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Preparation and properties of polymer matrix piezoelectric composites containing aligned $BaTiO_3$ whiskers

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A piezoelectric composite has been prepared with highly aligned $BaTiO_3$ whiskers as the active phase and polyvinylidene fluoride (PVDF) as the matrix. Its dielectric and electromechanical properties are characterized. It is found that the dielectric constant (ε), piezoelectric constant (d_{33}) and remnant polarization (Pr) are considerably higher in the whisker composite than in the corresponding composite containing $BaTiO_3$ powders as the active phase, while the loss factors follow the opposite trend. For the whisker composite, ε, d_{33} and Pr along the direction of the whisker orientation are much higher than the values normal to the whisker orientation. The reasons for the observed differences are discussed.

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1. Introduction

Composite piezoelectric has been widely used in transducer, ultrasonic medical imaging and non-destructive evaluation. In addition, they have also found application as actuators and in micro-motors. Ceramic-polymer piezoelectric composites have been extensively studied in the past four decades in the desire to obtain the optimum electromechanical and physical properties. Piezoelectric composites are classified according to their connectivity. For a diphasic composite, there exist 16 connectivity patterns [1, 2]. Of these, 0–3 and 1–3 composites are most studied because of their outstanding properties and relative ease of fabrication.

Composites with 0–3 connectivity are the easiest to make, simply by blending piezoelectric ceramic powders into polymer matrix. However, they are very difficult to get poled since only a small fraction of the poling electric field is imposed upon the ceramics, while the rest is exerting on the polymer matrix. The primary reason is that polymers normally have much higher electrical resistivity than ceramics.

Composites with 1–3 connectivity have been shown to have the highest sensitivity in pulse-echo mode and low acoustic impedance for good matching to the surrounding media, such as biological tissue, water and air [3]. The main problems are the difficulty in fabrication. Many techniques have been developed to manufacture 1–3 composites including rod replacement, dice-and-fill, lost mold and injection molding [4]. In 1–3 composites, the active piezoelectric rods or fibers are continuous in one direction, while the polymer is self-connected in all three directions. To improve electromechanical response and reduce the cross talking (noise), fine-scale structure is desired. However, with the existing processing methods, the scale of ceramic phase less than 100 μm can only be achieved with difficulty and tremendous technical complexity.

2. Rationale of the project

Piezoelectric whiskers are selected in this work as the active phase and polyvinylidene fluoride (PVDF) as the matrix. The properties of the resultant composites are examined. The objectives are to develop new composites that combine the merits of easy fabrication of 0–3 composites with the good properties of 1–3 composites.

Whiskers are acicular single crystals with very low density of defects. They usually have extremely high tensile strength, and thus are widely used as reinforcements in composites. Whiskers produced in the same batch tend to grow along the same crystallographic direction. For the $BaTiO_3$ whiskers used in this work, electron diffraction and XRD analysis have revealed that the growth axis is predominantly [100]. It is well known that the dielectric and piezoelectric properties of $BaTiO_3$ crystal vary markedly along different crystallographic axis. Therefore, when aligned, the whisker-containing composites might possess high anisotropy just like a [100] single crystal, and only then the excellent properties of the piezoelectric whiskers can be fully explored.

Fig. 1 shows schematically the connecting pattern of a composite containing aligned $BaTiO_3$ whiskers,

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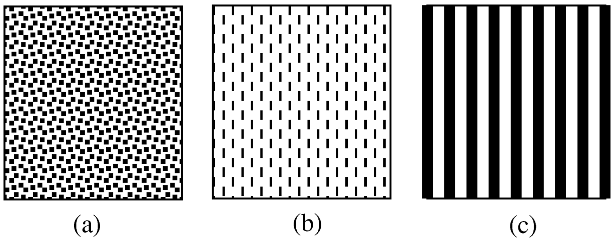

Figure 1 Schematics of piezoelectric composites with the active phases in the forms of: (a) particles, 0–3 composite, (b) whiskers and (c) ceramic rods, 1–3 composite.

together with 0–3 and 1–3 composites. Strictly speaking, the whisker composite has a 0–3 connectivity, because the active phase is not self-connecting. However, it is different from a typical 0–3 composite by its high anisotropy. It is also different from a 1–3 composite in that the active phase is not continuous in any directions. Moreover, the active phase is made up of extremely fine single crystals aligned along the directions of crystal growth, while in a typical 1–3 composite, the active phase is isotropic polycrystalline ceramic rods. The special microstructure of the whisker composite might have a profound effect on its dielectric and electromechanical properties.

3. Experimental procedure

Otsuks Chemical Co. Ltd., Japan, produced the $BaTiO_3$ whiskers. According to the producer's specifications, the average diameter and length were 0.3 and 3 μm respectively; the density was 5600 kg·m^{-3}. PVDF (density 1780 kg·m^{-3}, melting point 165–170°C) was used as the composite matrix. Although PVDF is piezoelectric, its contribution to piezoelectricity in this composite had been found to be much smaller than the whiskers and could be neglected.

The whisker alignment was realized using the technique developed by the present authors [5, 6]. Briefly, $BaTiO_3$ whiskers were dispersed into N,N-dimethylacetamide (DMA) at the presence of dispersant Hypermer KD-1. To reduce whisker agglomeration with the minimal whisker damage, the slurry was magnetically stirred for 5 h and then ultrasonically agitated for 10 min. PVDF solution of 30% in DMA was then added and the resultant fluid was stirred with a mechanical stirrer for 5 h to give a spinning dope. The volume fraction of the whiskers was fixed at 30% on the base of the total solid weight. For comparison, a 0–3 composite with hydrothermal $BaTiO_3$ powder as the active phase was also prepared following the same procedures. The average powder diameter was 0.3 μm, in the same order as the whisker diameter. The powders had well defined crystal morphology and narrow particle size distribution. The compositions of the spinning dopes are listed in Table I.

After vacuum de-aeration, the dope was extruded at 80°C to form fibers using a small-scale laboratory wet-spinning machine. The diameter of the spinneret orifice was 250 μm. A 30% DMA-H_2O solution was used as the coagulation liquid to precipitate the PVDF. Continuous washing in boiling water followed the coagulation. Finally, the fibers were collected at a winding speed of 15 m·min^{-1}. More detailed information can be found in the original paper [5].

TABLE I Compositions of wet-spinning dopes (% by mass) for the preparation of 30% $BaTiO_3$/PVDF composites

$BaTiO_3$ whisker/powder	PVDF	DMA	Hypermer KD-1
13.5	10	76.5	1% of $BaTiO_3$

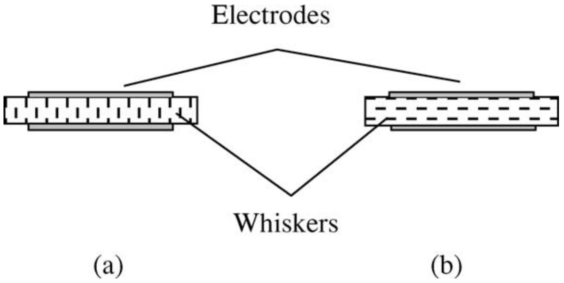

Figure 2 Specimens with the whisker orientation: (a) normal (normal specimen) and (b) parallel (parallel specimen) to the surfaces (the electrodes, when required, are also shown.

The as-spun fibers were dried and cut to length and unidirectionally placed into a rectangular steel die. Heating at 200°C and 0.3 MPa for 30 min densified the composite. After cooling, the composite was sectioned into specimens with the direction of the whiskers normal and parallel to the surfaces as shown in Fig. 2. They are referred to as normal specimen and parallel specimen respectively in the rest of the paper. The specimen thickness was about 0.5 mm.

Density measurement was based on Archimedes principle with distilled water as the liquid medium. XRD (Rigaku Rotaflex D/max-C XRD system) analysis and SEM (LEO-1530 Scanning Microscope) examination were performed on polished and ultrasonically cleaned sample surfaces. For the observation of whisker alignment, the polished samples were heated in air at 400°C for 600 min to completely remove the organics. The whiskers left were carefully transferred onto SEM stud and coated with gold to prevent electrostatic charging.

Piezoelectric constant d_{33} and polarization curve (P-E curve) were measured using the Radiant Technologies System, USA. Conductive paint was applied on the specimen surfaces prior to test to form the electrodes. Specimens were poled for d_{33} measurements at 3 kV·mm^{-1} for 30 min in silicone oil and at 80°C. A higher poling field resulted in the electric breakdown of the specimens used. P-E characteristic was tested at 80°C, 50 Hz and a field of 5 kV·mm^{-1}. Dielectric constant and loss were measured using LCR digital bridge (Model 4284A, Hewlett Packet Co.).

4. Results and discussion

The relative densities of the $BaTiO_3$ whisker-PVDF and the $BaTiO_3$ powder-PVDF composites were 96 and 98% respectively. This was consistent with the SEM examination (not shown), where only a small number of isolated pores were observable.

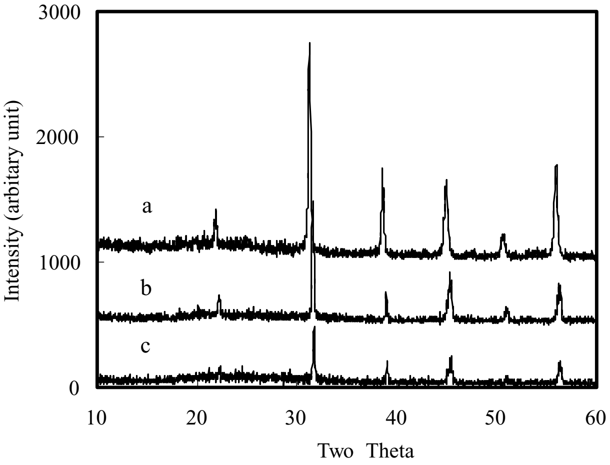

Figure 3 XRD profiles of: (a) powder-PVDF composite (b) parallel specimen and (c) normal specimen.

The XRD profiles for the powder composite, the normal and the parallel specimens are shown in Fig. 3. Analysis indicated that the whisker and the powder were all in tetragonal crystallographic form, characterized by the slight twin peaks at 44–46°(2θ), but the tetragonality of the whiskers was small in comparison with the powder. One reason may be the size of the whiskers. The tetragonality of $BaTiO_3$ is usually expressed by the c/a ratio, where c and a are the crystal lattice constants. It has been documented that c/a decreases with crystal dimension [7]. When the crystal size is below ~0.19 μm, c/a approaches to unity (i.e., $BaTiO_3$ becomes cubic) and piezoelectricity disappears, while when the crystals are larger than 0.27 μm, $BaTiO_3$ is in tetragonal form and piezoelectric. Although the average diameter of the whiskers was similar to that of the powders, some whiskers had diameters less than 0.27 μm. Moreover, the preparation method of the whiskers, which is unknown, might also be the cause of the low tetragonality. Nevertheless, for comparative study the low tetragonality should not affect the general trend of the property difference resulted from whisker orientation.

In all the composites, only peaks corresponding to $BaTiO_3$ phase had been detected. Other authors have also reported the absence of the PVDF diffractions in 0–3 composites [8]. It is believed due to low crystallinity of PVDF in the composites.

The most striking difference between the profiles of the normal and parallel specimens was that the relative intensity of the (100) peak was significantly lower in the normal specimen. This can be explained by the preferred whisker orientation. Because the whiskers are grown along the [100] axis, the alignment makes the (100) planes essentially parallel to the incident X-rays in the normal specimen (2θ is close to zero), and hence very limited XRD diffraction had occurred on these planes.

Fig. 4 shows the SEM photograph of the parallel specimen after the removal of the organic matrices. Whisker alignment was excellent, especially bearing in mind the extreme small size. The whisker aspect ratio remained unchanged from the raw material, as verified by statistic microstructural analysis, indicating that the piezoelectric phase had not suffered from any noticeable damage during the composite processing.

Table II gives the dielectric constants and loss factors of both the whisker-PVDF and the powder-PVDF composites. The dielectric constants of the whisker-PVDF composite were much higher than that of the powder-PVDF composite, while the loss factors were opposite. The dielectric constant of the normal specimen was more than double of the parallel specimen.

In a 0–3 composite, the dielectric constant (ε) can be expressed as [9]:

$$\varepsilon = \varepsilon_1 . \frac{2\varepsilon_1 + \varepsilon_2 - 2\phi(\varepsilon_1 - \varepsilon_2)}{2\varepsilon_1 + \varepsilon_2 + \phi(\varepsilon_1 - \varepsilon_2)} \qquad (1)$$

where 1 and 2 represent the matrix and the active phase respectively, and ϕ stands for the volume fraction of the active phase. In this work, ε_1, ε_2 and ϕ were 12, 1700 and 0.3, thus $\varepsilon = 27.1$. This value was in very good agreement with the experimental result of the

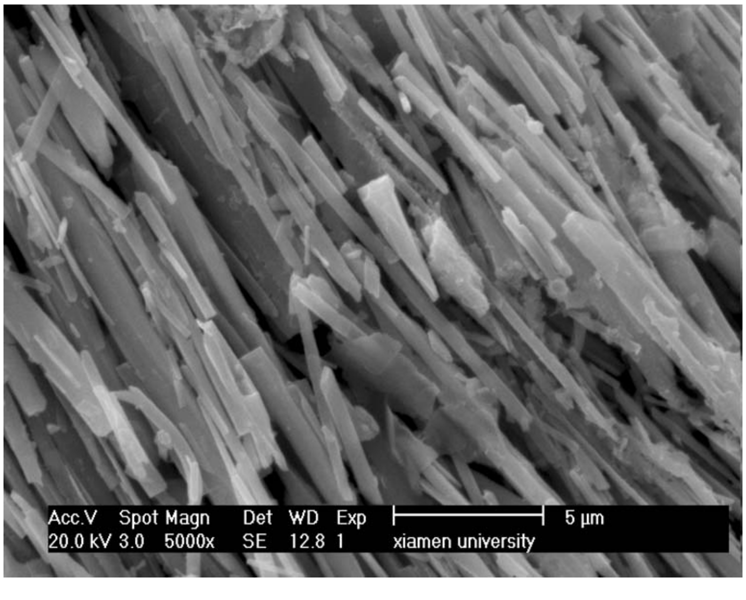

Figure 4 SEM photograph of the parallel specimen after the removal of the organics by heating at 400°C, showing the excellent whisker alignment.

TABLE II Relative dielectric constants and loss factors of whisker-PVDF and powder-PVDF composites

Sample	ε_r	$\tan\delta$
30% whisker-PVDF composite		
Normal	90.72	0.0746
Parallel	44.40	0.0325
30% powder-PVDF composite	23.89	0.2606

TABLE III The d_{33} values of whisker-PVDF and powder-PVDF composites

Sample	Poling field (kV·mm^{-1})	d_{33} (pC/N)
30% whisker-PVDF composite		
Normal	3	13.7
Parallel	3	10.6
30% powder-PVDF composite	3	4.4
	10	7.8

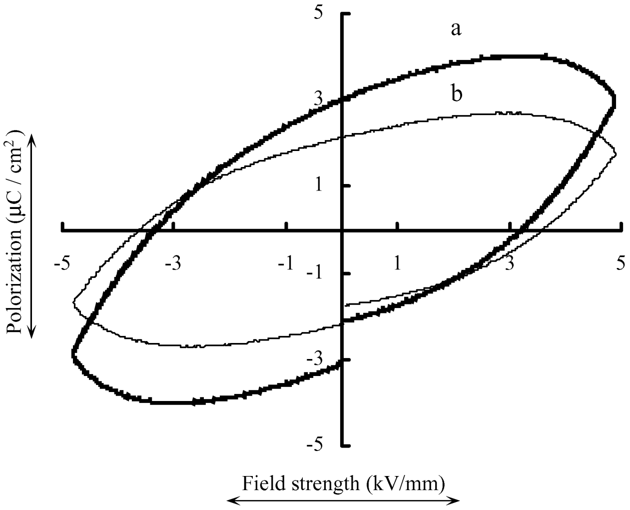

Figure 5 Ferroelectric hysteresis loops for 30% whisker-PVDF composite: (a) normal and (b) parallel specimens.

powder composite. However, in the whisker composite, the dielectric constants for both the normal and parallel specimens were several times higher than for the powder composite. This is believed to be the direct result of the different morphology of the active phases. To help elucidate these results, we may borrow some conclusions from the study on electrically conductive polymer matrix composites [10, 11]. In these composites, powders or fibers are by no means uniformly distributed. There exists a critical volume fraction of the conductive phase, above which the conductivity of the composite increases sharply. This critical value is called percolation threshold (P. T). Extensive research reveals that the particles or fibers form continuous electrical passages at P. T by contacting with one another. The P. T is strongly dependant upon the aspect ratio of the conductive phase. The greater the ratio is, the smaller the P. T is. Therefore, much lower volume fraction of (aluminum) fibers is needed to render the composite conductive than (aluminum) powders [10, 11]. In other words, for a given volume fraction, the density of the continuous passages in a fiber composite should be much higher than in a powder composite.

In the piezoelectric composites studied here, the formation of the connected passages is also expected to have significant influence on the dielectric and electromechanical properties. The connected passages are analogous to the ceramic rods in a 1–3 composite. The difference is that ceramic rods are continuous, but a very thin polymer film separates each powder or fiber in the connected passages. Furthermore, unlike ceramic rods the connected passages are not necessarily straight. In a 1–3 composite, the dielectric constant is governed mainly by the ceramic phase. Similarly in a piezoelectric composite, it believes to be influenced mainly by the connected passages. Equation 1 can be rearranged into the following form:

$$\varepsilon = \varepsilon_1 . \left[\frac{3(2\varepsilon_1 + \varepsilon_2)}{2\varepsilon_1 + \varepsilon_2 + \phi(\varepsilon_1 - \varepsilon_2)} - 2\right] \qquad (2)$$

Thus, ε increases with increasing ϕ (note: $\varepsilon_1 < \varepsilon_2$). When this relation is applied to the connected passages, ϕ is the fractional volume of the piezoelectric phase. Obviously ϕ is higher in the connected passages than in the non-connected regions. Consequently ε for these passages should also be higher. That is, the higher the connected passage density in the composites, the higher the overall ε. On the base of the above arguments and the results in Table II, the densities of the connected passages are descending from the normal specimen, the parallel specimen to the powder composite. The lower loss factors for the whisker composite support the connected passage hypothesis. Polymers have much higher loss factors than $BaTiO_3$. Therefore, the whisker specimens with a higher density of connected passages have lower dielectric loss.

The piezoelectric constants of the composites are given in Table III. Obviously the d_{33} are strongly dependent upon the whisker orientation. The d_{33} of the normal specimen is 30% higher than that of the parallel specimen. The d_{33} values of both the normal and parallel specimens are significantly higher than the composite with powder as the active phase.

Fig. 5 shows the ferroelectric hysteresis loops for the whisker composite. A maximum field of 5 kV·mm^{-1} was applied, above which the specimens were broken down. The remnant polarizations (Pr) are 3.0 and 2.1 μC·cm^{-2} for the normal and parallel specimens respectively. But under the same conditions, Pr of the powder-PVDF composite is only 1.8 μC·cm^{-2}.

Because the whiskers are much bigger in length than the powder, the size effect was initially thought to be one of the factors responsible for the difference in the electromechanical properties. Therefore, $BaTiO_3$ particles of various sizes ($d_{50} = 50$ nm, 0.3 and 7 μm) have been used to make 30% powder-PVDF composites to verify this assumption. The composite containing 0.3 μm powder was found to have the highest d_{33} and Pr values, or in other words, the piezoelectric properties are not directly proportional to the particle size. Clearly the sizes of the active phases cannot explain the observed difference.

Similar to the dielectric constants, the differences in d_{33} and Pr are also attributed to the different density of the connected passages for the different samples. In the connected passages polymer proportion is lower than in the rest part. Consequently the shielding effect of the polymer in these regions is less and a greater portion of electric field is exerted on the active phases, leading to a larger degree of polarization in these regions. The difference of the properties is actually the reflection of the different degree of polarization in these samples.

5. Conclusions

A piezoelectric composite has been prepared and characterized with highly aligned $BaTiO_3$ whiskers as the active phase and polyvinylidene fluoride (PVDF) as the matrix. Its dielectric constant (ε), piezoelectric constant (d_{33}) and remnant polarization (Pr) are considerably higher than the corresponding composite containing $BaTiO_3$ powder as the active phase, while the loss factors follow the opposite trend. For the whisker composite, ε, d_{33} and Pr along the direction of the whisker orientation are much higher than the values normal to the whisker orientation.

The concept of connected passage density has been put forth to explain the observed differences. In these passages, the polymer content is lower than the rest regions, and thus the shielding effect of the polymer on the external electric field is also less. As the result, a stronger field is exerted on the active phase, leading to a higher degree of polarization. Because whiskers have higher aspect ratio than powders, they are more likely to bridge or contact with one another to form the connected passages. The connected passage density is also a function of whisker orientation. It is higher along the direction parallel to the whisker axis than normal to the whisker axis.

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