Synthesis and Electrorheological Properties of Polyaniline-Coated Barium Titanate Composite Particles

Hua Yan, Zi Jun Liao, Xia Zhu, Xue Mei Wang, Yong Chen, Bin Zhang, Shui Lian Chen, Zhong Yong Za

Department of Petrochemistry, Logistic Engineering University, Chongqing, People's Republic of China

ABSTRACT: Polyaniline-coated barium titanate composite particles were synthesized by surface grafting polymerization, in which five silane coupling agents with different terminal groups were used. The structure of composite particles was characterized by SEM, XRD, FTIR, and TGA, and the electrorheological properties were tested by rotational rheometer. The results show that polyaniline was coated on the surface of barium titanate particles to form the shell-core structure. The yield stress of the electrorheological fluids based on polyaniline-coated barium titanate composite particles is higher than that of polyaniline and barium titanate. Compared with PANI-based electrorheological fluids (ERFs), the composite particles-based ERFs have lower field-off viscosity due to the molecular interaction. The yield stress of the ERFs, as well as density of the composite particles, was affected by the groups at terminal of silane coupling agents. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1960–1966, 2008

Key words: rheology; composites; core-shell polymers; conducting polymers

INTRODUCTION

Electrorheological Fluids (ERFs) are suspensions of polarizable particles in insulating oil, which exhibited a dramatic change in rheology in the presence of an electric field.[1] This change involved polarization and elongation of particles, and then migration of charge, formation of a chainlike or columnar structure oriented along the electric field direction over the gap between the electrodes, the fibrillation structure behaved like solid. When the electric field is removed, these particles return to the original random orientation distribution, and the fluid behaved like Newtonian fluid. Thereby, controllable viscosity, yield stress, fast and reversible response, and the simplicity of engineering designs using ERF have facilitated the development of many devices, such as auto damper, active engine mounts, clutches valves, and servo devices.

In an earlier study, various materials had been introduced as dispersed phase. However, hydrous ERFs based on inorganic and organic powdered materials have significant limitation and low electrorheological effect, which were associated with presence of water. From 1988, dry based systems were employed in ERFs, which exhibited higher yield stress and were used in broad temperature range.[2] Among various anhydrous ERFs, the dispersed phase materials have recently focused on conjugated polymer, because some drawbacks of conductive polymer became advantage for ERFs.[3] Nevertheless, the yield stress and modulus of ERFs were lower than those of magneto-rheological fluids. The performance of semiconducting polymer-based ERFs is still insufficient with respect to a successful development of application devices.

The shear stress of ERFs is equal to the rate change of the electric energy density with respect to the shear deformation. There are three ways to improve electric energy density at a certain electric field. However, there are many limitations to increase the electric energy density by increasing the volume fraction of the suspended particles and using additives.[4–6] With the framework of polarization, the yield stress of ERFs would be increased as the mismatch of dielectric constant between dispersed particles and insulating oil was increasing. Therefore, many materials with high dielectric constant, such as inorganic ionic compounds, are promising candidates as dispersed particles for ERFs. However, these kinds of ERFs cannot work in dry. Many groups turned to modify the dispersed particles for hydrous ERFs to improve the performance. Surface modified complexes strontium titanate microparticles were synthesized by sol-gel technique, the suspension composed of these particles immersed in silicone oil exhibited excellent electrorheological effect.[7]

WILEY InterScience®
DISCOVER SOMETHING GREAT

Novel electrorheological particles consisted of polymer core and electroconductive/nonconductive double layers shell were synthesized. The core was prepared by dispersion polymerization of methyl methacrylate to control the particle diameter and its distribution. The inner conductive and outer nonconductive layers were composed of silver and silica, respectively.[8] Wu and Conrad developed a nonohmic conduction model for the influence of a film on the particles on the ER response with DC field, prepared silica particles with an oxide film by heating in air for a special temperature and time, the ERFs showed good electrorheological effect.[9] Modified titania doped with rare earth were synthesized by means of sol/gel technique, the yield stress of the ERFs based on these particles changed with the mole ratio of RE/Ti, showed good ER performance at high temperature.[10] To obtain a large yield stress, optimizing the insulating layer coating thickness should strive, so that it would prevent shorting between the conducting and give a large yield stress, novel double coated particles with a conducting inner (nickel) and an insulating outer layer (TiO$_2$) were synthesized, the dramatic enhancement is obtained as the thickness got higher.[11] The granular aluminum hydroxide and flaky talc were used as substrates to prepare the composite particles coated with polyaniline. After the particles are coated with PANI, the ERFs for both inorganic particles at high electric field strength become comparing. In spite of the higher electroviscosity of suspension of PANI base particles, the ER efficiency expressed in term of relative electroviscosity, $(\eta_E - \eta_0)/\eta_0$, is similar to PANI-coated inorganic particles due to low field-off viscosity.[12] Lee et al.[13] synthesized the PANI/TiO$_2$ hybrid particles via an oxidation polymerization. The PANI/TiO$_2$-based ERFs in silicone oil showed strong EF effect. In addition, the region of plateau become wider with the strength of electric field, indicating the ER effect can be maintained up to higher shear stress.

Barium titanate is an inorganic ionic compound with high dielectric constant. Barium titanate-based ERFs have a high electrorheological effect, but it becomes poor in anhydrous state. By modifying the surface of BaTiO$_3$ with organic polymer to form core-shell composed particles, it may be the available method to prepare dispersed particles for ERFs.[14,15] Otherwise, the composite particles are easy to modify the dielectric and electric properties by doping or dedoping of polyaniline. In polymerization, PANI were coated on the surface of BaTiO$_3$, at the same time formed pure PANI. To increase the proportion of polyaniline-coated barium titanate composite particles, couplings agent should be used in the graft polymerization. Moreover, there are few reports about the influence of couplings agent for graft polymerization of aniline on BaTiO$_3$.

In this article, polyaniline-coated barium titanate composite particles were synthesized by surface grafting polymerization using silane couplings agent, and the structure and electrorheological properties were studied. The affection of silane couplings agent on grafting polymerization and the properties of ERFs have been explored.

EXPERIMENTAL

Materials for synthesis

Tetra-*n*-titanate and barium acetate (A.R.) were purchased from Chinese Medical Group. Silane coupling agents (KH570, KH560, KH550, NSC-151, SG-Si6O2, ≥97.0%) were from Nanjing Crompton Silcane Corp. Isopropyl alcohol, acetic acid, ammonium peroxysulfate, HCl, and alcohol were used as received without further purification. Aniline was distilled under nitrogen, and used as fresh.

Technology for characterization

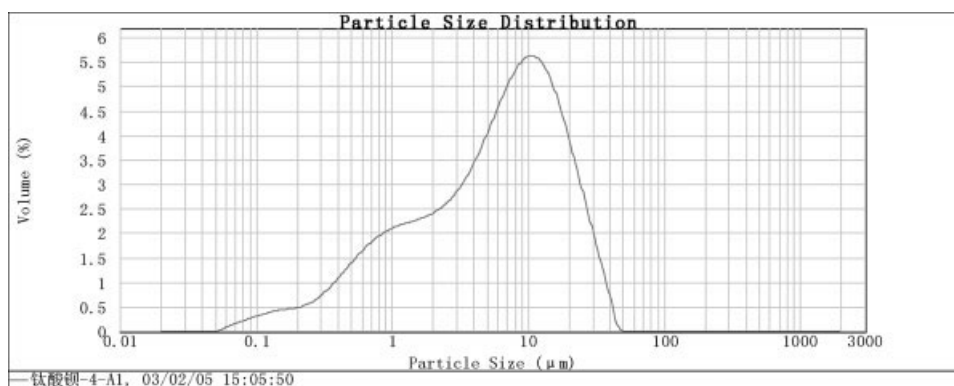Thermogravimeter were conducted on PE Q600 thermal analyzer to determine the relative content of

Figure 1 Particle size distribution of barium titanate.

TABLE I
Measured Result for Particle Size at Different Condition

Sample	Number average diameter (μm)	pH	Amount of water (mL)	Sintering temperature (°C)
1	10.34	3.5	64.9	750
2	8.71	3.5	64.9	780
3	16.82	3.5	58.4	750
4	12.34	3.5	51.9	750
5	14.57	3.5	77.9	750
6	13.92	3.4	64.9	780
7	18.07	3.2	64.9	780

barium titanate in polyaniline/barium titanate composite particles. All runs were carried out from room temperature to 1000°C in air stream with heating rate of 20°C/min. The number average particle diameter and size distribution were measured from MS 2000 (Mawen Co.), alcohol as dispersant. The density of barium titanate and polyaniline/barium titanate composite particles was measured by 50-mm Pycnometer. FTIR spectra were recorded on a PE 1725X FTIR spectrometer, the sample was prepared by compress disk of KBr. The morphology of particles was observed by scanning electron microscopy HITACHIS-57. X-ray diffraction analysis was carried out in XD-3 X-ray diffraction meter, fitted with copper target, Kα ray, scanning rate 4°/min for the recording data in the range of $2\theta = 5°$–$50°$(360 kV, 20 mA). The shear stress of the ERFs was measured with a rotary rheometer (NXS-11A, Chengdu Instrument Factory, China; the gap between the outer cup and inner bob was 2 mm) equipped with a high-voltage direct-current power source (GW5-2C,

Tiangjing Huida Electronic Component Factory, China).

Synthesis of barium titanate

The barium titanate was prepared by sol-gel technique. Tetra-*n*-titanate and barium acetate (0.1 mol) were dissolved in isopropyl alcohol, adding 0.3 mol acetic acid. The solution of acetic acid containing 0.1 mol barium acetic was dropped into above isopropyl alcohol solution. By hydrolyzing completely and adjusting the pH of the mixing to 3.5–3, the mixture was set in water bath 3 days for aging. The gel was sintering in oven at high temperature for 2 h, the barium titanate was obtained.

Synthesis of polyaniline-coated barium titanate composite particles

The suspension containing barium titanate particle (0.01 mol) was heated and stirred for 1 h, then the solution of silane coupling agent (1%) was added, reacted for another 1 h, and cooled to room temperature. A solution of aniline of 1*M* HCl was added, chilled, and stirred for another 2 h. The polymerization was initiated at 5°C by dropping of a prechilled solution of ammonium peroxysulfate of 1*M* HCl. The reaction was maintained for another 4 h. The composite particles were obtained after filtering, washing with distilled water, drying in vacuum, grinding with a ball mill, and passing through a 38-μ sieve. To obtain semiconducting particles, the composite particles were dedoped in aqueous NaOH, the pH of suspension was remained constant for 3 days. The dedoped particles were filtered and washed with distilled water, ethanol, and
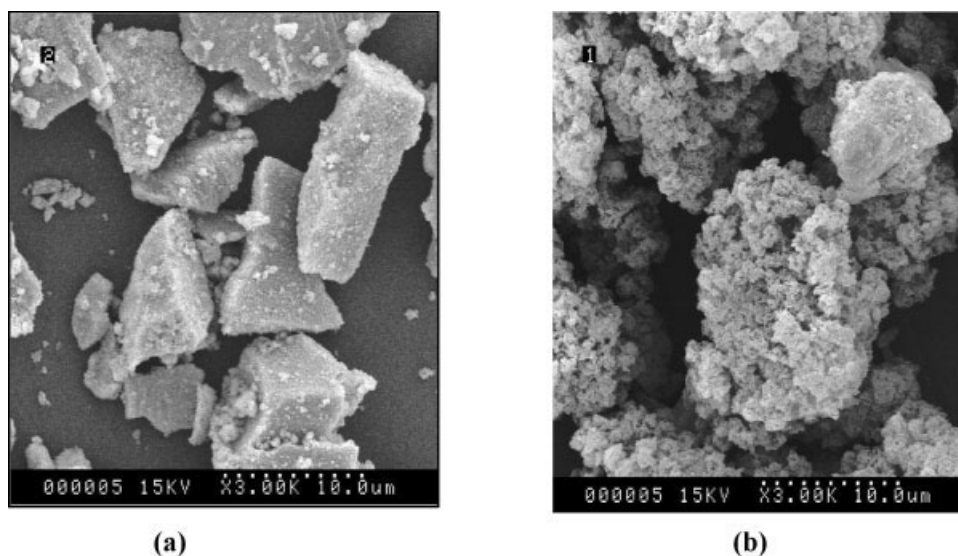

Figure 2 Scanning electron microscopy (SEM) of barium titanate particles (a) and polyaniline-coated barium titanate composite particles (b).
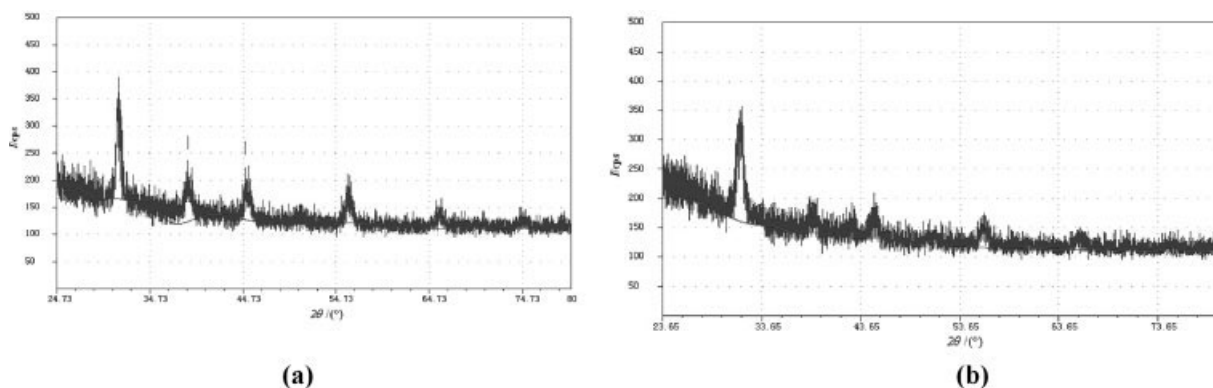
Figure 3 XRD pattern of barium titanate particles (a) and polyaniline-coated barium titanate composite particles (b).

cyclohexane to remove the oligomer and excess monomer and make the particle surface hydrophobic.

Preparation of ERFs

ERFs were prepared by dispersing the barium titanate and polyaniline-coated barium titanate compositive particles in silane oil, respectively. The mixture was grinded in muller for 20 min to disperse uniformly particles in oil, and then stored in vacuum oven before test.

RESULTS AND DISCUSSION

Properties of composite particles

Figure 1 is the size distribution of barium titanate particle. The number average particle diameter is 8.71 μm.

Several kinds of barium titanate had been synthesized at different conditions to explore the influence of the pH, the amount of water, and sintering temperature. Table I shows the result of particles size at different condition. The result showed that particle size was related with the pH, the amount of water, and sintering temperature. The number average particle diameter was increasing with the decreasing of

Figure 4 FTIR spectra of BaTiO$_3$, PANI and PANI/BaTiO$_3$.

the pH. At lower pH, the oxyalkyl of titanate was replaced by acetate, and had no chance to react with titanate. When pH is below 3, it cannot form the gel. With the increasing of amount of water, the concentration of polycondensity and the number average particle diameter were decreased. However, the particles had larger size due to the formation of OH and the crosslink when amount of water was greater than 64.9 mL. The particles size was decreasing as sintering temperature was higher.

Figure 2 showed the SEM photographs of barium titanate and polyaniline-coated barium titanate composite particles. Barium titanate particles have the abnormity shape, and the number average diameter is about 5–10 μm. By grafting polymerization on the surface of barium titanate, the composite particles are olivary and porous, and the number average diameter is about 10 μm.

Figure 3 exhibited the XRD analysis of barium titanate particles and polyaniline-coated barium titanate composite particles. Compared with distance between the layers, the barium titanate had the cubic crystallites structure, where d-spacing are 2.8500, 2.3280, and 2.0160 Å. The XRD pattern of composite particles, Figure 3(b), was similar to that of barium titanate, only decreasing in intensity due to coating by polyaniline. From SEM photographs and XRD analysis, the polyaniline was coated on the barium titanate and formed composite particles with shell-core structure.

FTIR spectra also confirm the structure for PANI/BaTiO$_3$. Figure 4 showed the FTIR spectra of barium
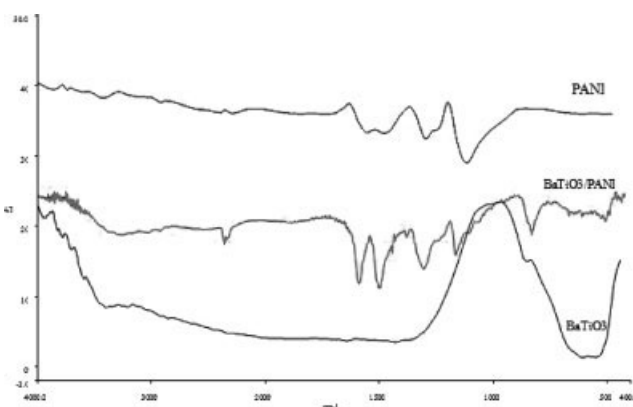
TABLE II
Molecular Structure of Silane Coupling Agent

	Samples	Molecular structure
1	KH570	$CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$
2	KH560	$CH_2CHCH_2O(CH_2)_3Si(OCH_3)_3$
3	KH550	$NH_2(CH_2)_3Si(OC_2H_5)_3$
4	SG-Si602	$NH_2(CH_2)_2NH(CH_2)_3SiCH_3(OCH_3)_2$
5	NSC-151	$CH_2=CHSi(OCH_2CH_3)_3$

Sample	BaTiO₃	PANI	KH570	KH560	KH550	SG-Si602	NSC-151
ρ (g/cm³)	6.0818	1.2914	1.5322	1.8012	1.5466	1.3581	1.8244
Content of PANI (%) from XRD data			46.54	33.29	39.90	48.72	33.50
Loss weight in 30 – 300°C (%)			4.439	2.080	6.850	6.350	1.960
Loss weight in 300 – 998°C (%)			28.853	29.705	26.255	28.405	28.47
Content of BaTiO₃ (%) from TGA			66.493	67.930	66.595	64.440	69.420

titanate, polyaniline, and polyaniline-coated barium titanate composite particles. The stretching vibration of quinondiimine and phenylene diamine display at 1568 and 1479 cm⁻¹, and the bend vibration of C—N in quinine is showed at 1131 cm⁻¹, these were associated with the polyaniline. The stretching vibration of C=C at 1650 cm⁻¹ was disappear due to the reaction between the double bond of KH570 with aniline, this also can be seen the appear at 710 cm⁻¹ for Si—C. The absorb peak at 600 and 400 cm⁻¹ is associated with the structure of perovskite.

Influence of silane coupling agents on structure of composite particles

Because of the handicap for polymerization on inorganic particle, silane coupling agent was used to modify the surface of BaTiO₃ for grafting surface polymerization. The molecular structure of silane coupling agent exhibited in Table II.

There are two kinds of silane couple agents, one has the reactivity groups at the terminal, such as double bonds and epoxy, and others have the NH₂ group. By simulation geometric configure of grafting on surface between silane couple agents and BaTiO₃ using soft Gaussian 03, the bond length of Si—O formed between them is shorter than that of Ti—O in BaTiO₃.[16] The silane couple agents with double bonds and epoxy groups are easier to form covalent bond with aniline than other silane couple agents.

The calculation results also showed that epoxy group is easier to reactive with aniline than double bonds due to the longer bond length for KH560.

Table III is the density of BaTiO₃, polyaniline, and composite particles. The density of composite particles is from 1.358 to 1.824 g/cm³, which is between that of BaTiO₃ and PANI. From XRD data, the content of amorphous in composite particles was calculated. Table III also gave the content of amorphous in composite particles, which is associated with the content of PANI. Figure 5 is the TG curve of composite particles. Before 300°C, the loss weight is the evaporation of low molecules, such as water, monomer, and HCl. The decreasing of weight between 300 amd 900°C is associated with the decomposing of PANI. After 998°C, the residual is the BaTiO₃. From Table IV, the content of PANI measurement by TG is consistent with that by XRD.

Electrorheological properties of ERF based on polyaniline/BaTiO₃ particles

Figure 6 (a) displayed the shear stress versus the shear rate for composite particles-based ERFs with volume fraction of 20 vol % at different electric field strength. The composite particles-based ERFs show higher shear stress than that of BaTiO₃-based ERFs in all the range of shear rate, the yield stress is as high as 720 Pa, but BaTiO₃-based ERFs has no yield stress. Figure 6 (b) is the shear stress versus the
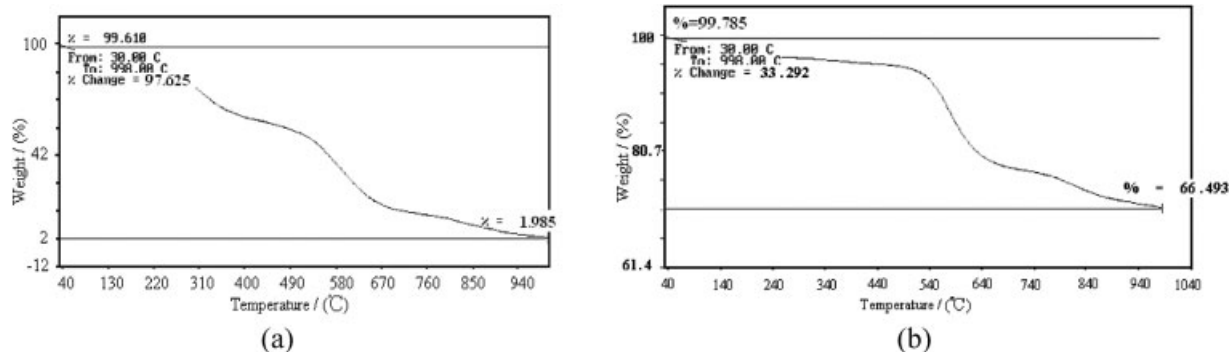
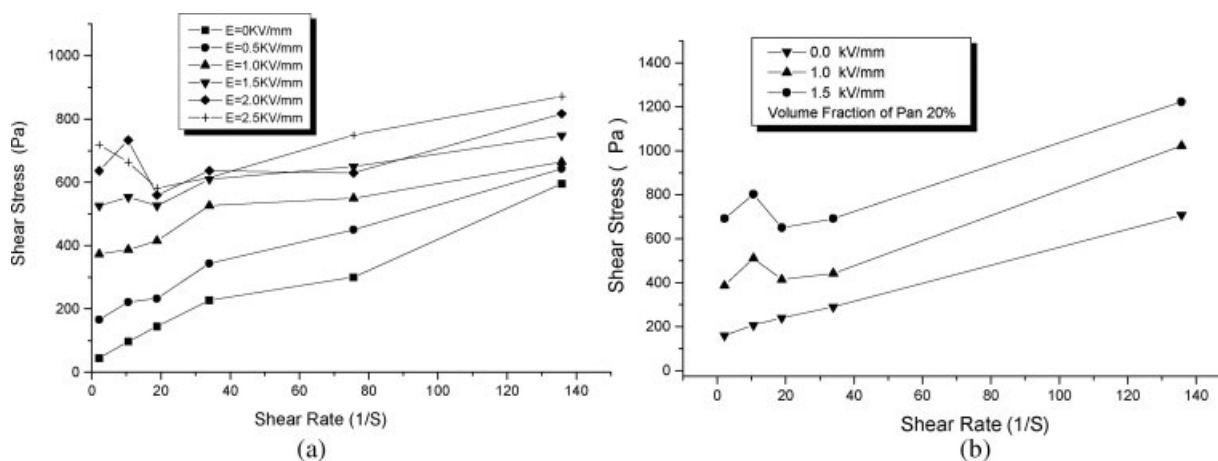**Figure 5** The TGA curve of PANI (a) and PANI/BaTiO₃ compound (b).

Figure 6 Shear stress versus the shear rate for (a) composite particles-based ERFs and (b) PANI-based ERFs.

shear rate for PANI-based ERFs at different electric field strength. Although PANI-based ERFs had comparable yield stress at lower electric field strength, but it has higher field-off viscosity, which was associated with the molecular interaction between particles at higher volume fraction. Otherwise, the PANI-based ERFs resulted in dielectric breakdown due to the high leaking current density at lower electric field strength in this higher volume fraction. The result showed the decreasing of shear stress at low shear rate, and the phenomena has been also found for other ERFs systems.[17]

Figure 7 exhibited the yield stress versus electric field strength of ERFs containing composite particles, which were synthesized by different silane couple agents. The yield stress of composite-based ERFs was greatly affected by the type of silane couple agents. The ERFs of composite particles synthesized by reactivity silane couple agents showed higher yield stress, it is poor for that of nonreactive silane couple agents. These are two types of polymerization for aniline. One is the polymerization of aniline on the surface of BaTiO₃, and other is the polymerization of aniline in solution. The former comes into being the polyaniline-coated barium titanate composite particles, and the latter forms the pure polyaniline. By using reactive silane couple agents, the covalent bonds were formed between modified BaTiO₃ and aniline, which is facile to graft polymerization on the surface of BaTiO₃ to form the composite particle. As a result, the mixture contained more composite particle, exhibited higher density, and the ERFs possessed higher yield stress. But for nonreactive silane couple agents, the bonds between BaTiO₃ and aniline are molecular interaction between amido, aniline formed pure PANI in mixture, in another words, the mixture contained more PANI particles, so the particles-based ERFs showed lower yield stress.

CONCLUSIONS

Polyaniline-coated barium titanate composite particles were synthesized by surface grafting polymerization, in which five silane coupling agents with different terminal groups were used. The number average particle diameter is 10 μm, with the olivary and porous. The particle size was related with pH, the amount of water, and sintering temperature. Characterized by SEM, XRD, FTIR, and TGA, the polyaniline-coated barium titanate composite particles with shell-core structure were formed.

The yield stress of the ERFs based on polyaniline-coated barium titanate composite particles is higher than that of based on polyaniline and barium titanate. Compared with PANI-based ERFs, the composite particles-based ERFs have lower field-off viscosity due to the molecular interaction. The yield stress of the ERFs, as well as density of the composite particles, was influenced by the groups at terminal of silane coupling agents.
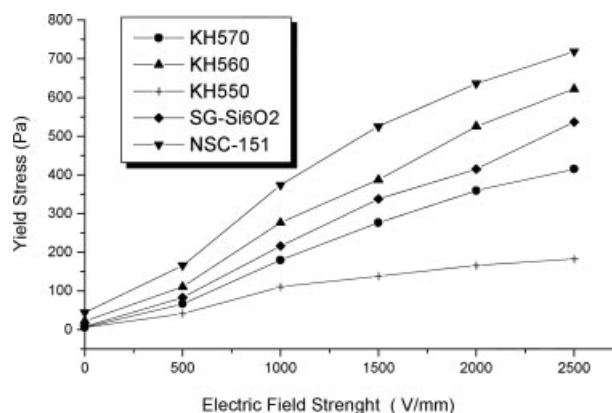

Figure 7 Yield stress versus the shear rate for ERFs of composite particles synthesized by different silane couple agents.

References

1. Whittle, M.; Bullogh, W. A. Nature 1992, 358, 373.
2. Block, H.; Kelly, J. P. J Phys D: Appl Phys 1988, 21, 1661.
3. Yan, H.; Chan, W. L.; Szeto, Y. S. J Appl Polym Sci 2004, 91, 2523.
4. Duan, X. D.; Chen, H.; He, Y. J. J Phys D: Appl Phys 2000, 33, 696.
5. Chin, B. D.; Park, O. O. J Rheol 2000, 44, 397.
6. Yan, H.; Liao, Z. J.; Mao, H. J. J Appl Polym Sci 2006, 101, 638.
7. Zhang, Y. L.; Zhang, S. H.; Lu, K. Q. Int J Mod Phys B 2001, 15, 596.
8. Saito, T.; Anzai, H.; Kuroda, S. I. Int J Mod Phys B 1999, 13, 1689.
9. Wu, C. W.; Conrad, H. Int J Mod Phys B 1999, 13, 1713.
10. Yin, J. B.; Zhao, X. P. Acta Mater Compos Sin 2002, 19, 64.
11. Wei, J. H.; Shi, J.; Liu, Z. Y.; Guan, J. G.; Yuan, R. Z. Int J Mod Phys B 2005, 19, 1423.
12. Lengalova, A.; Pavlinek, V.; Saha, P. J Colloid Interface Sci 2003, 258, 174.
13. Lee, I. S.; Lee, J. Y.; Sung, J. H.; Choi, S. J. Synth Met 2005, 152, 173.
14. Fang, F. F.; Kim, J. H.; Choi, H. J. Macromol Symp 2006, 242, 49.
15. Wei, J. H.; Guan, J. G.; Chen, W. Y.; Yuan, R. Z. Acta Phys Chim Sin 2002, 17, 653.
16. Liao, Z. J. Thesis, Logistic Engineering University, 2005.
17. Lee, H. S.; Cho, M. S.; Choi, H. J. Polymer 2005, 46, 1317.