

# Preparation and electrostriction of BaTiO<sub>3</sub>/polyurethane nanocomposite elastomers

Lin Baoping<sup>1</sup> Cong Yuqi<sup>1</sup> Chen Fanxiu<sup>2</sup> Wu Jianfeng<sup>3</sup> Li Jianqing<sup>3</sup> He Xiaoyuan<sup>2</sup>

(<sup>1</sup>Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

(<sup>2</sup>College of Civil Engineering, Southeast University, Nanjing 210096, China)

(<sup>3</sup>Department of Instrument Science and Technology, Southeast University, Nanjing 210096, China)

**Abstract:** BaTiO<sub>3</sub>/polyurethane (BaTiO<sub>3</sub>/PU) nanocomposite elastomers were prepared from barium titanate nanoparticles, polyester polyol, 2, 4-toluene diisocyanate, 1, 4-butanediol and 1, 1, 1-trimethanol propane by the one-step method. The density, hardness and dielectric constant of BaTiO<sub>3</sub>/PU nanocomposite elastomers increased with the increase of the content of BaTiO<sub>3</sub> nanoparticles in nanocomposites. The electrostrictive properties of BaTiO<sub>3</sub>/PU nanocomposite elastomers were investigated by the digital speckle correlation method (DSCM). It was found that through the on-and-off of the electric field, the electrostrictive strains of BaTiO<sub>3</sub>/PU nanocomposite elastomers revealed corresponding shrinkage and recovery. The electrostrictive coefficient of BaTiO<sub>3</sub>/PU nanocomposite elastomers was greater than that of the corresponding polyurethane elastomers, and the electrostrictive coefficient of composites decreased with the increase of the content of barium titanate nanoparticles.

**Key words:** nanocomposite elastomer; polyurethane; barium titanate; dielectric constant; electrostriction

Electrostriction is one of the electromechanical coupling effects of materials. Thermoplastic polyurethane elastomers are the materials that possess the electrostrictive strain of the order of few percents<sup>[1]</sup>. The electrostrictive strain of pure polyurethane elastomers is higher than that of ferroelectric ceramics, while the electrostrictive stress produced by pure polyurethane elastomers is not competitive with the electroactive ceramic. Hence, a combination of the two appears to be good alternative<sup>[2]</sup>. The inorganic-organic hybrid materials composed of hard and soft materials synergistically intertwined to provide both useful functionality and mechanical integrity<sup>[3]</sup>. The interaction between the inorganic and the organic compositions by physical force and chemical bond is important as a method for controlling the structure and properties of the inorganic-organic hybrid materials.

Sakamoto et al.<sup>[4-5]</sup> investigated the electro-mechanical properties of 0-3 vegetable based polyurethane and lead zirconate titanate composite (PU/PZT), and PU/PZT composite was used to prepare acoustic emission sensors. Wong et al.<sup>[2,6]</sup> prepared the electrostrictive composites of thermoplastic polyurethane elastomers with the ferroelectric lead zirconate ti-

tanate. It was found that the electrostrictive properties were affected by the content of lead zirconate titanate in the composites.

In this paper, BaTiO<sub>3</sub>/polyurethane (BaTiO<sub>3</sub>/PU) nanocomposite elastomers with lower BaTiO<sub>3</sub> content were prepared from barium titanate nanoparticles, polyester polyol, 2, 4-toluene diisocyanate, 1, 4-butanediol and 1, 1, 1-trimethanol propane by the one-step method. The effects of the content of BaTiO<sub>3</sub> nanoparticles on the structure, dielectric constant and electrostrictive properties were described.

## 1 Experimental

### 1.1 Materials

2, 4-toluene diisocyanate (TDI), 1, 4-butanediol (1,4-BD) and adipic acid (HA) were purchased from Shanghai Chemistry Reagent Company. 2, 2-dimethyl-1, 3-propanediol (NPG) was obtained from Bayer Chemical Company. TDI, 1, 4-BD, HA and NPG were respectively purified by distillation or recrystallization from solvent before use. The remaining chemical reagents were used without additional purification.

### 1.2 Preparation of polyester diol

The procedure of preparation of polyester diol is described as follows<sup>[7]</sup>: The adipic acid (1 mol), 1, 4-butanediol (0.65 mol) and 2, 2-dimethyl-1, 3-propanediol (0.65 mol) were added into a glass reactor with a condenser, a thermometer and a stirrer. When reacting

Received 2005-11-08.

**Foundation item:** The Natural Science Foundation of Jiangsu Province (No. BK2003063).

**Biography:** Lin Baoping (1958—), male, professor, lbp@seu.edu.cn.

temperature was raised to 120 °C, tetrabutyl titanate catalyst was dropped into the reactor. Then the reacting temperature was slowly raised from 120 °C to 220 °C within 10 h. After the water weight removed from the reaction system reached 70% of the theoretic value, the reaction continued *in vacuo* about 1 to 3 h. The reaction finished when the acid value of the product was smaller than 2.0 mg/g. The average molecular weight of prepared polyester diol was 1504.

### 1.3 Preparation of BaTiO<sub>3</sub> nanoparticles

BaTiO<sub>3</sub> nanoparticles were prepared according to Ref. [8]. 78 mmol of metatitanic acid, 61.8 mL of 30% hydrogen peroxide and 23.8 mL of 25% ammonium hydroxide were mixed and stirred at 0 °C for 2 h to obtain a clear solution of ammonium titanate. 75 mmol of barium acetate in 300 mL water was added to a stirred solution of ammonium titanate dropwise at ambient temperature to allow the light yellow precipitate to be formed. After suction filtration of the precipitate followed by washing with distilled water and anhydrous ethyl alcohol, the precipitate was dried at 105 °C for 8 h and calcined at 800 °C for 2 h to obtain BaTiO<sub>3</sub> nanoparticles. The molar ratio of barium to titanium measured by ICP was 1.002. The results measured by the XRD and the TEM show that BaTiO<sub>3</sub> nanoparticles have a typical perovskite structure and a diameter of 30 to 70 nm.

### 1.4 Preparation of BaTiO<sub>3</sub>/PU elastomers

The polyester diol and barium titanate nanoparticles dispersed in DMAc were mixed under mechanical stir, and the DMAc solvent in the formed polyester diol/BaTiO<sub>3</sub> mixtures was removed *in vacuo* at 160 °C for 1 h. Then quantitative 1, 4-Butanediol, 2, 4-toluene diisocyanate and 1, 1, 1-trimethylolpropane (TMP) were added into the mixture of the polyester diol and barium titanate nanoparticles at 80 °C, followed with vigorous stirring about 1 min. The obtained reactant was cast on a glass substrate. After curing at 120 °C for 10 h, a 1 mm thick film was obtained.

### 1.5 Measurement

The structure of BaTiO<sub>3</sub>/PU nanocomposite elastomers was characterized by the Fourier transform infrared spectroscopy (FTIR, Nicolet Magna IR650). The density was measured by the pycnometer method at 20 °C. The hardness was measured with an LX-A rubber hardness meter. Differential scanning calorimeter (DSC) measurement was conducted on a TA instrument Q10, under a nitrogen purge, at a heating rate of 10 °C/min. The dielectric constant was measured under

1 V bias voltage within the range of 100 Hz to 10 MHz with a 3532-50 HITESTER LCR analyzer.

The digital speckle correlation method was used to measure the strain induced by the electrical field. The schematic diagram of the experimental device is shown in Fig. 1.

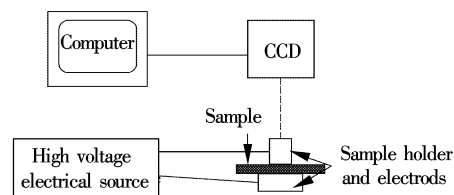


Fig. 1 Schematic diagram of the experimental device used to measure the field-induced strain

## 2 Results and Discussion

The components and some physical properties of BaTiO<sub>3</sub>/PU nanocomposite elastomers are listed in Tab. 1. When BaTiO<sub>3</sub>/PU nanocomposite elastomers were prepared, the molar ratios of TDI, polyester diol, 1, 4-BD and TMP were 2, 1, 0.12 and 0.52, respectively. The structures of BaTiO<sub>3</sub>/PU nanocomposite elastomers were confirmed with ATR-FTIR. The representative ATR-FTIR spectra of BaTiO<sub>3</sub>/PU nanocomposite elastomers are shown in Fig. 2. Comparing the spectra of PUE-1 and PUE-6, it was found that the spectra of PUE-1 and PUE-6 were about the same within the range of 4000 to 700 cm<sup>-1</sup>. The characteristic absorption at 1731 cm<sup>-1</sup> of C=O stretching in polyurethane was observed. The absorption of C—N stretching at 1600 cm<sup>-1</sup> was also observed. The characteristic N—H absorption in carbamate groups appeared at 3338 and 1535 cm<sup>-1</sup>. The absorption at 1172 cm<sup>-1</sup> was based on the aliphatic ester C—O in polyurethane. The observation of these absorption bands clearly indicated the existence of carbamate groups and aliphatic ester groups, and confirmed the successful synthesis of polyurethane either in the pure polyurethane or in BaTiO<sub>3</sub>/polyurethane nanocomposites.

Tab. 1 Components and some physical properties of BaTiO<sub>3</sub>/PU elastomers

Sample code	Content of BaTiO <sub>3</sub> /%	Density/(g·cm <sup>-3</sup> )	Hardness (Shore A)	T <sub>g</sub> /°C
PUE-1	0	1.1806	49.3	-31.1
PUE-2	0.5	1.1911	51.1	-26.8
PUE-3	1.1	1.1990	52.0	-25.0
PUE-4	1.5	1.2104	53.9	-27.8
PUE-5	1.8	1.2172	54.3	-28.4
PUE-6	2.3	1.2285	56.7	-27.5

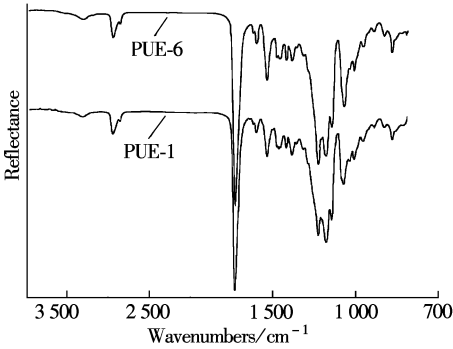


Fig. 2 ATR-FTIR spectra of BaTiO<sub>3</sub>/polyurethane nano-composite elastomers

The density and hardness of BaTiO<sub>3</sub>/PU nano-composite elastomers increased with the increase of the content of BaTiO<sub>3</sub> nanoparticles in nanocomposites, which meant that the compressed module of BaTiO<sub>3</sub>/PU nanocomposite elastomers increased with the increase of BaTiO<sub>3</sub> content. In general, the glass transition temperature  $T_g$  of organic-inorganic composites increased with the increase of inorganic content, however no clear trend with BaTiO<sub>3</sub> concentration was observed. The fact that this trend was not observed may reflect the variability in the degree of cross-linking and the morphology of these systems<sup>[9]</sup>.

The electrostrictive phenomena are relative to the dielectric constant of BaTiO<sub>3</sub>/PU nanocomposite elastomers. The prepared BaTiO<sub>3</sub>/PU elastomer films were coated with a thin gold layer on each surface as an electrode. Fig. 3 shows the relationship between the relative dielectric constant of BaTiO<sub>3</sub>/PU nanocomposite elastomers and the content of BaTiO<sub>3</sub> in nanocomposite elastomers at 1 kHz measuring frequency. The relative dielectric constant of BaTiO<sub>3</sub>/PU nanocomposites was higher than that of the corresponding polyurethane. And the relative dielectric constant increased with the increase of the content of BaTiO<sub>3</sub> in nanocomposite elastomers. The dielectric loss tangent value of these BaTiO<sub>3</sub>/PU elastomer films was within the range of 0.054 to 0.062.

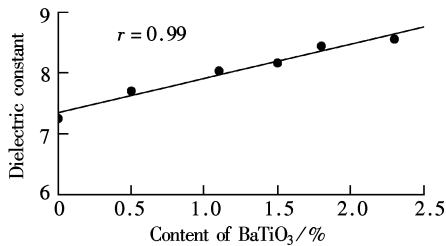


Fig. 3 Relationship between the relative dielectric constant of BaTiO<sub>3</sub>/PU elastomers and the content of BaTiO<sub>3</sub> in the elastomers at 1 kHz measuring frequency

The strain induced by electrostriction is proportional to the square of the electric field strength, which means the strain has nothing to do with the direction of the electric field. The electrostrictive strain of the PUE-3 at 3.5 and 6.5 kV electric field is shown in Fig. 4. In Fig. 4(a), the electric field was on at 60, 180 and 300 s and was off at 120, 240 and 360 s. The shrink of the PUE-3 sample was very quick when the electric field was conducted (it could reach its largest strain in 10 s), and the strain was stable under the steady voltage. After removing the electric field, the sample recovered gradually but the responding rate was slower than that of the shrink, and the film could not recover to the original thickness. The curve of PUE-3 at 6.5 kV electric field was similar to the one at 3.5 kV electric field (see Fig. 4(b)). The shrink of the PUE-3 sample at 6.5 kV electric field was larger than that at 3.5 kV electric field. It implied that the shrink of BaTiO<sub>3</sub>/PU nano-composite elastomers increased with the increase of driving electric field strength.

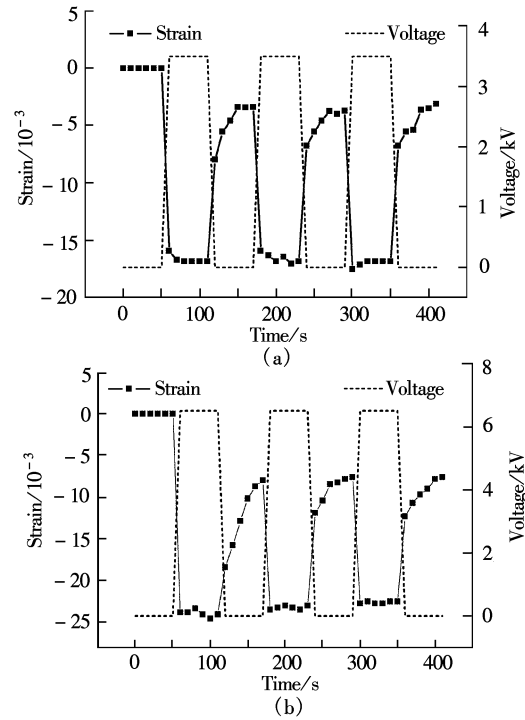


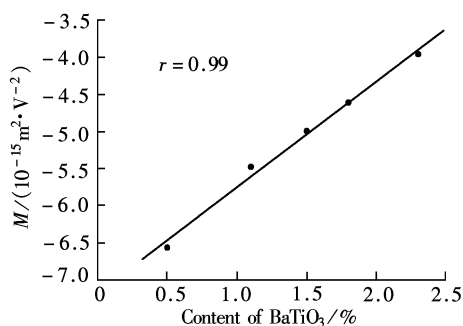
Fig. 4 Electrostrictive strain of PUE-3 at 3.5 and 6.5 kV electric fields, respectively. (a) 3.5 kV; (b) 6.5 kV

The electrostrictive coefficients of BaTiO<sub>3</sub>/PUE were calculated by<sup>[10]</sup>

$$S = ME^2$$

where  $S$  is the electrostrictive strain,  $M$  is the electrostrictive coefficient, and  $E$  is the applied electric field. Fig. 5 shows the results of the calculated electrostrictive coefficient  $M$ . Each  $M$  value in Fig. 5 is an average val-

ue of the electrostrictive coefficient measured at 3.5, 6.5 and 9 kV electric fields, respectively.



**Fig. 5** Relationship between  $M$  of BaTiO<sub>3</sub>/PU elastomers and the content of BaTiO<sub>3</sub> in elastomers

The average  $M$  measured at 3.5, 6.5 and 9 kV electric fields, respectively, was about  $-1.78 \times 10^{-15} \text{ m}^2/\text{V}^2$  for the pure polyurethane elastomers. The introduction of BaTiO<sub>3</sub> nanoparticles into polyurethane matrices would make the absolute value of  $M$  increase, which meant the electrostrictive strain increased with the introduction of BaTiO<sub>3</sub>. It may be attributed to the results of cooperation action of BaTiO<sub>3</sub> nanoparticles and the polyurethane matrix. However, with the increase of the content of BaTiO<sub>3</sub> nanoparticles in the polyurethane matrix, the absolute value of  $M$  decreased from  $6.56 \times 10^{-15}$  to  $3.95 \times 10^{-15} \text{ m}^2/\text{V}^2$ . It was believed that the group movability in the polyurethane was inhibited by the introduction of BaTiO<sub>3</sub> nanoparticles into the polyurethane matrix.

In general, the strain induced by electrostriction is proportional to the relative dielectric constant of materials<sup>[10]</sup>. Here the relative dielectric constant of BaTiO<sub>3</sub>/PU nanocomposites increased with the increase of the BaTiO<sub>3</sub> content in the nanocomposite elastomers, nevertheless the strain induced by electrostriction did not increase with the increase of the relative dielectric constant for BaTiO<sub>3</sub>/PU nanocomposite systems. These phenomena might be ascribed to the difference in the structure and morphology between the BaTiO<sub>3</sub>/PU nanocomposites and the pure polyurethane.

### 3 Conclusion

BaTiO<sub>3</sub>/polyurethane nanocomposite elastomers were prepared by the one-step synthetic method. The density, hardness and dielectric constant of BaTiO<sub>3</sub>/PU nanocomposite elastomers increased with the increase of the content of BaTiO<sub>3</sub> nanoparticles in the nanocomposites. The glass transition temperature of BaTiO<sub>3</sub>/PU nanocomposite elastomers did not present a clear trend with the varying of BaTiO<sub>3</sub> nanoparticles concentration

in BaTiO<sub>3</sub>/PU nanocomposites. The electrostrictive strain of BaTiO<sub>3</sub>/PU nanocomposite elastomers showed the corresponding shrink and recovery through the on-and-off of the electric field. The introduction of BaTiO<sub>3</sub> nanoparticles into the polyurethane matrix could increase the electrostrictive strain. However the absolute value of the electrostrictive coefficient  $M$  of BaTiO<sub>3</sub>/PU nanocomposite elastomers decreased with the increase of the BaTiO<sub>3</sub> content.

### References

- [1] Ma Z, Scheinbeim J I, Lee J W, et al. High field electrostrictive response of polymers [J]. *J Polym Sci, Part B: Polym Phys*, 1994, **32**(16): 2721 – 2731.
- [2] Wong Y, Tai L, Liu C X, et al. An investigation of the electrostrictive property of PZT/polyurethane particulate composites [J]. *Ferroelectrics*, 2001, **264**(1–4): 1715 – 1720.
- [3] Lu Y F, Yi Y, Alan A, et al. Self-assembly of mesoscopically ordered chromatic polydiacetylene/silica nanocomposites [J]. *Nature*, 2001, **410**(6831): 913 – 917.
- [4] Sakamoto W K, Dascupta D P. Electromechanical properties of 0-3 vegetable based polyurethane and lead zirconate titanate composite [A]. In: *Eighth International Conference on Dielectric Materials, Measurements and Applications* [C]. Edinburgh, 2000. 491 – 496.
- [5] Sakamoto W K, Marin-Franch P, Tunnicliffe D, et al. Lead zirconate titanate/polyurethane (PZT/PU) composite for acoustic emission sensors [A]. In: *2001 Annual Report Conference on Electrical Insulation and Dielectric Phenomena* [C]. Toronto, 2001. 20 – 23.
- [6] Liu C X, Zhu G Z, Wong Y H, et al. Electrostrictive of the composites of polyurethane with ferroelectric lead zirconate titanate ceramic particles [J]. *J of Functional Polymers*, 2001, **14**(3): 311 – 314. (in Chinese)
- [7] Sun Y P, Yang W Y. Study on method of polyester glycol synthesis [J]. *Ningxia Engineering Technology*, 2005, **4**(3): 262 – 264. (in Chinese)
- [8] Wang S Q, Liu X L, Chen J F, et al. Characterization and dielectric properties of nano-sized BaTiO<sub>3</sub> powders prepared by direct-reactive precipitation [J]. *Journal of Beijing University of Chemical Technology*, 2004, **31**(4): 32 – 35. (in Chinese)
- [9] Cornelius C J, Marand E. Hybrid inorganic-organic materials based on a 6FDA-6FpDA-DABA polyimide and silica: physical characterization studies [J]. *Polymer*, 2002, **43**(8): 2386 – 2400.
- [10] Asai K, Inoue S, Okamoto H, et al. The electric field strain-electrostrictive response of polyurethane elastomers [J]. *Kobunshi Ronbunshu*, 1999, **56**(2): 68 – 76. (in Japanese)

# BaTiO<sub>3</sub>/聚氨酯纳米复合物弹性体的制备与电致伸缩性能

林保平<sup>1</sup> 丛羽奇<sup>1</sup> 陈凡秀<sup>2</sup> 吴建锋<sup>3</sup> 李建清<sup>3</sup> 何小元<sup>2</sup>

(<sup>1</sup>东南大学化学化工系,南京 210096)

(<sup>2</sup>东南大学土木工程学院,南京 210096)

(<sup>3</sup>东南大学仪器科学与工程系,南京 210096)

**摘要:**以聚酯二元醇、甲苯二异氰酸酯、1,4-丁二醇、1,1,1-三羟甲基丙烷和纳米钛酸钡粉体为原料,采用一步法制备了一系列 BaTiO<sub>3</sub>/聚氨酯复合物弹性体. BaTiO<sub>3</sub>/聚氨酯复合物弹性体的密度、硬度和介电常数随钛酸钡含量的增加而增加. 采用数字散斑相关测量方法研究了复合物弹性体在电场诱导下的应变与复合物中钛酸钡含量的关系. 结果表明:BaTiO<sub>3</sub>/聚氨酯复合物弹性体在外加高压电场的作用下,随着高压电源的开合,其应变也随之呈现出相应的收缩与回复. 复合物的电致伸缩系数高于相应的聚氨酯弹性体,但复合物的电致伸缩系数随复合物中钛酸钡含量的增加而逐渐减小.

**关键词:**纳米复合物弹性体;聚氨酯;钛酸钡;介电常数;电致伸缩

**中图分类号:**O63