hydrazine to Fe and reaches a constant value at 4. Even at the high applied field of 20 kOe, the hybrid shows no decrease in magnetic induction, which implies that magnetic particles are highly dispersed without agglomeration in organic matrix through chemical bonding. The hybrids show typical superparamagnetic behavior as a result of the nano-crystalline size. The saturation magnetization was found to increase with increasing the amount of added water for hydrolysis, which is attributable to the increases in size and crystalline regularity of iron oxide spinel particles in organic matrix. Methylhydrazine was more effective than hydrazine for the reduction of Fe(III) to Fe(II). The corrected saturation magnetization of the hybrid is about 75 emu/g in 40 mass% of organic matrix.

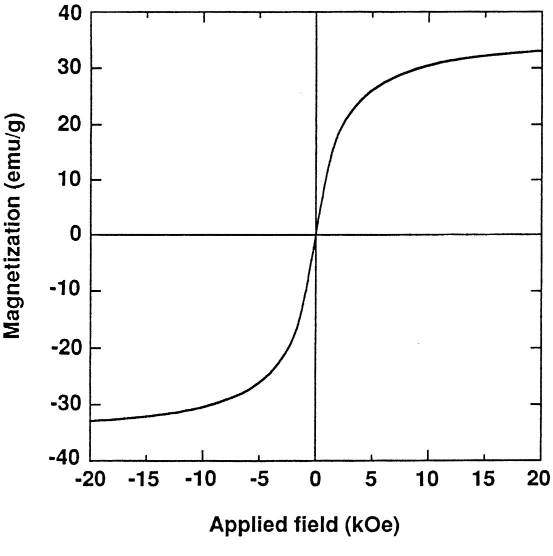

Fig. 5. Magnetization curve of iron oxide/organic hybrid measured at 25°C synthesized at Fe:hydrazine:H_2O = 1:4:10.

3. Processing and characterization of nano-sized dielectric particle/organic hybrids[8–10]

3.1. $BaTiO_3$/polymer hybrids

Fig. 6 illustrates the representative processing scheme used for the synthesis of $BaTiO_3$/polymer hybrids. A starting precursor of methacryltriisopropoxytitanium (MTPT) was prepared by the reaction of methacrylic anhydride ($(CH_2{=}C(CH_3)CO)_2O$) and titanium isopropoxide. Barium metal reacted in a mixture of ethanol and 2-ethoxyethanol (EGMEE) (volume ratio of 20) was added to MTPT solution and reacted at 80°C for 20 h. The precursor of Ba-MTPT was polymerized at 100°C, and then hydrolyzed with various amounts of water at 80°C. The product was oligomeric with the molecular weight below 2000. Styrene was copolymerized with Ba-MTPT using AIBN at 80°C. The bulk $BaTiO_3$/polymer was placed between two steel plates with heating elements, and pressed to fabricate films.

The polymeric hybrid formed from Ba-MTPT/water ratio of 1.0 was analyzed by DTA-TG to be composed of about 30 mass% of organics. TEM and electron diffraction revealed the formation of nano-sized crystalline $BaTiO_3$ particles (median diameter of 2 nm) homogeneously dispersed in polymer matrix. The dielectric constant was 7 and shows no maximum around 120°C on the hybrid film synthesized at a molar ratio of styrene to Ba-MTPT of 1.0 with 1.0 equiv. water. The loss tangent was about 0.025 at 100 kHz. The quite small size of $BaTiO_3$ particles is responsible for the absence of dielectric maximum relating to the Curie temperature.

3.2. $PbTiO_3$/polymer hybrids

Fig. 7 shows the processing scheme for the synthesis of hybrids. Commercially available lead methacrylate hydrate ($(CH_2{=}C(CH_3){=}COO)_2Pb{\cdot}H_2O$) was heated at

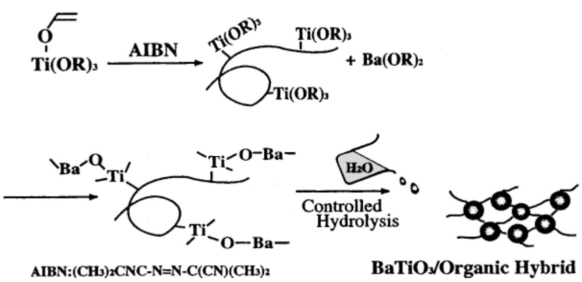

Fig. 6. Processing of $BaTiO_3$/organic hybrid.

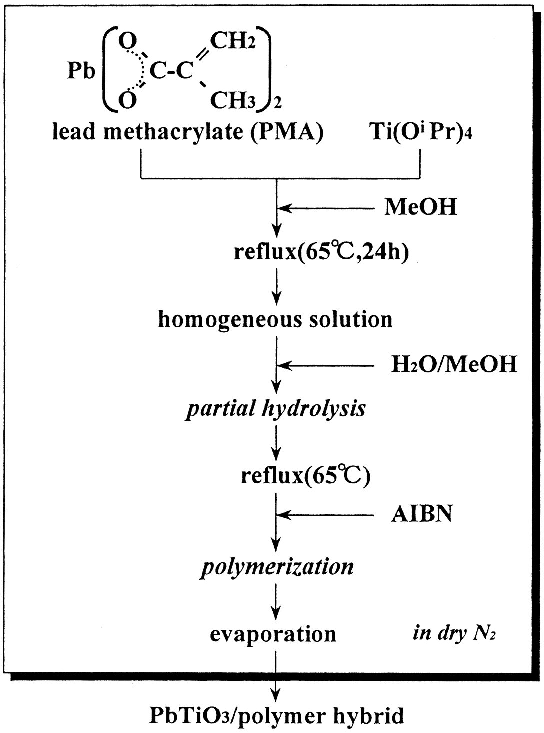

Fig. 7. Processing of $PbTiO_3$/organic hybrid.

56°C for 24 h over phosphorus pentoxide under vacuum with a drying apparatus producing dehydrated lead methacrylate. Lead methacrylate (754 mg, 2.0 mmol) and titanium isopropoxide (554 mg, 2.0 mmol) were weighed with a molar ratio of 1.0 and dissolved in 20 ml dried methanol. The mixture was reacted at 65°C for 24 h to form a clear precursor solution, which was hydrolyzed with various amount of CO_2-free water diluted with 10 ml of methanol. The solution was evaporated in vacuo at 10 Pa to form a solid product, which was then charged in a glass tube with AIBN and methanol. The glass tube was immersed in liquid nitrogen at −190°C followed by evacuation at 10 Pa. The frozen product was then melted at 20°C at 10 Pa. The glass tube was sealed at 10 Pa, after the freezing-melting treatment was repeated five times to remove oxygen. The mixture in the sealed glass capsule was polymerized at 100°C. Films were prepared by placing the prepared solid powder between electrically heated platens, which were pressed and heated at about 170°C and 80 kg/cm^2.

Fig. 8 shows a TEM photo of the hybrid hydrolyzed with 30 equiv. water, revealing finely dispersed $PbTiO_3$ crystalline particles. The ratio of Pb to Ti of the particles was found to be 1:1 by EDX analysis. The size of particles can be adjusted by controlling the amount of water and reflux time for hydrolysis resulting in the growth of PT particles. The results of TEM and Raman spectroscopy exhibit that the nanoparticles of around 10 nm are crystalline tetragonal $PbTiO_3$.

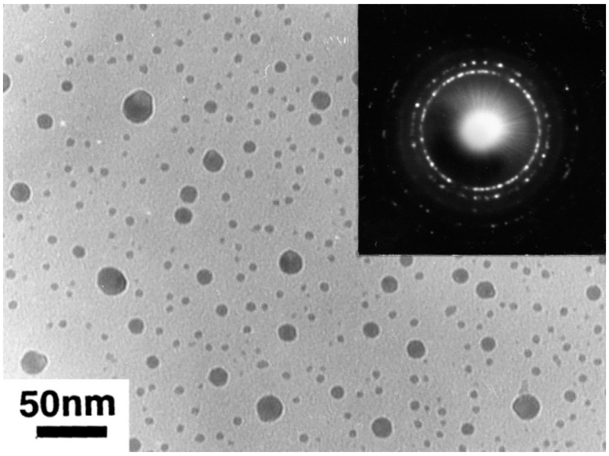

Fig. 8. TEM photograph of $PbTiO_3$/organic hybrid with a selected area diffraction of black particles.

A 200 μm thick hybrid film was prepared from the PT precursor hydrolyzed with 30 equiv. water followed by polymerization at 100°C. The dielectric constant is 5.2 at 10 kHz at room temperature, while the dielectric constant of matrix poly(methyl methacrylate) (PMMA) film is 2. The hybrid is composed of $PbTiO_3$ particles and the PMMA matrix. The dielectric constant was calculated by a model equation using the dielectric constant and density of tetragonal $PbTiO_3$ particles in continuous polymer matrix. The calculated dielectric constant was 5.1, which is comparable with the measured value.

The electro-rheological behavior was evaluated with hybrid dispersed in silicon oil. Fig. 9 shows a stress–strain curve of the hybrid, which exhibits the typical electro-rheological behavior, depending upon the applied voltage. This behavior can be held without degradation, because the finely dispersed particles are bonded to the organic matrix.

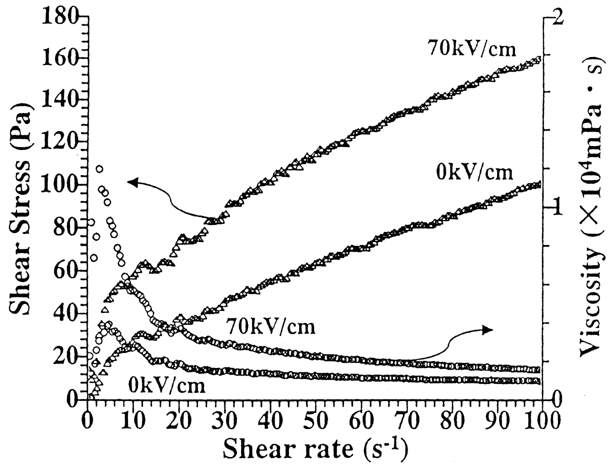

Fig. 9. Shear stress and viscosity changes as a function of shear rate on $PbTiO_3$/organic hybrid.

4. Conclusions

The concept described in this article can be applied to the processing of novel functional hybrids with controlled nano-sized ceramic particles in polymer matrix. The design of metalorganic precursor is a key to control the crystallization of particles and microstructure of the hybrids. The structure of metallorganics is composed of alkoxy group and C=C unsaturated double bonds which are subjected to the hydrolysis for oxide formation and the polymerization, respectively. Magnetic iron oxide, $BaTiO_3$ and $PbTiO_3$ can be crystallized below 100°C by designing the precursor molecules. The particle size can be controlled by selecting the reaction scheme and the amount of water for hydrolysis. The hybrids with nano-sized particles exhibit the quantum size effect. The hybrids composed of nanocrystalline magnetic particles show the typical superparamagnetic behavior. The hybrids with crystalline $BaTiO_3$ and $PbTiO_3$ particles behave electrorheologically on applying the electric field, which creates the future strategy of new material families.

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