行政院國家科學委員會個別型計劃成果報告

計畫名稱 : 鉍系列的鐵電智慧材料 (3/3)
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We have prepared polyacrylate containing bismuth titanate nanoparticles as a new ferroelectric smart material using sol-gel process. The bismuth titanate nanoparticles are amorphous, less than 50 nm and well dispersed in the polymer matrix. The material can be easily processed into various shapes such as films and monoliths. The material exhibits ferroelectricity and is transparent in visible light. It has shown good dielectric and thermal properties. The material has potential applications in capacitors, actuators, sensors and optoelectronic devices.

Key Words：bismuth titanates, acrylates, ferroelectricity, smart material, nanoparticles.

1. Introduction

Ferroelctric materials are responsive to external fields and can perform active smart functions such as actuating and sensing. They usually are high in dielectric constant and exhibit hystersis behaviors. Polymeric organic materials usually can be processed easily, low cost, good adhesive strength and impact resistance; however, they are low in the dielectric constant and no ferroelectricity. On the other hand, many inorganic materials exhibit ferroelectric properties with high dielectric constant but they are difficult to process, heavy, brittle and expensive.[1] Recently, organic/inorganic hybrid materials have been emerged as a new class of materials by taking advantages of the merits of each material.[2,3]

Bismuth titanate ceramics have been studied widely due to their electro-optical property, piezoelectricity, ferroelectricity, ionic conductivity, and low sintering temperature. The materials are useful in applications as: actuators, capacitors, nonvolatile memory devices,[4] microwave filters,[5] etc. Polyacrylates are polar and good dielectrics. We have used sol-gel process to combine both materials at molecular level and study their properties.

2. Expertimental

Synthesis of Materials

The polymerizable titanium bismuth 2-methacryl ethoxide is the precursor of bismuth titanate polyacrylate. It was synthesized through alcohol exchange of conventional metal alkoxide with 2-hydroxy ethyl methacrylate. The infrared spectrum (IR) of bismuth titanium 2-methacryl ethoxide exhibits the Ti-O and Bi-O absorptions at 655, 593, 526 and 487 cm^{-1}.

Preparation of Samples

Film Sample

An about 20 grams of 10% (vol.) aqueous hydroxy ethyl methacrylate was added into a mixture of 100 grams (96 gram of polymerizable metal alkoxide and 4 gram of 2,2-dimethoxy-2-phenyl acetophenone (photo-initiator)) to hydrolyze the mixture. The exact amount of water used in the hydrolysis was dependent on the gel rate of the mixture. The mixture was hydrolyzed for 2 minutes, then the hydrolyzed mixture was spin or cast coated on substrate. The sample was irradiated with an UV light (UVP Co. Model UVGL-25) at 254 nm for 3 min. and 365 nm for 3 min to cure the samples.

Monolith Sample The photoinitiator of above mixture was replaced by a 0.5 wt % of 2,2'-azobis(isobutyronitrile) thermoinitiator. The mixture was poured into a Teflon mold. The sample was hydrolyzed overnight, then the hydrolyzed sample was cured at, 60°C/24hrs and 70°C/24hr, 90°C/24 hrs., 110°C/24hrs

Thermal Analyses (TGA and TMA)

The thermal stability of samples was analyzed at 10°C/min from 70 to 700°C in nitrogen using DuPont 9900 TGA 954 instrument. The Tg and coefficient of thermal expansion of samples were analyzed at 10°C/min from 70 to 200°C in air using TA Instrument 2940.

Transmission Electron Microscope (TEM) Analysis.

Hitachi H-7100 TEM instrument was used to analyze the particle size of bismuth titanate in the sample.

X-Ray Diffraction (XRD)

Philips PW1830 X-ray diffractormeter was used to study the crystalline behaviors of the material.

Dielectric Measurements

The dielectric constants and dissipation factors of samples were measured using a Wayne Kerr Precision Magnetics Analyzer PMA 3260A at 25°C from 100 to $2x10^6$Hz. The hystersis loop of samples was measured at voltage from 5 to 20V by Radiant Technologies RT-66A.

3. Results and Discussion

The material was prepared from polymerizable titanium bismuth 2-methacryl ethoxide precursor. It was synthesized through alcohol exchange of conventional metal alkoxide with 2-hydroxy ethyl methacrylate. The precursor was hydrolyzed and condensed into bismuth titanate in an acrylate monomer, then the mixture was subsequently polymerized either by heat or UV radiation. The polymerized hybrid materials contain bismuth titanate inorganic phase and polyacrylate organic phase. Samples with three molar ratios of Ti:Bi:acrylate (1:0.37:8; 1:0.56:8;1:0.74:8) were prepared.

The sample is transparent as shown in Figure 1. The transmission electron microscopy study shows that bismuth titanate particles are less than 50 nm in diameter and well dispersed in the polymer matrix (Figure 2). The materials can not dissolve in acetone and swell in N-methyl pyrrolidone, so they have a crosslinked structure. The materials have shown higher thermal stability (Figure 3) and lower coefficient of thermal expansion (Figure 4) over neat polymer. The results are expected from crosslinked organic-inorganic hybrid network and are consistent with literature reports.[6]

The X-ray diffraction studies show the sample is amorphous and less order than polymer (Figure 5). The presence of bismuth titanate phase in polymer decreases the molecular folding and hydrogen bonding from the hydroxy ethyl group of the acrylate that results in a less order structure. Figure 6 shows the dielectric constant of the material increases with the concentration of bismuth titanate. Figure 7 shows that the material exhibits ferroelctric behavior. It is interesting to note that the amount of dielectric constant increases (~250%) in the hybrid material is higher than expected (~60%) from the simple addition rule of mixing organic material and inorganic material. The pure bismuth titanate with a molar ratio compositon of Bi:Ti = 0.74: 1.00 has a ε_r~12 which accounts about 20% by weight in hybrid material. The high dielectric constant of the hybrid material may be due to effective nanoscale interactions between the organic phase and inorganic phase under electric field. The detailed mechanisms are currently under investigation.

4. Conclusions

Ferroelectric bismuth titanate polyacrylate has been prepared via sol-gel process using polymerizable titanium bismuth methacryl ethoxides precursor The material exhibits high transparency due to the well dispersed bismuth titanate nanoparticles in polymer matrix. It has good thermal and dielectric properties. The material is useful in the applications of capacitors, actuators, sensors and opto-electronic devices.

Acknowledgement

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5. References

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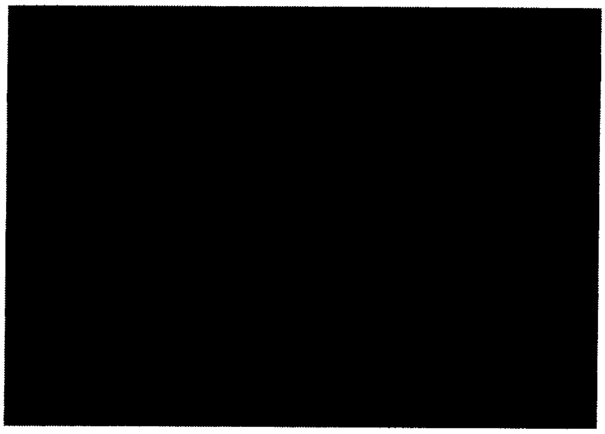

Figure 1 Bismuth titanate polyacrylates-2 shows good transparency in visible light (UV cured sample is on the top of the Bi symbol)

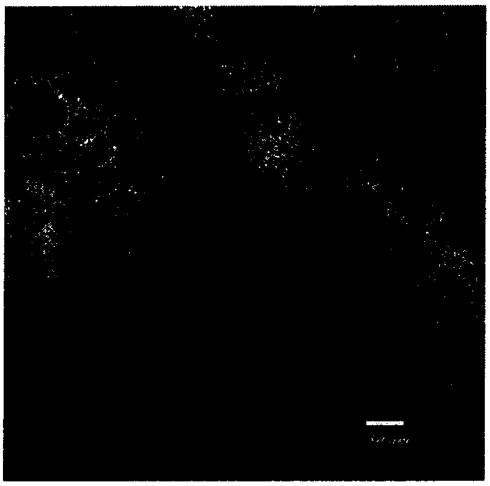

Figure 2 Transmission Electron Microscope Photo of Bismuth titanate polyacrylates-1

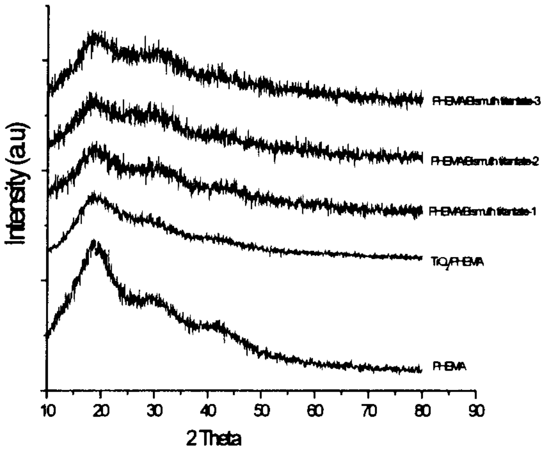

Figure 5 X-ray Diffraction Patterns of Bismuth titanate polyacrylates as compared with Polyacrylate

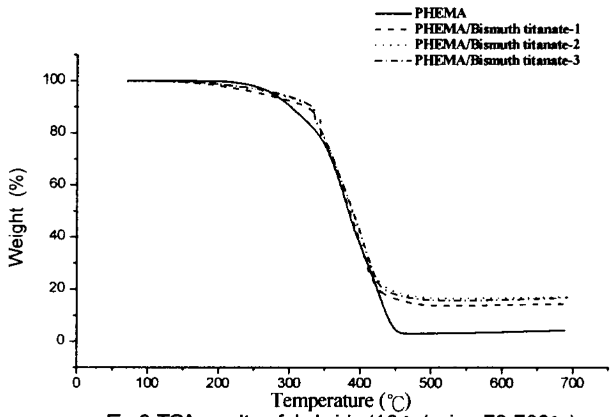

Fig 3 TGA results of hybrids (10 ℃/ min, 70-700℃)

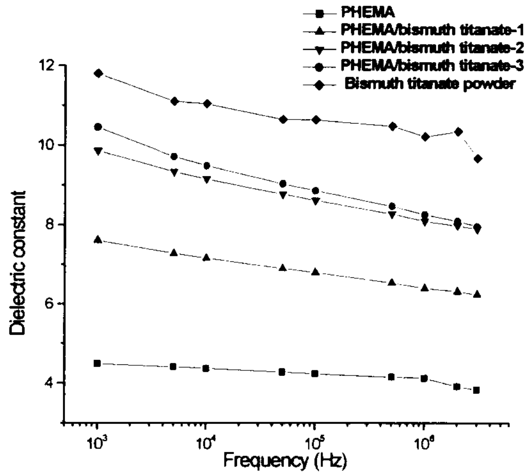

Figure 6 Plots of Dielectric Constant vs. Frequency of Bismuth titanate polyacrylates as compared with polyacrylate

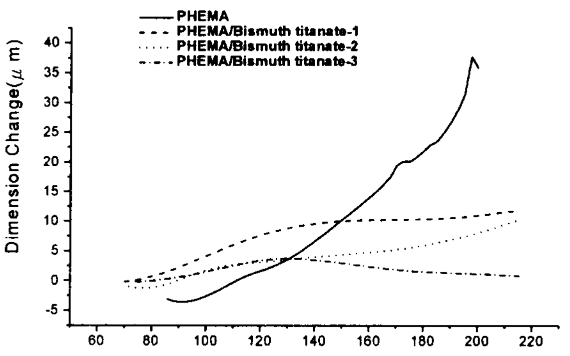

Fig 4 TMA results of hybrids (10℃ /min, 70-200℃)

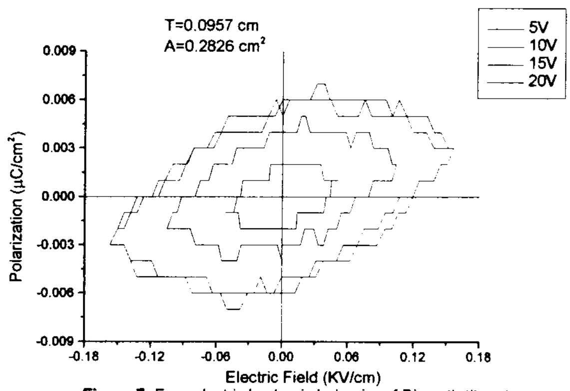

Figure 7 Ferroelectric hysteresis behavior of Bismuth titanate polyacrylates under different voltages.