Preparation and Electromechanical Properties of PVDF Matrix Piezoelectric Composites Containing Highly Oriented $BaTiO_3$ Whiskers

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The piezoelectric composites containing highly oriented $BaTiO_3$ whiskers as active phase and PVDF as matrix have been prepared by micro-hole extrusion and orientation in carried fibers. The morphology of oriented $BaTiO_3$ whiskers and microstructure of the composites were observed by SEM. As for its electromechanical properties, it is found that the dielectric constant, piezoelectric constant and remnant of polarization in the $BaTiO_3$ whisker-PVDF composite are considerably higher than that in the $BaTiO_3$ powders-PVDF composite, while the loss factors follow the opposite trend. For the $BaTiO_3$ whisker-PVDF composite, the values of ε, d_{33} and $P_{\rm r}$ parallel to the whisker orientation (normal specimen) are much higher than that perpendicular to the whisker orientation (parallel specimen). The significant effects of the connective passages of active phase on electromechanical properties of the piezoelectric composites has also been investigated.

KEY WORDS: Piezoelectric composite, $BaTiO_3$ whiskers, Electromechanical properties, Polarization, Connective passages

1. Introduction

The piezoelectric composites combined with piezoelectric ceramic phase and polymeric phase are multi-functional composites, and they take important part in smart materials and structural systems. Ceramic-polymer piezoelectric composites have been usually made in a variety of devices such as transducer, sensor, and actuator, and have many applications in the fields of nondestructive evaluation, biological medical imaging system, marine acoustics and electric acoustics, sensor technology *etc*[1~3]. Recently, the piezoelectric composites with PZT and $BaTiO_3$ ceramic as active phase and polyvinylidene fluoride (PVDF) as matrix have attracted much attention because of its excellent electromechanical and physical properties[4,5].

According to connective patterns of phases, there are 10 connectivities existing in the piezoelectric composites with dual-phase components[6,7]. Of these, the 0-3 and 1-3 type composites are most studied. Composites with 0-3 connectivity are the easiest to make, simply by blending piezoelectric ceramic powders with 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, and that has normally 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[8]. The main problem is the difficulty in fabrication. Many techniques have been developed to manufacture the 1-3 type composites, including rod replacement, dice and fill, lost mold and injection molding[9]. 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.

Whiskers are acicular single crystals with very low density of defects. They usually have extremely high tensile strength, and thus are widely used as reinforcing agents in composites. For the $BaTiO_3$ whiskers, it is demonstrated that the growth axis is predominantly [100], and its dielectric and piezoelectric properties vary markedly along different crystallographic axis. Therefore, when $BaTiO_3$ whisker is oriented, the whiskers composites might possess high anisotropy just like a [100] single crystal, and thus the excellent electromechanical properties of the whiskers can be fully explored.

In this work, $BaTiO_3$ whiskers are selected as the active phase and PVDF as the matrix, where the whiskers were extruded and oriented in carried fibers. The objective is to develop a new composite that combine the merit of ease of fabricating the 0-3 type composite with the good properties.

2. Experimental

2.1 Raw materials

The $BaTiO_3$ whiskers were produced by Otsuka Chemical Co. Ltd., Japan. Its average diameter and length we are 0.3 and 5 μm, respectively, and the density was 5.6 $g\cdot cm^{-3}$. The Hypermer KD-1, provided by Aldrich Co. Ltd, USA, was used as dispersant of the $BaTiO_3$ whiskers. DMA (N, N-dimethylacetamide) was used to dissolve PVDF. The $BaTiO_3$ powders were synthesized by hydrothermal synthesis method in this laboratory. The average size was 0.3 μm, and it had well defined crystal morphology and narrow particle size distribution, in the same order as the whisker diameter. PVDF was used as the composite matrix. Although PVDF was a piezoelectric material, its contribution to piezoelectricity in this composite has been found to be much smaller than the $BaTiO_3$ whiskers and can be neglected.

2.2 Fabrication

The whisker alignment technique was realized using extrusion and orientation in carried fibers by some researchers[10~12]. To reduce whisker agglomeration with minimal whisker damage (reduction of aspect ratio), 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 gain a spinning dope. The volume fraction of the $BaTiO_3$ whiskers was fixed at 30 vol. pct. For comparison, a 0-3 type composite with hydrothermal $BaTiO_3$ powders as active phase was also prepared using the same procedures. The compositions of the wet-spinning dopes were batched containing 13.5 wt pct $BaTiO_3$ whisker/powder, 10 wt pct PVDF and 76.5 wt pct DMA. The dispersant was approximately equal to 1 wt pct of the $BaTiO_3$.

The whisker orientation was accomplished by micro-hole extrusion of spinning dope, then a carried fiber containing oriented $BaTiO_3$ whiskers can be obtained. More detailed in

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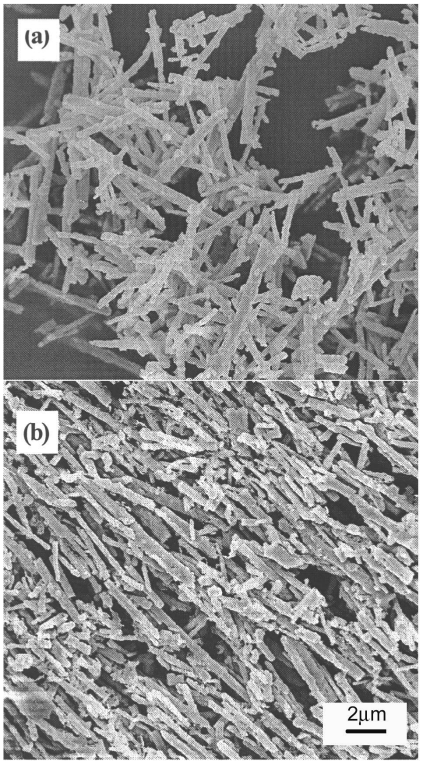

Fig.1 SEM photographs of $BaTiO_3$ whiskers of (a) starting whiskers and (b) oriented whiskers after removing PVDF in air at 600°C

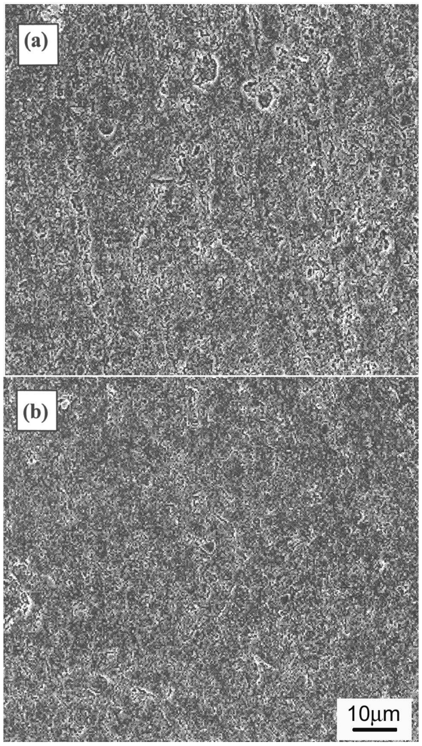

Fig.2 SEM photographs of $BaTiO_3$ whisker-PVDF composite of parallel specimen (a) and normal specimen (b)

formation can be found in literature [10]. The as-spun fibers were dried and cut to length and unidirectionally placed into a rectangular steel die. To obtain the dense composite, the die was heated to 200°C at the pressure of 0.3 MPa for 30 min. After cooling, the composite was sectioned into specimens with the direction of the whiskers normal and parallel to the surfaces. They were hereafter referred to as normal specimen and parallel specimen respectively. The specimen thickness was about 0.5 mm.

2.3 Measurement and analysis

Density was measured by Archimedes method and distilled water was used as the liquid medium. Phase analysis was carried out using XRD (Rigaku Rotaflex D/max-C XRD system) and specimen surface and whisker alignment were observed by SEM (LEO-1530 scanning microscope) after the sample surface was polished and ultrasonically cleaned. For the observation of whisker alignment, the samples were heated in air at 600°C for 30 min to completely remove the organics. The residual whiskers were carefully transferred onto SEM stud and coated with gold to prevent electrostatic charging.

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

3. Results and Discussion

3.1 Microstructure and phase compositions

Figure 1 shows SEM photographs of starting $BaTiO_3$ whiskers and oriented whiskers after removing PVDF in air at 600°C. In Fig.1(a), the $BaTiO_3$ whiskers are rod-like single crystals with length of 3∼10 μm and random alignment. After orientation (Fig.1(b), parallel specimen), almost all $BaTiO_3$ whiskers has a unidirectional direction along the direction of fiber extrusion. Whisker alignment is excellent, especially bearing in mind the extreme small size. Imaging processing analysis revealed that the whisker aspect ratio remains unchanged, indicating that the active phase ($BaTiO_3$ whiskers) has not suffered any noticeable damage during the composite processing.

SEM photographs of $BaTiO_3$ whisker-PVDF composites at different section are shown in Fig.2. In Fig.2(a), a small number of isolated pores are observable along whisker orientation. After removing PVDF, the $BaTiO_3$ whisker alignment appear in agreement with the direction of fiber extrusion (see Fig.1(b)). On normal specimen (Fig.2(b)), only a few fine-scale pores can be observed. It is believed that these pores formed during extrusion process of carried fiber and distributed along the direction of fiber extrusion. Density measurement indicated that the relative density of the $BaTiO_3$ whisker-PVDF composites is 97%, which is consistent with SEM examination.

XRD curves for the starting $BaTiO_3$ whiskers and oriented whisker-PVDF composites are shown in Fig.3. Only peaks corresponding to $BaTiO_3$ phase appear for all the tests. XRD analysis results show that the $BaTiO_3$ whisker is in tetragonal crystallographic form, indicated by the slight double peaks at 44°∼46° (2θ), but the tetragonality is small in comparison with the powder. One reason may be the small 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[13]. When the crystal size is below ∼0.19 mm, c/a approaches to unity (*i.e.* $BaTiO_3$ becomes cubic) and piezoelectricity disappears; however, when the crystal size is larger than 0.27 μm, $BaTiO_3$ is in tetragonal form and piezoelectric. Although the average diameter of the whiskers is similar to that of the powders, some whiskers have diameters less than 0.2 μm. Nevertheless, for comparative study the low tetragonality should not affect the general trend of the property difference resulted from whisker orientation.

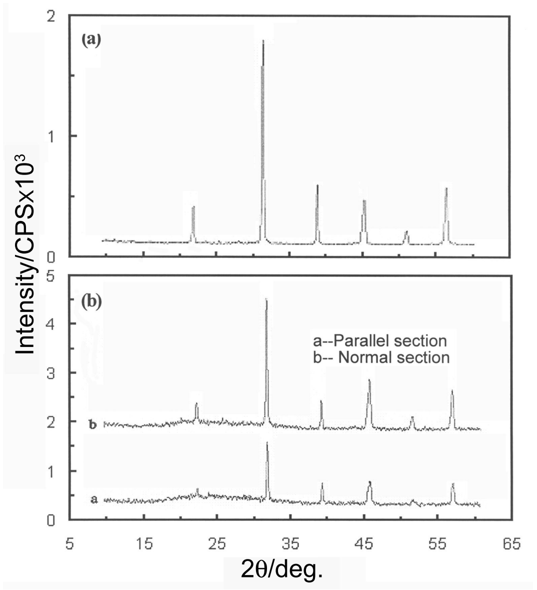

Fig.3 XRD profiles of starting $BaTiO_3$ whiskers (a) and oriented whisker (b) composite on parallel and normal section

Table 1 Relative dielectric constants and loss factors of both the whisker and powder-PVDF composites

Materials	ε	$\tan\delta$
$BaTiO_{3(w)}$/PVDF(normal)	90.72	0.0746
$BaTiO_{3(w)}$/PVDF(parallel)	44.40	0.0325
$BaTiO_{3((p)}$/PVDF	23.89	0.2606

Notes: ∗ $BaTiO_{3(w)}$ stands for $BaTiO_3$ whiskers; $BaTiO_{3(p)}$ is $BaTiO_3$ powder

In Figs.3(a) and (b), the position of the main peaks of $BaTiO_3$ crystals is the same, and the most striking difference between the curves of the normal and parallel specimens is that the relative intensity of the (100) peak is 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 occurred on these planes. No peaks corresponding to PVDF have been detected. Other authors have also reported the absence of PVDF diffraction peaks in the 0-3 type composite[4,14]. It is believed to be due to low crystallinity of PVDF in the composite.

3.2 Dielectric properties

Table 1 gives the relative dielectric constants and loss factors of both the whisker-PVDF and powder-PVDF composites. The dielectric constants of the whisker-PVDF composite are much greater than that of the powder-PVDF composite, while the loss factors are opposite. For the oriented whisker-PVDF composite, the loss factor of the normal specimen is more than that of the two parallel specimens.

In an electrically conductive polymer composite, there exists a critical volume fraction of the conductive phase, which is called percolation threshold (P.T). The P.T is strongly dependant upon continuous electrical passages formed by the particles or fibers[15,16], and much lower volume fraction of fibers is needed to render the composite conductive than the powders. Similar to the continuously connective passages in electrically conductive polymer, the density of the continuous passages in a whisker composite should be much higher than that of powder composite. If the volume fraction of $BaTiO_3$ active phase, loss factor of $BaTiO_3$ whiskers and PVDF are 0.3, 1700 and 12, respectively, by means of theoretical formula of the powder composites (0-3 type)[17], the loss factor of composite will be 26.97. This value is in well agreement with the experimental results in this work. However, in the whisker composite, the dielectric constants for both the normal and parallel specimens are several times higher than that for the powder composite. This is believed to be the direct result of the different morphology of the active phases.

In whisker-piezoelectric composites, the connective passages formed by oriented $BaTiO_3$ whiskers are analogous to the ceramic rods in the 1-3 type composite. Unlike ceramic rods, the connective passages are not necessarily straight. In the 1-3 type composite, the ε is governed mainly by the ceramic phase. Similar to the 1-3 type composite, it is believed to be influenced mainly by the connective passages. Due to much lower loss factor, the effect of PVDF on the loss factor of composite can be neglected, so the loss factor of the 1-3 type composite was mainly governed by oriented $BaTiO_3$ whiskers. Obviously the volume fraction of the oriented $BaTiO_3$ whiskers is higher in the connected passages than that in the disconnected regions. Consequently loss factor for these passages should also be higher. Therefore, more connective passages mean higher overall ε for the composite. For all composites in this work, the densities of the connective passages are descending from the normal specimen, the parallel specimen to the powder composite. Microstructure observation by SEM illustrated that the pores in parallel specimen, originally occupied by PVDF, are elongated along the direction of whisker orientation, as the result there should be a higher density of connected passages for the normal specimen.

The lower loss factor of the whisker composites supported the connected passage hypothesis. Polymers have much higher loss factors than $BaTiO_3$. Therefore, the whisker specimens having higher density of connected passages, have lower dielectric loss.

3.3 Piezoelectric and ferroelectric properties

Table 2 lists the piezoelectric constants of both the $BaTiO_{3(w)}$-PVDF and $BaTiO_{3(p)}$-PVDF composites. 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. Moreover, the d_{33} values of both the normal and parallel specimens in $BaTiO_3$ whisker-PVDF composites are significantly higher than that of the composites with powder as the active phase.

Figure 4 shows the ferroelectric hysteresis loops for the oriented $BaTiO_3$ whisker-PVDF composite. A maximum field of 5 $kV\cdot mm^{-1}$ was applied, above that the specimens were broken down. The P_r are 3.0 $\mu C\cdot cm^{-2}$ and 2.1 $\mu C\cdot cm^{-2}$ for the normal and parallel specimens respectively. But under the same conditions, the P_r of the $BaTiO_3$ powder-PVDF composite is only 1.8 $\mu C\cdot cm^{-2}$.

Similar to the dielectric constants, the differences in d_{33} and P_r are also attributed to the different density of connective passages for the different samples. In the connective passages polymer proportion is lower than that in the rest part. Consequently its shielding effect 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 electromechanical properties of active phase are directly related to the degree of dipole poling. Therefore, the different poling ability between the whiskers and powders should directly result in the difference in its properties. The $BaTiO_3$ whiskers with high quality single crystals can be easily poled at a field less than 1 $kV\cdot mm^{-1}$. Remnant of polarization, 25 $\mu C\cdot cm^{-2}$, is obtainable for (100) crystals. However, the $BaTiO_3$ powders, usually consisting of a cluster of crystallites (aggregates), are not mono-dispersed. Extensive bonding (necking) between the crystallites can be observed easily, the aggregates may be roughly considered as sintered ceramic. Bulk $BaTiO_3$ ceramic needs much higher field to get poled, usually more than 2 $kV\cdot mm^{-1}$. The resultant P_r is also much smaller, about 7.5 $\mu C\cdot cm^{-2}$. Obviously, the diffe-

Table 2 Piezoelectric constants of both the $BaTiO_{3(w)}$-PVDF and $BaTiO_{3(p)}$-PVDF composites

Materials	Poling field/kV·mm^{-1}	$d_{33}/\mu C \cdot N^{-1}$
$BaTiO_{3(w)}$/PVDF(normal)	3	13.7
$BaTiO_{3(w)}$/PVDF(parallel)	3	10.6
$BaTiO_{3(p)}$/PVDF	3	4.4
$BaTiO_{3(p)}$/PVDF	10	7.8

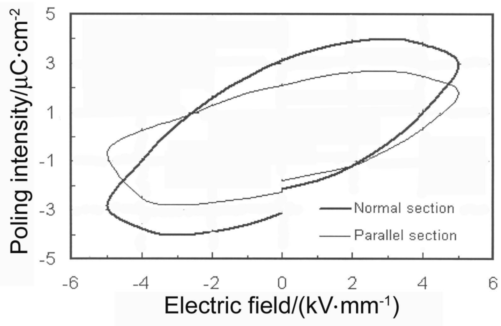

Fig.4 Ferroelectric hysteresis loops of the oriented $BaTiO_3$ whisker-PVDF composite

rence in the initial size and dispersity between whiskers and powders may be the other reason for affecting their properties. Usually, the ceramic powders are made up of aggregates of many $BaTiO_3$ crystallites. Each aggregate behaves like sintered ceramic. The difference in poling ability between single crystal and bulk ceramics also contributes to the observed difference in electromechanical properties. Nevertheless, this hypothesis needs further tentative confirmation.

The remnants of polarization among $BaTiO_3$ whisker composite, $BaTiO_3$ single crystals and dense $BaTiO_3$ bulk ceramic are different. The primary reason is that the piezoelectric active phase in present composites is only 30 wt pct, while the active phases both of single crystals and dense bulk ceramic can be referred as 100 wt pct, the density of connective passages and the degree of dipole poling of whisker composites is much lower than that of single crystal and dense bulk material. Moreover, the relative density of whisker composite is about 97%, and a portion of active phase was detached by PVDF around whisker, which resulted in a low density of connective passages and lowered the electromechanical properties. As a result the remnant of polarization in this work is lower than those of both $BaTiO_3$ single crystals and dense bulk ceramic.

4. Conclusions

The piezoelectric composites consisting of highly oriented $BaTiO_3$ whiskers as active phase and PVDF as matrix have been prepared by micro-hole extrusion and orientation in carried fibers. The experimental results showed that the ε, d_{33}, and P_r in the $BaTiO_3$ whisker-PVDF composite are considerably higher than those in the $BaTiO_3$ powders-PVDF composite, while the loss factors follow the opposite trend. For the whisker composites, the values of ε, d_{33} and P_r along the direction of the whisker orientation (normal specimen) are much higher than those of normal to the whisker orientation (parallel specimen).

The connective passages of active phase have significant effects on electromechanical properties of the piezoelectric composites. In the whiskers composites, the oriented $BaTiO_3$ whiskers are more likely to bridge or contact with one another to form connective passages, the stronger poling electric field exerting on the active phase led to a higher degree of polarization. As the result, the oriented whisker composites possess good electromechanical properties.

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